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Modelling the chemically induced liquid crystalline phases in mixtures of disc-shaped mesogens: the phase diagram of quadrupolar Gay–Berne discs revisited

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We investigate the phase behaviour of pure systems and mixtures of quadrupolar Gay–Berne discs. The interaction potential mimics that of disc-shaped molecules which exhibit chemically induced phases with a structure based on columns of alternately stacking species. The phase diagram of the pure system is determined over a range of pressures, and the phase sequence is shown to include tilted columnar and nematic phases. The mixtures, in which the species have equal but opposite quadrupole moments, are investigated over a range of pressures using semigrand canonical simulations, such that the composition of the system is allowed to change. The fact that the composition is not fixed is especially important at the phase transitions, where the compositions of the coexisting phases may not necessarily be the same. In this situation, preparation of a system in the ‘biphasic region’ will lead to phase separation into the two distinct phases of differing compositions. The resulting phase diagram obtained using semigrand canonical simulations indicates that the columnar nematic phase observed in previous fixed composition simulations of this model [*Liq. Cryst.*, **24**, 229 (1998)] is not stable with respect to phase separation into an isotropic phase rich in a single component and a hexagonal columnar phase composed of roughly equal quantities of the two components. The structure of the columnar phase for the mixture is shown to be based on the alternate stacking of the different species. The relative concentrations of the different species in this phase may deviate up to approximately 60:40 mol %, after which any further material added will separate into the pure isotropic state.

1. Introduction

Binary mixtures of liquid crystalline materials can often lead to either new liquid crystal phases not observed in the corresponding pure systems or the extension of the temperature range over which the mesophases are stable [1, 2]. The enhancement of the liquid crystalline region often occurs because of the depression of the melting point, which reaches a minimum at the eutectic composition. However, for certain materials, it is also possible to observe chemically induced liquid crystal phases [3–10]. Rather than depressing the melting point, these phases are formed by the alternative strategy of tailoring the molecular interactions between the components to increase the liquid crystal–isotropic liquid transition temperature [3–7]. Some of the first observations of chemically-induced liquid crystal phases in low molar mass systems were made by Praefcke and co-workers [3–7], for systems of alkyl pentakis(phenylethynyl)phenyl ethers doped with the electron acceptor 2,4,7-trinitrofluorenone (TNF). These are large disc-shaped molecules, although none of the pure systems exhibit liquid crystalline behaviour. However, the multiyne:TNF binary mixtures

can exhibit both nematic and columnar phases and, depending on the length of the alkyl chain in the multiyne, different types of phase diagram are found. For ‘short’ chains, the phase diagram is similar to that schematically illustrated in figure 1(a). Close to the equimolar concentration, a hexagonal, ordered columnar phase is observed with the columnar–isotropic transition temperature well above the melting points of the individual species, indicating that this phase has been chemically induced. As the system is doped with more TNF, the transition temperature starts to fall and a nematic phase appears instead of the columnar phase. X-ray diffraction studies indicate that the different molecules alternate along the columns of the columnar phase. Intriguingly, a similar local structure is observed for the nematic phase, thus the nematic phase is thought to consist of short columns in which the components alternate as in the more ordered columnar phase. Once formed into short columns, it is the anisotropic interactions between these which should be responsible for the formation of the nematic phase and so this phase has been called a columnar nematic. For ‘long’ chains, the phase diagram

lacks the columnar phase, and if the mixture contains between 30 and 70 mol% TNF, a columnar nematic phase is observed over a reasonable temperature range; see figure 1(b).

A related local packing behaviour was observed by Bushby and co-workers [8] for hexaalkoxytriphenylene (HAT) based systems doped with hexakis(4-nonylphenyl)-dipyrazino[2,3-f:2'3'-h]quinoxaline (PDQ9). However, here the resulting phase diagrams were found to be significantly different. The strong face-to-face interaction between the unlike disc-shaped molecules again leads to the formation of columns in which the species stack alternately. However, microphase separation is observed in these systems leading to a phase diagram similar to that schematically illustrated in figure 1(c). Here mixed systems not at the equimolar concentration microphase separate into the 1:1 columnar structure with the excess in the pure isotropic state; that is, the 1:1 'compound' formed is immiscible with excess of either of the components. No columnar nematic phase is observed. It is, therefore, intriguing why these two systems, which exhibit apparently similar alternate stacking behaviour at the molecular level, have very different phase diagrams; namely, the induction of the columnar nematic phase (with apparently neither phase separation nor fractionation of the system at the transitions in the multiyne:TNF systems), along with complete miscibility of the induced phases with excess material, as compared with the fractionation of the HAT:PDQ9 system into a columnar phase composed of equal amounts of the two species and an isotropic phase rich in one species.

To explore the formation of the columnar nematic phase, in a previous paper [11] we described computer simulations of idealized model mesogens interacting through the Gay-Berne potential [12], with the enhanced face-to-face binding of the different species described by a quadrupolar interaction. However, in these simulations the concentrations of the components were taken to be fixed, and a phase diagram similar to that indicated in figure 1(a) was observed. Thus a columnar phase with alternating species along the columns was observed for a 50:50 mixture, which melted directly to the isotropic phase on heating. For a 75:25 mixture, what was considered to be a columnar nematic phase was observed; namely, short columns in which the discs stacked alternately. As there was an excess of one of the components, the columns were 'diluted' and so could not assemble into a columnar phase. However, the non-zero nematic order parameter indicated that the resulting phase was liquid crystalline and this was deemed to be a columnar nematic. This phase undergoes a transition to the isotropic phase at a temperature lower than that of the 50:50 mixture, again similar to the experimental behaviour shown in figure 1(a). Note that for this idealized system,

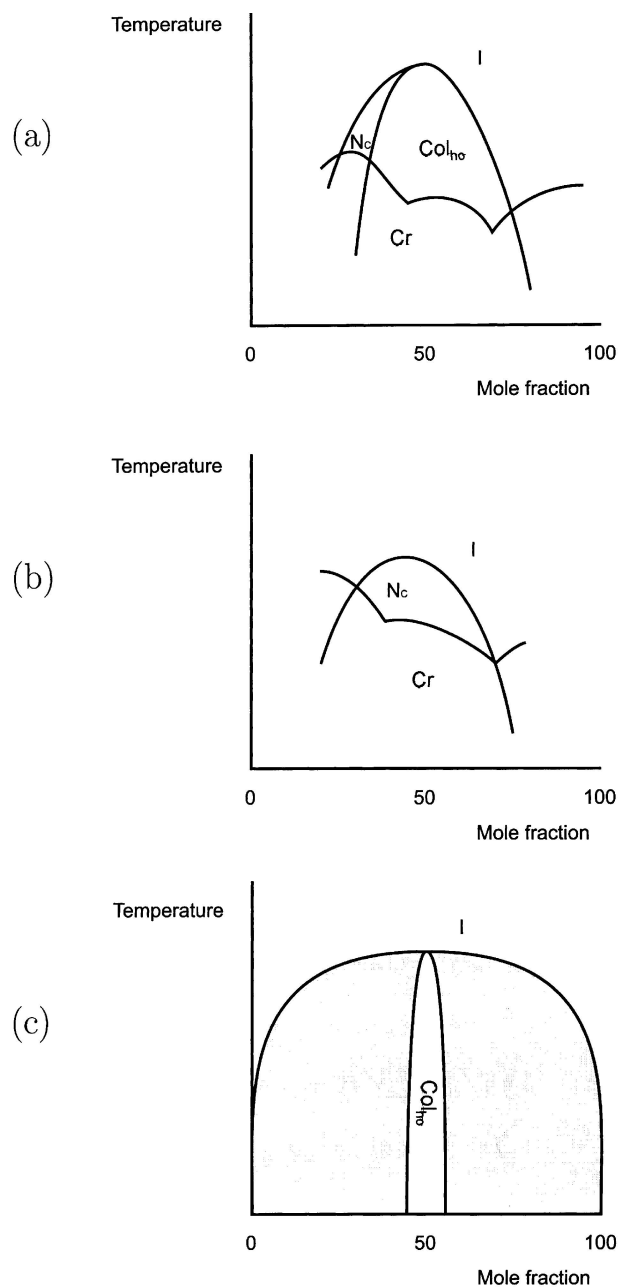


Figure 1. Schematic composition-temperature phase diagrams of liquid crystalline systems exhibited by mixtures in which the molecules assemble into alternate stacks. (a) 'Short chain' multiyne:TNF mixtures [4, 7], (b) 'long chain' multiyne:TNF mixtures [4, 7] and (c) HAT:PDQ9 mixtures [8]. The mole fraction axis refers to the multiyne species in (a) and (b) and to HAT in (c). The shaded area in (c) is a biphasic region, in which the system phase separates into the 1:1 Col_{ho} columnar phase and the isotropic phase rich in the excess component.

the components were identical except that their quadrupole moments were equal but opposite, and so a 25:75 mixture has the same phase behaviour as the 75:25 one, leading to a symmetrical phase diagram.

However, in interpreting these results, it is important to remember that the systems studied were at fixed concentrations. For the relatively small systems studied, this is important since, even if phase separation should occur in a macroscopic system, it may not be due to finite size effects [13]. That is, even though the system might phase separate if it was macroscopic in size, it might not in practice for the small system due to the large surface free energy associated with this separation, and so misleading results may occur in the simulations. To overcome this, we have performed a new, extensive series of semigrand ensemble simulations using the same model in which the composition of the system is allowed to change during the simulation. In addition, the simulations of the pure system have been extended over a large range of pressure. The paper is arranged as follows. In §2, the background of the model is described. The simulations and phase behaviour of the pure system is described in §3, and the mixtures are described in §4. A summary and our conclusions are presented in §5.

2. Modelling interactions between mesogenic molecules

Our understanding of supramolecular systems has been considerably advanced by computer modelling. There are, in general, two different but complementary approaches to modelling such systems. The first is to model each molecule using accurate, pseudo-atomic forcefields. As this approach is computationally expensive, typically only a few molecules can be modelled and so the structure of the phase cannot be investigated. However, modelling systems in this way can indicate the conformations in which specific molecules prefer to bind to each other, and also the binding energies for specific pairs of molecules. Thus predictions can be made about transition temperatures between, for example the columnar and isotropic phases of the binary mixtures previously discussed, and so general conclusions can be made about whether stable columnar-based phases can be formed depending on the chemical structure of the molecules in question. Indeed, this approach has been used to analyse the local structure and the formation and stability of the 1:1 ‘compounds’ of HAT:PDQ9-based systems [9]. However, a different approach is necessary if we wish to investigate the longer range structure characteristic of the liquid crystalline phase. This is important if we wish to distinguish, for example, a columnar phase and a columnar nematic phase. As atom-based models are computationally expensive, it is typical to use models in which the chemical detail is stripped away but the essential physics of the problem remains [14–16]. Thus a cheaper, more generic model is necessary to study how the arrangement of a pair of molecules will propagate at larger separations. A particularly successful model for liquid crystal simulations is that devised by Gay and Berne [12], in which each

molecule is modelled by a single site, which dramatically reduces the computational effort necessary to calculate the interaction between two molecules. Therefore, this model is particularly suited to the simulation of liquid crystal systems containing 1000s of molecules, rather than just two or three. The use of the Gay–Berne potential to investigate liquid crystal behaviour has been discussed in detail elsewhere [15, 16].

The important feature common to both the multiyne:TNF and HAT:PDQ9 systems is that the molecules tend to stack alternately in the mesophases. There have been a number of proposed mechanisms for the origin of the interaction responsible for the local stacking. One argument based on the colour change on mixing of the multiynes and TNF is that a charge transfer interaction occurs between the unlike molecules, although there is some doubt that this interaction is strong enough to induce a liquid crystal phase. An alternative argument is that the enhanced interaction between unlike molecules is due to electrostatic forces. Evidence for the electrostatic interaction comes from the simpler benzene:hexafluorobenzene system [17], in which the quadrupolar interaction between benzene and hexafluorobenzene, which have quadrupole moments of opposite signs, is dominant [18]. However, as a first approximation, we require a simple model in which the correct symmetry of the interaction is present; that is, we require that the face-to-face interaction between a pair of unlike molecules is enhanced compared with that for a pair of like molecules. Knowledge of the origin of the interaction at this somewhat crude level of modelling is not necessary. Of course, this means that we cannot answer questions such as, is it the charge transfer interaction or the quadrupole interaction which is dominant. For this the complementary technique using atomic forcefields combined with electronic electron distribution models (such as that used in the XED modelling suite [19]) on a couple of molecules is more appropriate [9]; indeed, this has been done for the HAT:PDQ9 systems by Lozman and Bushby [9], and this interaction appears to be electrostatic in nature. However, given that there is a favourable interaction which occurs between unlike species, we use a generic model to represent it.

We have chosen, out of convenience, to model this interaction using a point quadrupole model [20]. The equations governing the interaction potential between pairs of molecules and definitions of the various parameters are given in a previous paper [11]. The underlying disc shape of the molecule is modelled with the GB(0.345, 5.0, 1, 2) potential [21] (see appendix A of ref. [22] for the naming convention of GB mesogens). To enhance the favourable face-to-face attraction between unlike molecules we add a point quadrupole potential, with the quadrupole located at the centre of the molecule

and oriented along the short molecular axis, to the underlying GB potential. For like molecules, the point quadrupole leads to a destabilization of the face-to-face interaction and the energy minimum for a pair of molecules shifts to a slipped-parallel arrangement, in which the intermolecular vector is aligned at about 30° to the two (parallel) molecular axes. We should point out that even though we use a quadrupole model, we are not necessarily assuming that the favourable face-to-face interaction between the molecules is dominated by a quadrupolar interaction rather than a charge transfer interaction. We are using the point quadrupole model because this is a convenient way to model the correct symmetry and short-ranged nature of the interaction between both like and unlike pairs of molecules, in the same way that the Gay-Berne potential is used to model the essential features of rod- or disc-shaped molecules [15, 16] rather than specific chemical structure of a real mesogen. The quadrupole moment used in this study is the stronger of those used in ref. [11], $Q^* = 0.1$ ($Q^* = Q/(4\pi\epsilon_0\epsilon_o\sigma_o^5)^{1/2}$), where ϵ_o is an energy parameter and σ_o is a distance parameter. All quantities are given in standard reduced units (see, for example, refs. [11, 15, 16]), such as temperature $T^* = kT/\epsilon_o$ and pressure $P^* = P\sigma_o^3/\epsilon_o$.

3. Phase behaviour of the pure system

Simulations of the pure system of quadrupolar Gay-Berne discs, with shape and energy parameters $\sigma_f/\sigma_e = 0.345$, $\epsilon_f/\epsilon_e = 5.0$, $\mu = 1$, $\nu = 2$ and $Q^* = 0.1$ (see ref. [11] for full details of the model potential) have already been performed [11]. Here, we extend these simulations to include the columnar phase and construct the phase diagram over a range of pressures.

To examine the structure of the columnar phase, constant pressure simulations were performed with 960 molecules in which the box dimensions were allowed to change independently. However, rather than allowing the molecules to rotate freely as normal, they were all rotated in unison to remain parallel. To ensure that the system kept its columnar structure, the relative x and y coordinates of the molecules were kept fixed on a hexagonal lattice, whilst the molecules were free to translate in the z direction. These two constraints allow the system to remain in an idealized columnar phase with perfect orientational order and 2D positional order, whilst allowing the director to vary with respect to the direction of the column axis. As the simulations are performed at constant pressure the distances between the columns are free to change, although the constraints on the x and y molecular coordinates ensures that the molecules remain in a columnar structure. Moreover, as the box dimensions can change independently, structure changes to a rectangular arrangement formed by stretching the hexagonal lattice are possible, as are changes

to a structure in which the columns interdigitate; that is, although the underlying lattice is hexagonal, transformations which stretch or compress the system independently in the two different in-plane axes are allowed. Such structure changes are important to allow for, since it is feasible that the intercolumn spacing may depend on the magnitude of the tilt angle of the columns and also on the direction of the tilt, especially at high tilt angles.

The resulting tilt angle of the molecules was found to be essentially independent of the pressure, at approximately 30° to the column axis. This is not surprising given the energy minimum between a pair of parallel molecules occurs when the intermolecular vector is at this angle. The tilt angle is also found to be essentially independent of temperature, at least for low temperatures at which the columnar phase is still stable once the constraints are removed. We can, therefore, be confident that the low temperature phase of this model is a tilted columnar phase, and that this is independent of the pressure, at least over the pressure range in which we have studied the non-constrained system, as will now be described.

The tilted columnar structures obtained from the constrained simulations were slowly heated at fixed pressure, monitoring thermodynamic properties such as the enthalpy H^* , the second rank orientational order parameter \bar{P}_2 and the density ρ^* to determine the location of any phase transitions. Examples of these are shown in figure 2 for the simulations at pressure $P^* = 10$. It is clear that two transitions occur at $T^* = 1.83 \pm 0.01$ and $T^* = 1.99 \pm 0.01$; and the changes in \bar{P}_2 indicate that the lower temperature transition is between two liquid crystalline phases and that the higher temperature transition is between a liquid crystalline phase and the isotropic liquid. The order parameter $\bar{P}_2 \approx 0.6$, combined with structural analysis via a columnar distribution function (not shown, but see ref. [11]), indicate that the intermediate phase is a nematic. The phase diagrams for each pressure studied have been collated in figure 3, where the transition temperatures, order parameters at the transitions and densities at the transitions are shown as functions of pressure.

At very low pressures, $P^* \approx 2$ and below, the columnar structure melts directly to the isotropic liquid. The order parameter jumps from zero to essentially one, indicating that the transition is between a highly orientationally ordered and disordered phase, and there is a corresponding large density change. For all pressures $P^* = 5$ and above, the nematic phase is observed on melting the columnar phase. The phase boundaries in the temperature-pressure plane are essentially linear, indicating that dP^*/dT^* is independent of temperature and pressure for each phase transition; see figure 3(a). As for other

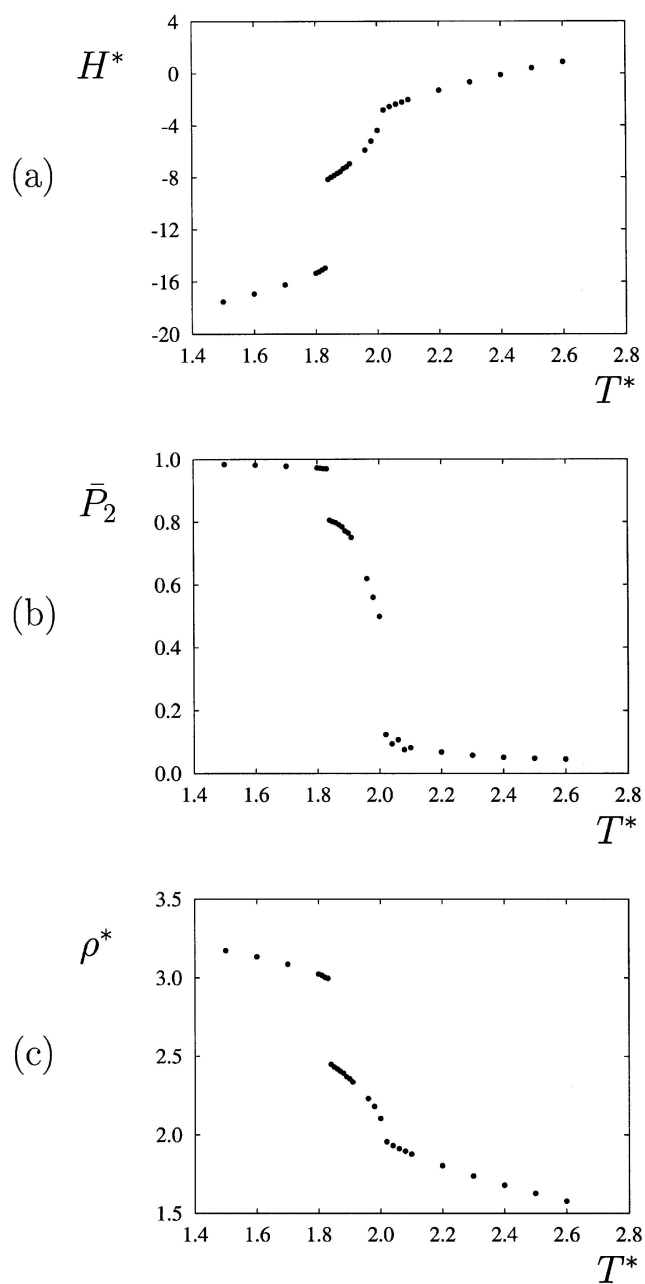


Figure 2. The temperature dependences of (a) the enthalpy (per molecule) H^* , (b) the second rank orientational order parameter \bar{P}_2 and (c) the density ρ^* for the pure quadrupolar Gay-Berne system at a pressure $P^* = 10$.

Gay-Berne models [22], dP^*/dT^* is larger for the columnar-nematic (or smectic-nematic for rod-shaped molecules) transition than for the nematic-isotropic transition. As the pressure is increased, the coexistence density of the columnar phase is essentially unchanged whilst that of the nematic phase increases. This is somewhat expected, since the more ordered columnar phase cannot be compressed as much as the more liquid-like nematic phase. A similar increase is observed in the

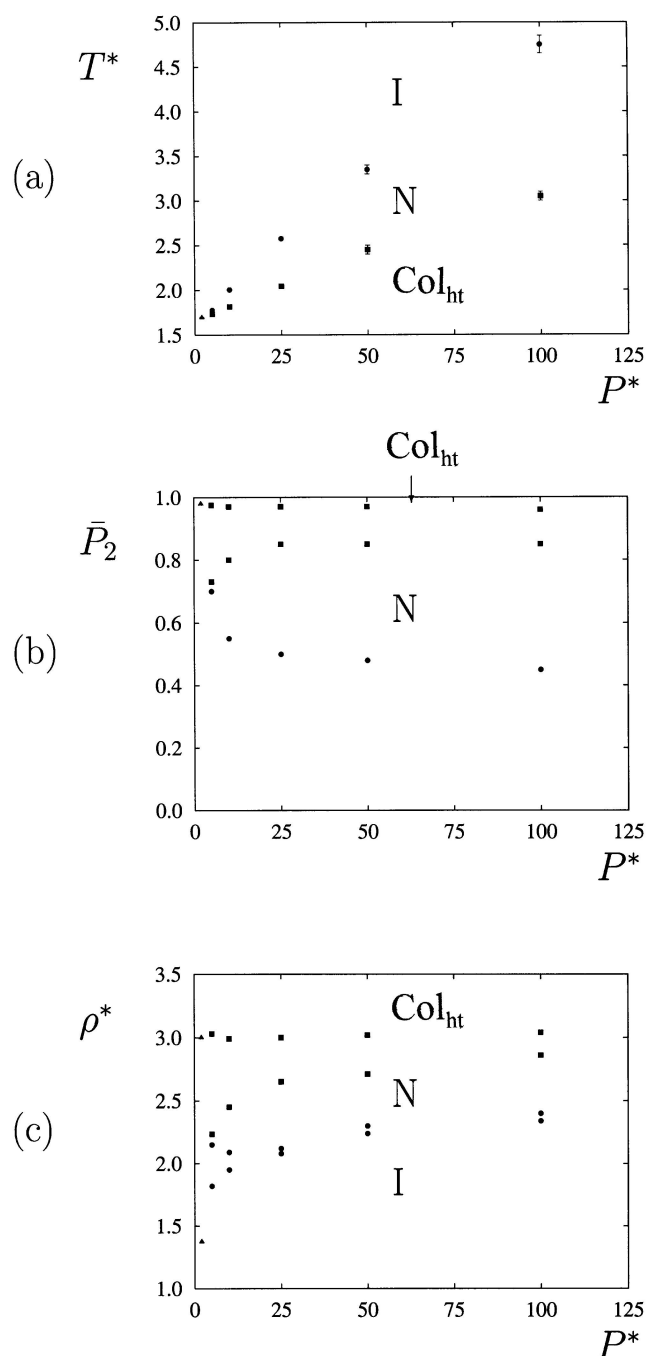


Figure 3. The influence of pressure on the pure quadrupolar Gay-Berne system. (a) The temperature-pressure phase diagram, (b) the pressure dependence of the coexistence order parameters at the transitions and (c) the coexistence densities at the transitions.

coexistence densities for the nematic-isotropic transition on increasing pressure. However, note that the order parameter of the nematic phase at coexistence with the isotropic phase drops as the pressure is increased, even though the density increases with pressure. This is due

to the large change in the transition temperature at this transition as the pressure is increased. To summarize, the pure system exhibits a tilted columnar–nematic–isotropic phase sequence over the majority of the pressures studied, although the nematic phase is not stable at low pressures, where the columnar phase melts directly to the isotropic phase. Note that the pure model system studied here is different to those investigated experimentally [3–10], in that the pure system has a nematic phase. Therefore, when considering the mixtures, we will study only temperatures above the nematic–isotropic transition, to ensure that any liquid crystal phases observed are chemically induced phases, and do not occur because the pure system would have a nematic phase at the same temperature.

4. Phase behaviour of the mixtures

The mixtures studied experimentally [3–10] are clearly complicated, in that the sizes and shapes of the components are different due to the different molecular structures. In principle, the parameters used in the pair potentials to model the mixtures should also be different to take this into account. However, to reduce the number of independent variables in the simulation, we choose that the underlying Gay–Berne potential parameters are the same for each component, thus assuming equal size and shape. Moreover, we choose the magnitude of the quadrupolar interaction to be the same for each species. The components differ only in the sign of their quadrupole moments and so, as the quadrupolar interaction is quadratic in Q , this means that the pure systems are equivalent and so the phase diagrams will be symmetric about the 50% molar fraction line. The different behaviour of the mixture compared with that of the pure systems results solely from enhanced face-to-face interaction arising from the negative sign of the product $Q_i Q_j$, compared with the positive sign of the products $Q_i Q_i$ and $Q_j Q_j$. Typical potential energy contours of the interaction between pairs of like and unlike molecules are shown in ref. [11].

To study the phase behaviour of the mixtures, we have used constant pressure semigrand canonical simulations [13]. Rather than fix the concentration, we fix the chemical potential difference between each species and allow the relative concentrations to change. In this way, we can ensure that when the system undergoes a phase transition, the chemical potential of each species as well as the temperature and pressure are the same in both phases, the necessary conditions that we are at thermodynamic equilibrium. The simulations are performed in exactly the same way as standard constant pressure simulations, apart from the fact that there is an extra type of trial, in which the identity of one molecule is changed from one species to the other, and the accept-

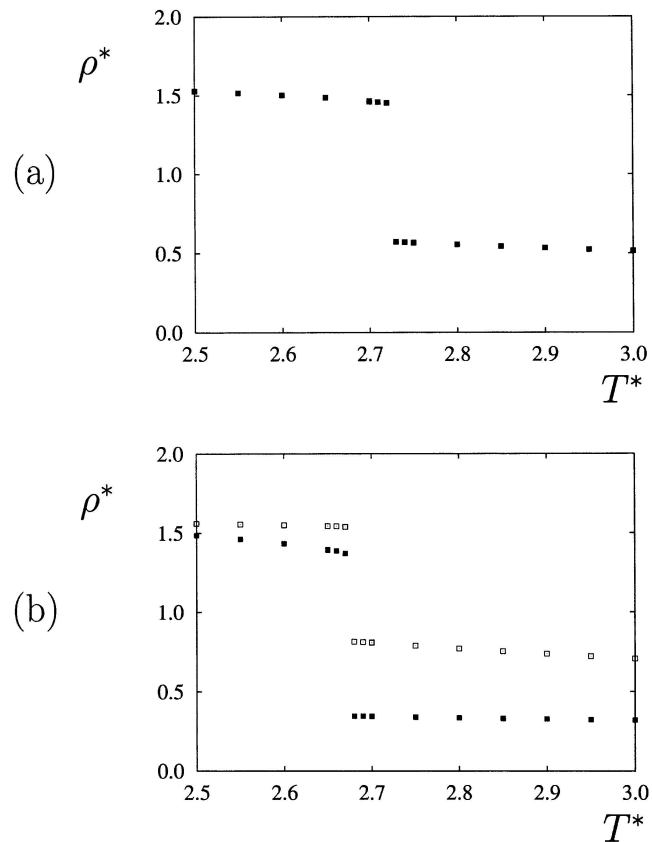


Figure 4. The temperature dependence of the density for mixtures of quadrupolar Gay–Berne discs at a pressure $P^* = 5$. (a) Chemical potential difference $\mu_d = 0.0$, (b) $\mu_d = 5.0$. Open squares: component A, filled: B.

ance or rejection of this trial is based on the imposed chemical potential difference [13]. The phase diagrams can be constructed in much the same way as for the pure systems, except that now we have two species rather than just one.

The simulations were performed as for the pure systems, namely starting from a constrained columnar system to determine the structure at low temperature. For the mixtures it is necessary to run a number of simulations, with different chemical potential differences between the species, which will lead to a variation of the composition of the system. In all cases, except for extreme chemical potential differences, the low temperature phase was found to be based on a mixed columnar structure. For relatively large chemical potential differences, even though a disordered system would prefer to lower its free energy by being a highly unsymmetrical mixture, the strong face-to-face interaction between unlike molecules in the columnar phase forces the system to have a composition of about 50:50. If extreme chemical potentials are used, the free energy cost of converting to the ‘rare’ species is so high that the system contains just

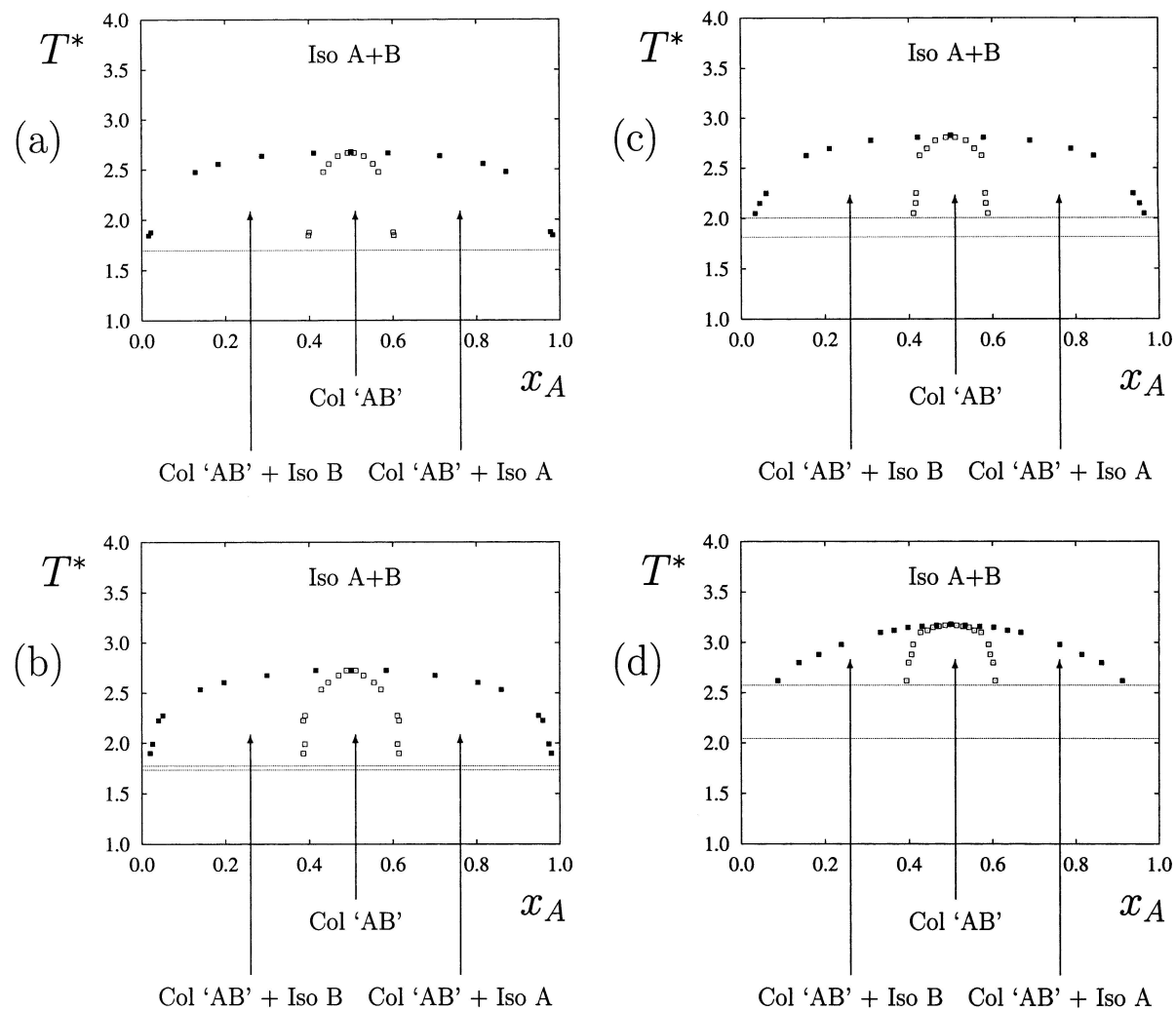


Figure 5. Temperature–composition phase diagrams for mixtures of quadrupolar Gay–Berne discs at pressures (a) $P^* = 2$, (b) 5, (c) 10 and (d) 25. Open squares: coexistence composition of the columnar phase, filled: isotropic. Col ‘AB’ means that the columnar phase is of composition roughly 1:1, Iso A means that the isotropic phase is richer in A than in B. The horizontal lines indicate the columnar–nematic and nematic–isotropic transition temperatures for the pure system (just columnar–isotropic for $P^* = 2$), see figure 3(a).

a single component. For each chemical potential difference studied, the temperature was then increased for an unconstrained system to determine the phase behaviour.

Examples of the temperature dependence of the density of the two species are shown in figure 4, for two simulations with different chemical potential differences (one zero and one finite). For the system where the chemical potential difference between the two species is zero, the density of each component is the same for all temperatures, 4(a); the columnar phase is composed of a 50:50 mixture, which melts to an isotropic phase with the same composition. In contrast, when there is a finite chemical potential difference between the species, 4(b), the columnar structure is no longer a perfect 50:50 mixture, since the columnar phase can lower its free energy by containing more of the species with lower

chemical potential; although as we shall see, there is a limit on how much of the system can convert before the columnar phase is disrupted. On melting, we observe that the densities of the two components drop as before. However, note that the composition of the system is now quite different. In the columnar phase, the system was roughly 50:50, but on melting the density of one component has more than twice the density of the other. This enables us to determine the coexistence compositions of the system, and the transition temperatures, as a function of chemical potential difference.

To compare with experimental data, it is the transition temperature as a function of composition which is most useful, and this is shown in figure 5. The form of the temperature–composition plot is independent of pressure, although, as for the pure system, we observe an increase

in transition temperatures with increasing pressure. For each pressure, we observe that there is a relatively large area of the phase diagram which has been chemically induced. That is, the columnar phase is stable over a reasonable temperature range above the temperature at which the pure system would melt to the isotropic phase. Note also that there is a large region in which the system would phase separate into the mixed columnar phase and an isotropic phase very rich in one component. The columnar phase is constrained to the middle of the phase diagram; that is, if the composition of the system strays outside of the 60:40 region, the system will phase separate into a columnar phase of roughly equal proportions and an isotropic phase richer in the excess material.

To examine the structure of the columnar phase, we have calculated the columnar distribution functions $g_{\text{col}}^{\alpha\beta}(r^*)$ [11]. These give the probability of finding a molecule of type β at a distance r^* from one of type α along a column. Full details of the algorithm are given in ref. [11]. This function is shown in figure 6 for a 50:50 columnar structure and one at approximately 60:40. For the 50:50 mixture the function is the same for A-A pairs as for B-B pairs, as we may expect given the symmetry of the model. The first peak appears at $r^* \approx 0.4$ in the A-B function, indicating that the unlike face-to-face interaction is highly favoured; indeed, the A-A and B-B peaks are zero, from which we can conclude that the like interactions (AA or BB) are so unfavourable that like pairs do not approach this close. The second peaks occur at two molecular spacings ($r^* \approx 0.8$), in the A-A and B-B functions; these arise from the ABA and BAB stackings. Further peaks can be analysed in the same way, and lead us to the conclusion that the structure of the columns is ... ABABABAB... The peaks gradually decrease in height and tend to widen with increasing distance along the column, indicating the liquid-like nature of the packing along the columns. At first sight the functions for the unsymmetrical 60:40 columnar phase look similar, and indeed help us to characterize the phase as a columnar phase. However, as species A is in excess, the packing can no longer be ... ABABABAB... On closer inspection, it is clear that, although the A-B peak is dominant at one molecular spacing ($r^* \approx 0.4$), there is a small contribution at this distance in the A-A function. Thus we can conclude that AA pairs do exist, although the majority of molecules can pair up as AB; no BB pairs are observed.

This is easily explained; as species B is the rarer species, all B molecules can find A partners. The second peak is again strong for the A-A and B-B functions, arising from ABA and BAB structure as for the 50:50 columnar phase. However, we also observe a small peak in the A-B function which, given that AA (and not BB)

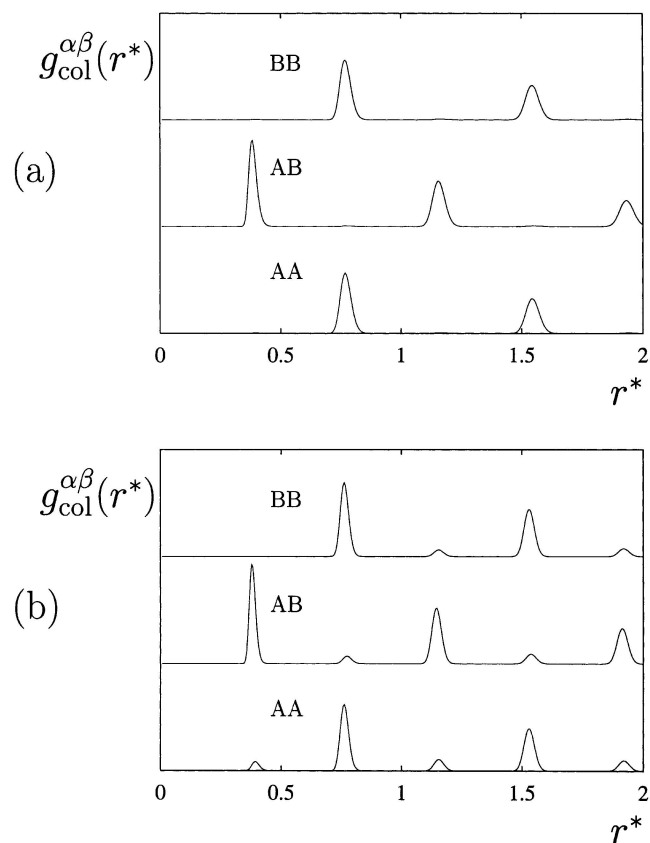


Figure 6. Columnar distribution functions in the columnar phase of (a) a symmetrical 50:50 system ($\mu_d = 0.0$, $P^* = 5$) and (b) an unsymmetrical 60:40 system ($\mu_d = 15.0$, $P^* = 5$). The separations are given as $r^* = r/\sigma_0$, in which $\sigma_0 = 0.345$ is the Gay-Berne parameter governing the distance at which the attractive and repulsive terms cancel in the face-to-face arrangement. Units for $g_{\text{col}}^{\alpha\beta}(r^*)$ are arbitrary.

nearest neighbour pairs can occur, means that this must arise from an AAB or BAA structure. The larger distance peaks can again be analysed in the same way. This leads us to the conclusion that the structure is based on an ... ABABABAB... structure, but on adding the excess of species A, the columnar phase can incorporate this into the columns such that AA nearest neighbours do exist. However, if too much excess A is added such that the composition exceeds 60:40, the columnar phase can no longer accommodate this excess and this will lead to phase separation. The columnar phase will exist in the limiting 60:40 composition, with the excess forming an A rich isotropic phase.

The phase behaviour that we observe in the simulations is very similar to that observed for the HAT:PDQ9 systems [8, 9], where the 1:1 'compound' cannot be diluted by adding an excess of one of the components, but rather the excess material phase separates. In these simulations, we do not observe the columnar nematic

phase, and so we might wonder why this phase was observed in earlier simulations [11]; here, at a fixed concentration of 75:25, the columnar phase was observed to melt at $T^* \approx 2.5$ to form a columnar nematic phase, and then at $T^* \approx 2.8$ to the isotropic phase at a pressure $P^* = 25$. This behaviour can be explained using the phase diagram constructed from the semigrand canonical simulations at this pressure, shown in figure 4(d). Below $T^* = 2.5$, a system of composition 75:25 should phase separate into two distinct phases, one of 60:40 composition and one almost pure. As the systems studied in the simulations are necessarily small compared with real systems, the two phases do not phase separate due to the large free energy cost of forming the interface between them. Indeed, at this temperature both the mixed and the pure phases will be columnar, and so the resulting structure observed in the 75:25 mixture will be columnar. As the temperature is increased past $T^* = 2.5$, the pure system should melt, whilst the 60:40 one will remain in a columnar structure. This is the reason a disordered columnar structure was observed in the earlier simulations [11]; there are columns due to the columnar phase, but the overall phase structure is not a perfect columnar phase since this has been diluted with excess material which cannot fit into the columnar structure. This was interpreted as a columnar nematic phase, but it is now clear that this is due to phases of different composition which should phase separate but cannot in the fixed composition simulation.

If we return to the phase diagram, and the system is heated further, the composition (and thus the total amounts) of the two phases will change until at $T^* \approx 2.8$ the whole 75:25 system will have melted into the isotropic phase. This accounts for the change in the slope of the volume per particle for the temperature region between $T^* = 2.5$ and 2.8 [11]. It is also possible to understand the behaviour of the fixed 50:50 concentration system [11], in which the mixed columnar phase was observed directly on cooling from the isotropic phase at $T^* \approx 2.8$ –2.9. In the semigrand canonical simulations, the 50:50 mixture would remain columnar on heating until temperatures $T^* \approx 3.1$, where the entire system melts to the isotropic phase of the same composition. Thus there is no progressive phase separation, and the (false) columnar nematic phase was not observed in the fixed composition simulations. Note that this hysteresis observed in the simulations for the transition temperatures on heating and cooling is not uncommon for transitions between highly ordered and disordered phases.

5. Conclusions

We have simulated pure systems and mixtures of Gay–Berne quadrupolar discs. The mixtures are of interest because they provide a crude model with which to

understand the behaviour of real systems in which the components are tailored such that they stack into columns, along which the species alternate. The simple mixtures model presented here exhibits a phase behaviour which has much in common with the HAT:PDQ9 systems studied experimentally by Bushby and co-workers [8, 9]. Namely, a columnar phase is induced in the mixtures which is stable over a large temperature region, in comparison with the original melting temperatures. We have also shown that care must be taken when analysing the phase behaviour of mixtures, in that the phase behaviour reported in this paper is radically different from that for the same model using fixed composition simulations [11].

Since the model is quite crude, we cannot answer the question as to what stabilizes the columnar nematic phase observed by Praefcke and co-workers [3–7]. It is clear that the basic formation of the alternate stacks must be due to a strong face-to-face interaction between unlike molecules, such as that studied in this paper. The origin of the disruption of the columns to form a nematic phase is not known. However, the existence and length of the alkyl chains are clearly crucial for the formation of the columnar nematic, although chains attached to the periphery of the discs do not guarantee the formation of this phase, as it is not observed in the HAT:PDQ9 systems [8, 9]. To understand the role of chains on the phase behaviour, more advanced models which explicitly take these into account are necessary. Although such molecular features are taken into account in the atomic-based modelling based on pairs of molecules (such as for the HAT:PDQ9 systems [9]), their role in the formation of the columnar nematic phase from the columnar phase is still not clear.

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