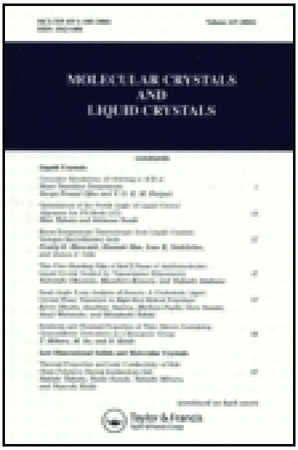

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Physical Properties of an Ester/Biphenyl Mixture Exhibiting an Injected Smectic Phase

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To cite this article: D. A. Dunmur , R. G. Walker & P. Palffy-muhoray (1985): The Physical Properties of an Ester/Biphenyl Mixture Exhibiting an Injected Smectic Phase, Molecular Crystals and Liquid Crystals, 122:1, 321-338

To link to this article: http://dx.doi.org/10.1080/00268948508074762

Mol. Cryst. Liq. Cryst., 1985, Vol. 122, pp. 321–338
0026-8941/85/1224-0321/$20.00/0

Printed in the United States of America

The Physical Properties of an Ester/Biphenyl Mixture Exhibiting an Injected Smectic Phase

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(*Received September 10, 1984*)

Measurements are reported of the phase-coexistence temperatures, transition enthalpies, refractive indices and electric permittivities of a series of mixtures of 4-*n*-pentyl 4'cyanobiphenyl (component 1) and 4 *n*-pentylphenyl 4 *n*'-pentyloxybenzoate (component 2). The temperature composition phase diagram shows the presence of an injected smectic phase, and the nature of this phase together with its effect on the adjacent nematic phase is discussed in the light of the measured physical properties. The results suggest that the injected smectic A to nematic transition is second order (or very weakly first order) for mole-fractions of component 1 greater than 0.55, but at lower mole-fractions the nature of the transition alters to become more characteristic of a first order phase change.

In the nematic phase above the injected smectic, the orientational order is reduced, as evidenced by enthalpy measurements, refractive indices and electric permittivities. Using a recent adaptation of mean field theory, the component order parameters in the mixture have been calculated, and hence values predicted for the optical and dielectric anisotropies. There is reasonable agreement between the theoretical and experimental results provided that an empirical scaling procedure is adopted for the component order parameters in the mixture. Finally the presence of coexisting phases in the phase diagram is considered, and implications for the structure of the injected smectic phase are discussed.

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†Paper presented at the 10th International Liquid Crystal Conference, York, 15–21 July 1984.

1. INTRODUCTION

Most applications of liquid crystals use mixtures of mesogens to adjust the temperature range of the mesophase and to optimise their physical properties. There is consequently much interest in understanding the properties of liquid crystalline mixtures, so that better materials may be produced for applications. Various theoretical approaches have been developed to explain mesogenic mixture properties based on lattice theories[1-3] hard particle theories,[4,5] or various adaptations of mean field theory.[6-8] Calculations so far have been restricted to binary mixtures consisting of two mesogens or one mesogen and one non-mesogen, and theoretical predictions have for the most part been concerned with the nematic/isotropic phase behaviour of such mixtures. There have been many experimental studies of binary phase diagrams of mesogens,[9] and the physical properties of mixtures have been measured by a number of groups.[10-14] A recent extension of the Maier–Saupe mean field theory to binary mixtures[15] has shown that order parameters of the components of a mixture can be calculated, and so predictions of various anisotropic physical properties can be made. Theoretical attention has been mainly restricted to the nematic mesophase of mixtures, but regular solution theory has been used to provide a phenomenological description of more complex phase behaviour.[16]

One of the more unusual aspects of the phase behavior of binary liquid crystal mixtures is the formation of smectic phases from components which do not themselves show smectic properties.[17-18] Accompanying the formation of the injected smectic phase is a marked deviation of the nematic/isotropic transition temperature from a linear dependence on composition. Injected smectic phases are often formed in mixtures of "unlike" nematogens, and the consequent stabilization of a translationally ordered phase must reflect more efficient packing of dissimilar molecules in layers. A quantitative theory of this is difficult since it requires the inclusion of position-dependent attractive and repulsive interactions for both components. Wagner[19] using the McMillan model[20] for smectics calculated a phase diagram showing an injected smectic phase. The appearance of this phase was a consequence of neglecting all smectic terms in the mixture pseudo-potential except that for the unlike interaction; the calculation did not predict the observed behaviour of the nematic/isotropic phase boundary. Clearly the interaction between component molecules of different species must be important in the formation of injected smectic phases, and it is to be expected that it will influence the nematic phase properties in the vicinity of an injected smectic region of the phase diagram.

In an attempt to understand the formation of injected smectic phases and their influence on adjacent nematic phase properties, we have carried out an extensive investigation of the physical properties of binary mixtures of 4 *n*-pentyl 4′cyanobiphenyl and 4 *n*-pentylphenyl 4′ *n*-pentyloxybenzoate. Measurements are reported for the nematic/isotropic and smectic/nematic transition enthalpies, and for electric permittivities and refractive indices of the mixtures. The experimental results obtained in the nematic region of the phase diagram are compared with the predictions of our mean field theory. A plan of the paper is as follows: in section 2 we record the experimental results and observations. Our mean field theory of mixtures is summarized in section 3, and the predicted nematic mixture properties are compared with experiment. In section 4 the implications of our observations for the injected smectic phase are considered, and we advance some tentative ideas concerning the nature of the phase transition along the nematic/smectic coexistence line.

2. EXPERIMENTAL OBSERVATIONS

2.1. Phase diagram

The temperature-composition phase diagram for the binary system of 4 *n*-pentyl 4′ cyanobiphenyl (component 1) and 4 *n*-pentylphenyl 4′*n*-pentyloxybenzoate (component 2) is shown in figure 1. This was compiled from the results of a variety of experiments. The nematic/isotropic coexistence line was determined from microscopic observation of 15 mixtures. A narrow two-phase coexistence region was sometimes observed microscopically, but direct measurement of the extent of this region was possible for mixtures in the centre of the phase diagram from refractive index measurements. The boundary of the injected smectic region was also found microscopically, but the extent of the associated two-phase region is largely based on dielectric measurements and will be commented upon below.

2.2. Transition enthalpies

The enthalpies of transition associated with the nematic/isotropic and nematic/smectic phase changes were measured at the University of Hull using a Perkin Elmer DSC-2C Differential Scanning Calori-

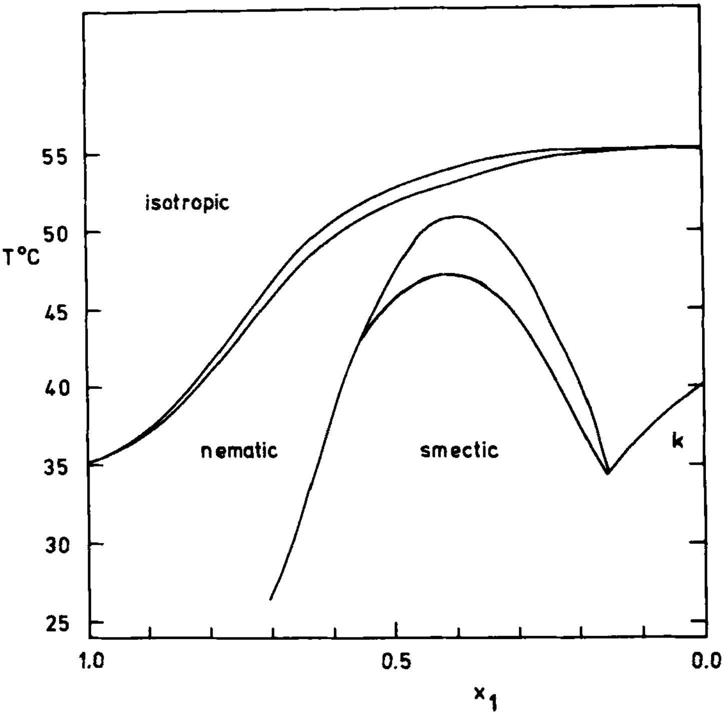

FIGURE 1 Temperature/composition phase diagram for the binary system of 4 *n*-pentyl 4′cyanobiphenyl (1) and 4 *n*-pentylphenyl 4′*n*-pentyloxybenzoate (2). x_1 is the mole-fraction of component 1.

meter. A scan rate of $2\frac{1}{2}°$ per minute was used, and for each mixture there was good agreement between the integrated peak areas for heating and cooling scans. Transition enthalpies are given in table I, and the quoted limits indicate the difference between values obtained on heating and cooling. In figure 2 the results of table I have been converted to transition entropies and plotted as a function of composition. A very clear qualitative conclusion is apparent from these results. The entropy change (ΔS_{SN}) associated with the smectic/nematic transition is largest in the centre of the phase diagram near the maximum in the injected smectic phase region. With increasing concentration of component 1 there is a rapid decrease in ΔS_{SN} suggesting that for $x_1 > 0.5$ the nature of the smectic/nematic phase change is different from that for $x_1 < 0.5$. The increase in ΔS_{SN} in the centre of the phase diagram is accompanied by a decrease in ΔS_{NI}, which indicates that the nematic phase above the injected smectic region is relatively disordered.

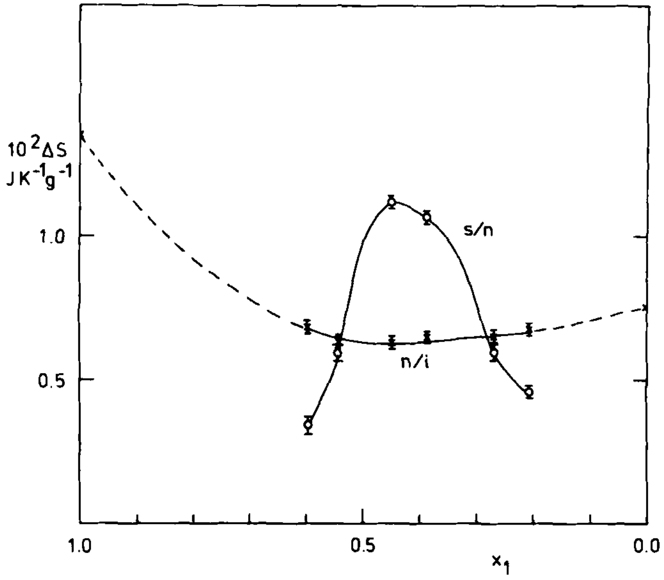

FIGURE 2 Transition entropies (ΔS) as a function of mole fraction of component (1): O = smectic/nematic transition, and x = nematic/isotropic transition.

TABLE I

Transition enthalpies for mixtures of 4 *n*-pentyl 4′cyanobiphenyl (1) and 4 *n*-pentylphenyl 4 *n*′-pentyloxybenzoate (2). ΔH_{SN} is the enthalpy of the smectic/nematic transition and ΔH_{NI} is the enthalpy of the nematic/isotropic transition.

mole fraction of (1)	$\Delta H_{SN}/Jg^{-1}$	$\Delta H_{NI}/Jg^{-1}$
0.205	1.48 ± 0.07	2.24 ± 0.02
0.268	1.97 ± 0.13	2.20 ± 0.06
0.384	3.51 ± 0.42	2.17 ± 0.08
0.447	3.70 ± 0.21	2.08 ± 0.13
0.543	1.90 ± 0.10	2.09 ± 0.08
0.596	1.15 ± 0.08	2.24 ± 0.19

2.3. Refractive Indices

Measurements of refractive indices were made as a function of temperature using a homeotropically aligned film on the prism sur-

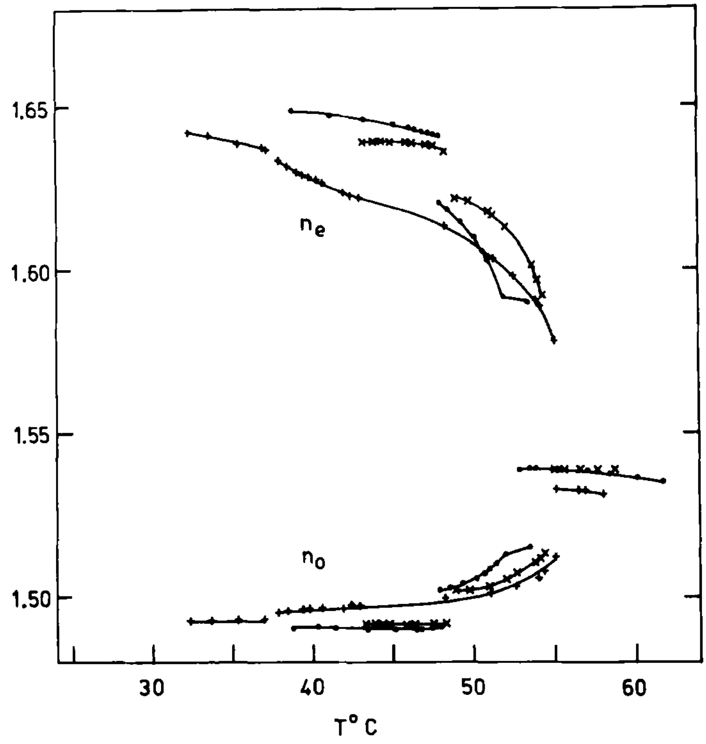

FIGURE 3a Refractive indices as a function of temperature for mole-fractions (x_1) of component (1), + (x_1 = 0.154); x(x_1 = 0.305); ●(x_1 = 0.400).

face of an Abbé or Pulfrich refractometer. The light source used was a helium-neon laser operating at a wavelength of 633 nm. In order to destroy the speckle pattern from the laser and so improve the definition of the image, a vibrating thin opalescent disc was inserted in the beam to destroy its coherence. Results of our refractive index measurements are given in figures 3a and 3b. For some mixtures in the centre of the phase diagram the extent of the two phase coexistence region was measured directly, since it was possible to measure three refractive indices (n_e, n_0 and $n_{\mathrm{isotropic}}$) simultaneously; a more detailed description and analysis of the measurements is given in an earlier publication.[21] The results for mixtures with $x_1 < 0.45$ (fig. 3a) show a sharp discontinuity at the smectic/nematic transition, and the birefringence ($\Delta n = n_e - n_0$) is considerably greater in the smectic phase than the nematic. These observations would be consistent with a first order smectic/nematic transition, and indicate a relatively high degree of orientational order in the smectic phase. In contrast the

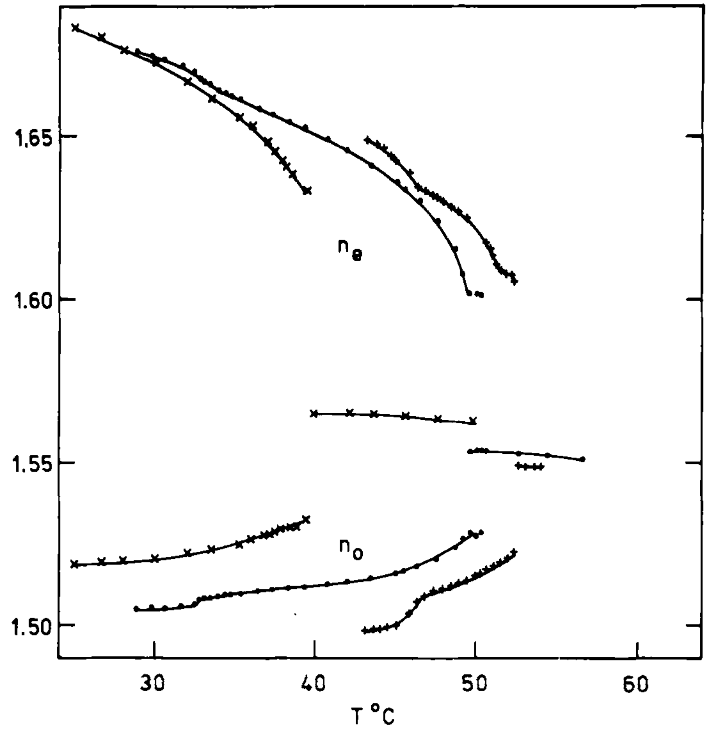

FIGURE 3b Refractive indices as a function of temperature formole-fractions (x_1) of component 1, +(x_1 = 0.460); ●(x_1 = 9.645); x(x_1 = 0.812).

refractive indices for mixtures with $x_1 > 0.45$ are continuous at the smectic/nematic transition, indicative of a weak first order or second order transition.

2.4. Electric permittivities

Our dielectric measurements were made at 1592 Hz using a thermostatted metal cell with parallel electrodes separated by about 1 mm. The cell was calibrated with standard dielectric liquids, and the liquid crystal samples were aligned in a magnetic field of 1.1 to 1.4 Tesla. Alignment of the smectic phase was achieved by slow cooling from the nematic phase in the presence of the magnetic field. Results are presented in figures 4a and 4b. The first point to note is that in contrast to measurements on pure materials there is no sharp discontinuity in the measured permittivity components ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$) at the nematic/isotropic transition. This is consistent with the existence of a two-phase region, since the measured permittivity component will be

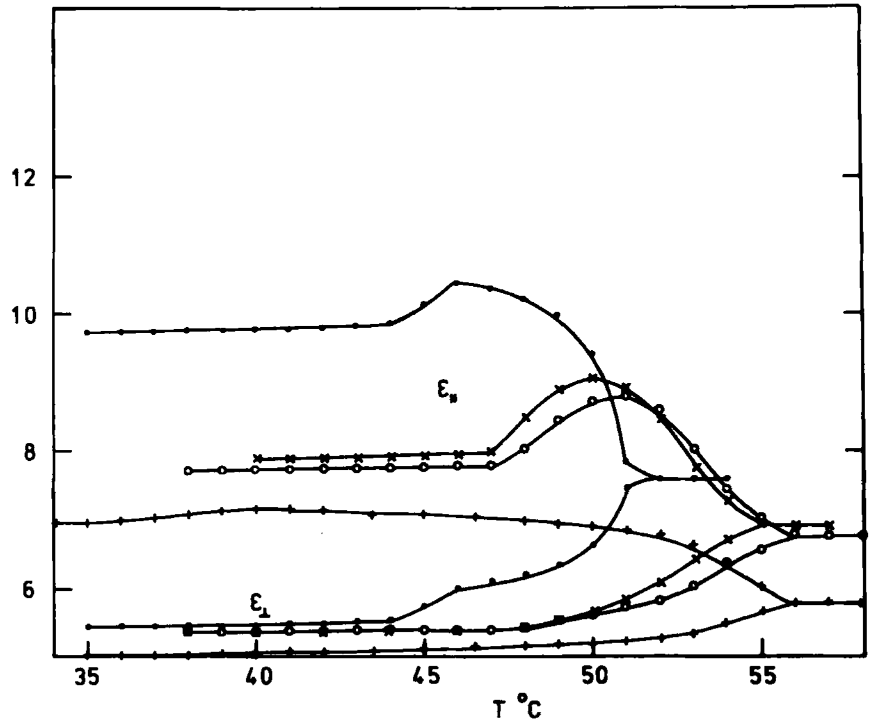

FIGURE 4a Electric permittivities as a function of temperature for mole-fractions (x_l) of component (1), +(x_l = 0.208); O(x_l = 0.384); x(x_l = 0.447); ●(x_l = 0.501).

an average of contributions from the two coexisting phases. As with the refractive index measurements we find that mixtures to the right of the phase diagram ($x_l < 0.5$, fig. 4a) show a significant step in the permittivity components at the smectic/nematic transition: both components being less in the smectic phase. The conclusion from our refractive index measurements is that the order parameter increases at the nematic→smectic transition for these mixtures, and we deduce that enhanced dipole-dipole correlation in the smectic phase outweighs the effect of increased order and leads to a net reduction in the parallel component of the permittivity. The change in the permittivity components at the smectic/nematic transition is not sharp, but extends over 1 to 3°C. This would be consistent with the existence of a two phase region at this transition as indicated on our phase diagram (fig. 1). Unfortunately we were not able to observe the refracted rays from these coexisting phases in the refractometer, probably because the strong image from the smectic phase obscured

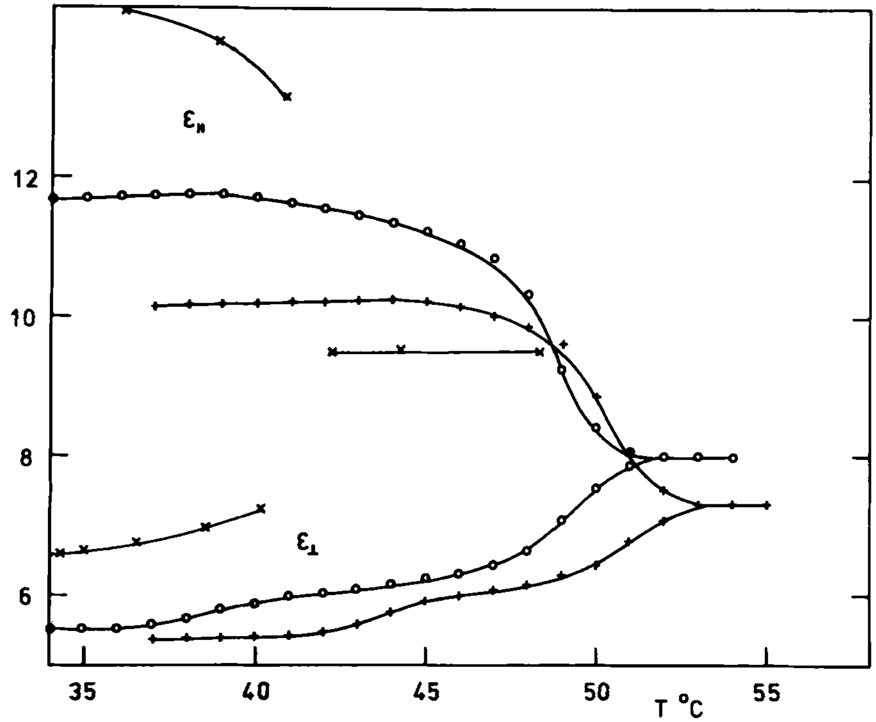

FIGURE 4b Electric permittivities as a function of temperature for mole-fractions (x_1) of component 1, + ($x_1 = 0.548$); O($x_1 = 0.596$); x($x_1 = 0.80$).

any other images. In fig. 4b we give results for mixtures with $x_1 > 0.5$. Once again there is evidence for two-phase coexistence at the nematic/isotropic phase transition, but there is no longer a jump in the permittivity components at the smectic/nematic transition, consistent with it being a weak first order or second order transition.

3. COMPARISON WITH THEORY

Our mean field theory of binary nematic mixtures has been described in other publications,[15,22] and will only be reviewed briefly here. We assume that the pseudo-potential for components in a mixture can be written as:

$$\epsilon_i = \epsilon_i^0 - \left[u_{ii}\rho_i S_i + u_{ij}\rho_j S_j \right] \left[P_2(\cos\theta_i) - \tfrac{1}{2} S_i \right] \qquad (1)$$

where i and j refer to the components 1 and 2 ($i \neq j$). ϵ_i^0 is the isotropic part of the potential, S_1 and S_2 are the component order parameters for species 1 and 2, and ρ_1 and ρ_2 are their corresponding number densities. The Helmholtz free energy for the mixture is given by:

$$F = -kT\rho_1 \ln\left(\frac{1}{\rho_1}\right)\int \exp(-\epsilon_1/kT)\,d(\cos\theta_1)$$

$$-kT\rho_2 \ln\left(\frac{1}{\rho_2}\right)\int \exp(-\epsilon_2/kT)\,d(\cos\theta_2) \qquad (2)$$

and minimising this with respect to the component order parameters leads to the usual self-consistent equations:

$$S_i = \frac{\int P_2(\cos\theta_i)\exp(-\epsilon_i/kT)\,d(\cos\theta_i)}{\int \exp(-\epsilon_i/kT)\,d(\cos\theta_i)} \qquad (3)$$

For a mixture of given composition at a particular temperature eq. (3) can be solved to yield the component order parameters and hence the free energy F. The solution is considerably simplified if the geometric mean rule is assumed for the unlike interaction energy, $u_{ij} = (u_{ii}u_{jj})^{1/2}$. Using eqs. (2) and (3) in the manner previously described[15,21] gives a theoretical phase diagram for the system. Parameters of the theory are the ratios of the nematic/isotropic transition temperatures ($T_{\mathrm{NI}i}$) for the pure components, and the ratios of their molecular volumes (v_i). Our calculated phase diagram for the system studied experimentally is given in figure 5: $T_{\mathrm{NI}1}/T_{\mathrm{NI}2} = 0.94$, and $v_1/v_2 = 0.70$. When plotted against mole-fraction the nematic/isotropic boundary is slightly convex, but the deviation from linearity is not as strong as that observed experimentally; the extent of the two-phase coexistence region is also much less than is measured. It is worth noting that when plotted against volume-fraction the transition temperature of the mixture is a linear function of composition: this is probably a consequence of adopting the geometric mean rule for the unlike interaction energy.

In order to calculate the anisotropic physical properties of mixtures it is necessary to evaluate the component order parameters. Results of these calculations are presented in figure 6 for different mixture compositions. At a particular temperature the order parameter of the larger component is greater than that of the smaller component, while the volume-fraction average of the component order parameters is close to the Maier–Saupe values for pure mesogens (see ref. 21). In

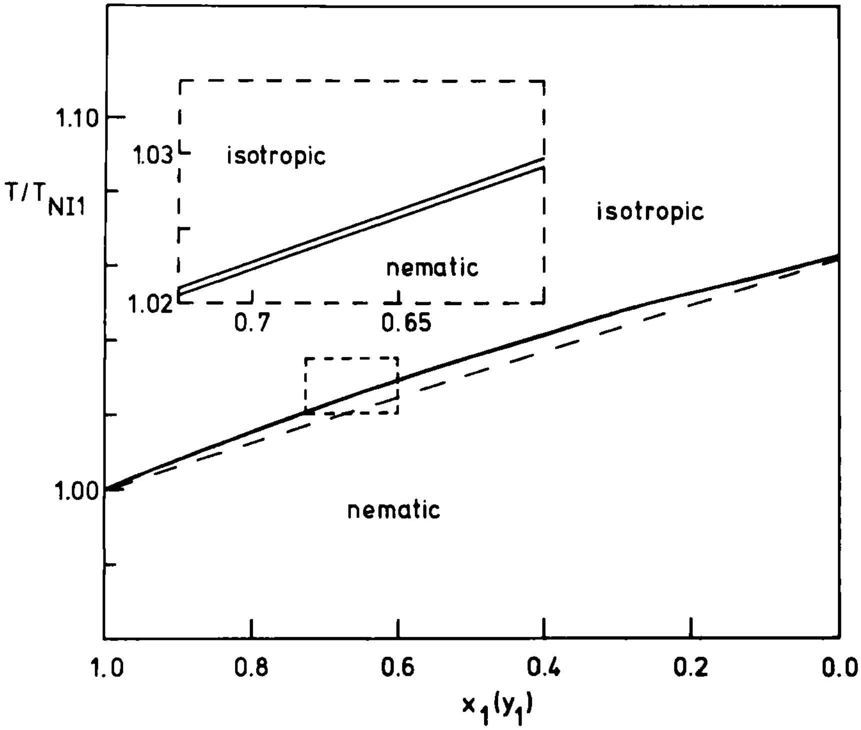

FIGURE 5 Calculated phase diagram for a mixture with $T_{NI1}/T_{NI2} = 0.94$ and $v_1/v_2 = 0.70$. The full line is the coexistence temperature plotted as a function of mole-fraction (x_1) of component (1), while the dashed line represents the same data plotted against volume-fraction (y_1). The inset shows the small two phase coexistence region around the nematic/isotropic transition.

fig. 6 the dotted lines indicate the component order parameters for a reduced temperature $T_R = 0.99$.

To proceed further one needs a mixture theory for the various anisotropic physical properties. Magnetic susceptibility anisotropy, birefringence and dielectric anisotropy are to a first degree of approximation single particle properties and they can be written as linear functions of the number density and order parameter. For such properties a simple mixing law can be proposed of the form:

$$X(T)_{\text{mix}} = \sum_i y_i X_i S_i(T) \tag{4}$$

where y_i and S_i are the component volume-fractions and order parameters, $X(T)_{\text{mix}}$ is the mixture property at some temperature T,

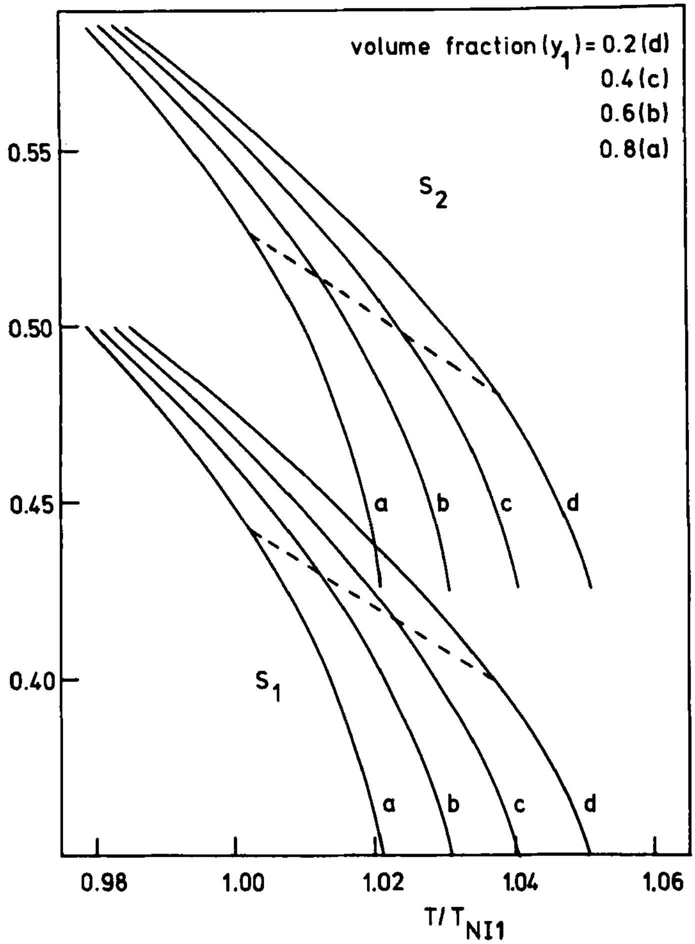

FIGURE 6 Calculated component order parameters S_1 and S_2 plotted as a function of reduced temperature T/T_{NI1} for mixtures of different volume fractions. The dotted lines are the component order parameters in mixtures corresponding to a reduced temperature of $T_R = T/T_{NI}(\text{mixture}) = 0.99$.

and the X_i are characteristic properties of the pure components, independent of temperature and number density. Eq. (4) takes on a particularly simple form for the magnetic susceptibility anisotropy, and the X_i would be simply related to the anisotropy in the molecular magnetic susceptibility.

A function of refractive indices can be defined that is proportional to the order parameter, and the corresponding mixing law becomes:[21]

$$\left(\frac{n_e^2 - n_0^2}{\bar{n}^2 - 1}\right)_{12} = y_1\left(\frac{\Delta\alpha}{\bar{\alpha}}\right)_1 S_1 + y_2\left(\frac{\Delta\alpha}{\bar{\alpha}}\right)_2 S_2 \qquad (5)$$

where $\Delta\alpha$ is the polarizability anisotropy and $\bar{\alpha}$ is the mean polarizability. For dielectric properties the situation is more complicated. Using the Meier and Meier equations it is possible to write an expression for the dielectric anisotropy that apparently depends linearly on the number density (N) and the order parameter:

$$\Delta\epsilon = \frac{NLF}{\epsilon_0}\left[\Delta\alpha + \frac{Fg\mu^2}{2kT}(3\cos^2\beta - 1)\right]S \qquad (6)$$

In eq. (6) L and F are cavity field and reaction field factors, μ is the molecular dipole moment which makes an angle of β with the axis of maximum polarizability and g is the Kirkwood dipole correlation factor. L and F depend indirectly on the order parameter, g is a function of number density and in a mixture will depend on composition. However as a first attempt we propose to use the simple additivity rule:

$$(\Delta\epsilon)_{12} = y_1\left(\frac{\Delta\epsilon}{S}\right)_1 S_1 + y_2\left(\frac{\Delta\epsilon}{S}\right)_2 S_2 \qquad (7)$$

in which $(\Delta\epsilon)_{12}$ is the dielectric anisotropy of the mixture, and $(\Delta\epsilon/S)_i$ is evaluated for the pure components at the same reduced temperature.

Unfortunately a further difficulty arises when applying mean field theory to the interpretation of mixtures, which is that mean field theory is not followed by the pure components, i.e., the pure component order parameters are not usually in agreement with the M-S universal curve. To overcome this problem we have *scaled* the calculated component order parameters by the volume-fraction average of the ratio of the experimental to calculated order parameters for the pure components. Using this scaling procedure and eqs. (5) and (6) we are able to calculate the birefringence and dielectric anisotropy for the mixtures, and our results for $T_R = 0.99$ are given in figures 7 and 8. The agreement between theory and experiment for the refractive index function is surprisingly good, and confirms the reduction in orientational order for the mixtures in the centre of the phase dia-

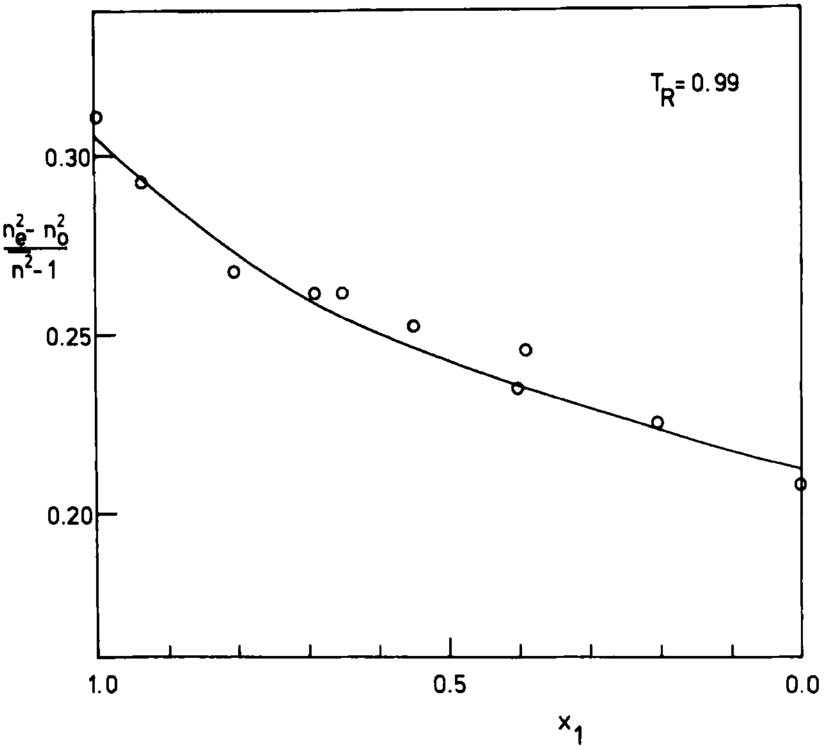

FIGURE 7 The refractive index function of the nematic phase plotted against mole-fraction (x_1) for a fixed reduced temperature $T_R = 0.99$. The open circles (○) are experimental points, and the full line represents the calculated values.

gram. Given the many approximations in the theory, the calculated result for the dielectric anisotropy is in fair agreement with experiment, although for mixtures close to the injected smectic region there are clearly additional contributions to the permittivities which have been neglected in the theory. Short range effects of the reduction in order on the dipole correlation factor may be responsible for the observed experimental behaviour.

4. DISCUSSION AND CONCLUSIONS

The formation of an injected smectic phase in a binary mixture clearly influences the properties of the proximate nematic phase. For the system studied in this work the appearance of an injected smectic region in the phase diagram has the effect of pushing-up the nema-

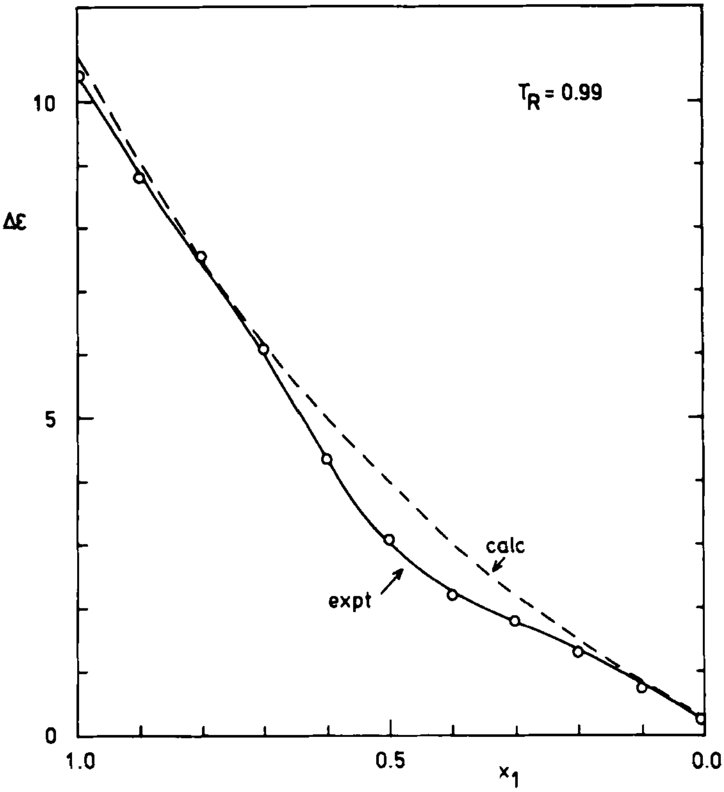

FIGURE 8 The dielectric anisotropy $\Delta\epsilon$ of the nematic phase plotted against mole-fraction (x_1) for a fixed reduced temperature of $T_R = 0.99$. The open circles (○) are experimental points, and the dashed line represents the calculated values.

tic/isotropic coexistence line. In a related system of 4 *n*-nonyl 4'cyanobiphenyl and 4 *n*-pentylphenyl 4' *n*-pentyloxybenzoate,[23] the injected smectic phase intrudes into the nematic phase to the extent that there is an enantiotropic transition from smectic to isotropic for mixtures in the centre of the phase diagram. Results of our calorimetric, refractive index and dielectric measurements indicate that the orientational order in the nematic phase is reduced in the region above the injected smectic, with a consequent increase in the strength of the smectic/nematic first order phase transition.

Although not reported in this paper, we have made measurements of the splay (k_{11}) and bend (k_{33}) elastic constants of selected mixtures in the nematic region using the Freedericksz transition in planar cells. The interpretation of elastic constant measurements on mixtures is complicated because they are two particle properties and depend directly on the pair distribution function. Like the second virial coefficients of gas mixtures, elastic constants for liquid crystal mixtures are difficult to analyse quantitatively. However our elastic constant measurements do support the general conclusions of this work. There is a considerable reduction in k_{33} and k_{11} in the centre of the phase diagram consistent with a reduction in the nematic order parameter in that region.

Perhaps the most consistent result of the experiments reported here is the apparent change in the nature of the smectic/nematic phase transition with mixture composition. Measurements on mixtures to the right of the temperature-composition phase diagram ($x_1 < \sim 0.5$) show a discontinuity at the smectic/nematic transition, but for mixtures of higher concentration of component 1 the physical properties are continuous at this transition. We believe that the injected smectic phase is S_A, at least over the range of temperatures studied in our experiments, and a qualitative conclusion based on measurements of refractive indices and permittivities could be that the order of the S_A/N transition changes from first order for $x_1 < \sim 0.5$ to second order for $x_1 > \sim 0.5$. There is some supporting evidence for this from the enthalpy data, but it must be pointed out that strong pretransitional effects can easily obscure the transition, and our temperature control of ±0.1°C is not enough to be able to resolve the transition totally. Recent work by the Bordeaux Group[24–26] has lead to the identification of a number of smectic A phases characterized by density waves of different wave-vectors, and it is likely that the injected S_A phase studied in our work is a monolayer S_{A1} to the right of the phase diagram and a partially overlapped bilayer S_{Ad} to the left: the latter is characteristic of smectic phases formed from cyano-biphenyls. We are not aware of any X-ray measurements on the system reported here, but for a related cyano-biphenyl/ester mixture[27] the smectic layer spacings change across the injected smectic region from bilayer to monolayer values with increasing ester concentration.

Associated with a strongly first order smectic/nematic transition, one would expect a significant two phase coexistence region: no such region will exist for a second order S_A/N transition. Our interpretation of the dielectric measurements suggests that for mixtures with $x_1 < 0.55$ there are two phases coexisting around the smectic to nematic transition temperature. A change in the order of the S_A/N transition from first to second order would occur at a tricritical point, and this would also mark the termination of a two phase coexistence region. If such a point exists it would also locate the end of the coexistence line separating the S_{Ad} and S_{A1} phases in the injected smectic region. The critical composition associated with this tricritical point is of some significance. If it occurs at $x_1^{t.c.} < 0.5$, then the coexisting phases at the S_A/N transition are smectic and nematic, but if $x_1^{t.c.} > 0.5$ then a region of nematic-nematic coexistence can emerge at the top of the injected smectic. Recent theoretical work has demonstrated that nematic-nematic coexistence is predicted in binary mesogenic mixtures by mean field[22,28] and hard particle[29] theories. It is expected that for most systems such phase separation would only occur at temperatures well below solidification, however the effect of the injected smectic phase could be to push-up the nematic/nematic coexistence region into a temperature range where it is detectable.

In this paper we have shown that mean field theory can be used to predict and interpret a number of physical properties of mesogenic mixtures, and given the relative simplicity of the model, the calculations are in fair agreement with experiment. Addition of a steric term to the mean nematic potential and inclusion of smectic ordering terms would greatly extend the theory. The need to scale component order parameters in calculating mixture properties would be removed, and nematic/smectic phase equilibria in mixtures could be quantitatively investigated. From both an experimental and theoretical standpoint it is important to explore fully the two-phase coexistence regions. Our experimental work has raised the possibility of a tricritical point existing in binary mesogenic mixtures which exhibit an injected smectic phase, and the location of this point has some interesting consequences for the phase diagram.

Acknowledgements

Financial support from the U.K. Ministry of Defence and Science and Engineering Research Council, and from the Canadian National Science and Engineering Research Council is gratefully acknowledged. Our thanks are also due to BDH Chemicals Ltd. for their support and for generously providing us with liquid crystal samples. We are grateful to Professor G. W. Gray FRS and Mrs. C. Hogg (Department of Chemistry, University of Hull) for the DSC measurements, and to Mr. I. H. A. Jabbar and Mr. S. A. Bellamy (Department of Chemistry, University of Sheffield) for assistance with some of this work. One of us (RGW) thanks the UK SERC and BDH Chemicals Ltd. for the aware of a CASE Research Studentship.

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