The phase behavior of a binary mixture of rodlike and disclike mesogens: Monte Carlo simulation, theory, and experiment

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The phase behavior of a binary mixture of rodlike and disclike hard molecules is studied using Monte Carlo NVT (constant number of particles N, volume V, and temperature T) computer simulation. The rods are modeled as hard spherocylinders of aspect ratio $L_{HSC}/D_{HSC}=5$, and the discs as hard cut spheres of aspect ratio $L_{CS}/D_{CS}=0.12$. The diameter ratio $D_{CS}/D_{HSC}=3.62$ is chosen such that the molecular volumes of the two particles are equal. The starting configuration in the simulations is a mixed isotropic state. The phase diagram is mapped by changing the overall density of the system. At low densities stabilization of the isotropic phase relative to the ordered states is seen on mixing, and at high densities nematic–columnar and smectic A–columnar phase coexistence is observed. Biaxiality in the nematic phase is not seen. The phase diagram of the mixture is also calculated using the second virial theory of Onsager for nematic ordering, together with the scaling of Parsons and Lee to take into account the higher virial coefficients. The disc–disc and rod–disc excluded volumes are evaluated numerically using the exact overlap expressions, and the lower-order end-effects are incorporated. The exact rod–rod excluded volume is known analytically. In the case of the theoretical calculations, which are limited to translationally disordered phases, coexistence between two uniaxial nematic phases is predicted, as well as the stabilization of the disc-rich isotropic phases. As found in the simulation, biaxial nematic phases are not predicted to be stable. The phase equilibria of an experimental system is also reported which exhibits a behavior close to the system studied by computer simulation. As in the model mixtures, this system exhibits a marked destabilization of the ordered phases on mixing, while nematic–columnar demixing is observed at lower temperatures (the higher-density states). © *2003 American Institute of Physics.* [DOI: 10.1063/1.1598432]

I. INTRODUCTION

Binary mixtures of rodlike and disclike molecules are of interest in the context of phase behavior as they may exhibit liquid crystalline phases such as calamitic nematic (N+), discotic nematic (N−), columnar (Col) or smectic (SmA), in addition to the more common isotropic liquid and solid phases. Even in the case of mixtures of hard molecules, the interplay between the orientational, translational and mixing entropic contributions gives rise to a wealth of phase behavior comparable to that observed in simple mixtures with attractive interactions. In a series of recent papers[1–5] the theory of Onsager for isotropic–nematic transitions has been used to investigate the global phase behavior of mixtures of discs and rods. As well as the expected isotropic–nematic phase coexistence and azeotropy, nematic–nematic and isotropic–isotropic demixing, and heteroazeotropy can be observed for particular combinations of molecular parameters. In addition, much interest surrounds the possible existence of the nematic

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biaxial phase. Biaxial nematic phases are characterized by three directions of preferred alignment, though only two are independent. In theory, a biaxial nematic phase can form if the three axes of the constituent molecules align in a fluid, though the experimental evidence for such phases is still contentious.[6] A biaxial nematic phase was identified and characterized in a lyotropic nematic system of anisotropic micelles by Yu and Saupe,[7] although whether the transitions truly involve a biaxial nematic phase or a change in the shape of the micelles has recently been subject of debate.[8,9] On the other hand, biaxial nematic phases have been stabilized in a number of computer simulation studies involving pure model systems of hard[10] and Gay–Berne[11] ellipsoidal biaxial particles.

An alternative route to biaxial fluid phases could be provided, in principle, by mixing uniaxial rodlike and disclike particles. In an orientationally aligned fluid the axes of the cylindrically symmetrical rods and discs tend to adopt perpendicular orientations, resulting in a macroscopically biaxial phase. Alben[12] was the first to report the existence of a biaxial nematic phase in a mixture of rodlike and disclike molecules using a mean-field lattice model, but further examination of the model indicates that phase separation into two uniaxial nematic phases is likely to be a preferred equilibrium state.[13] A stabilization of the biaxial nematic phase with respect to nematic–nematic demixing can be induced in the presence unlike attractive interactions.[14,15] A very small difference in free energy separates the biaxial nematic phase and the nematic–nematic demixed state in these systems, so that the phase behavior is very sensitive to the theoretical approximations assumed in each case. It is thus not yet clear if the biaxial nematic phase initially proposed theoretically can be stable. Stroobants and Lekkerkerker[16] have considered a symmetric mixture of rods and discs (in which the like excluded volumes are equal) using the theory of Onsager together with a second-order Legendre expansion to evaluate the kernels of the orientational distribution function. Following from this work Varga *et al.*[3] have evaluated the kernels numerically and examined the phase behavior for a large number of aspect ratios (all corresponding to symmetric mixtures). As with the earlier study of Stroobants and Lekkerkerker, biaxial nematic phases are predicted. However, experiments carried out for mixtures with highly asymmetric rod and disc molecules (with aspect ratios of about 15 and 1/15) have shown that demixing into rod-rich and disc-rich phases is observed instead of a biaxial nematic phase.[17,18] The same system has also been studied using the theory of Onsager with the scaling of Parsons[19] and Lee,[20] using Gaussian trial functions to determine the equilibrium orientational distribution functions.[1] Good qualitative agreement with experiment is obtained, but the stability of the biaxial phase was not considered in the work. The biaxial phase was later considered[2] using a slightly different approximation. In this case stabilization of a biaxial nematic phase is predicted only for the less asymmetric mixtures. For aspect ratios close to those of the experimental mixture, the biaxial nematic phase is always found to be metastable with respect to nematic–nematic demixing. On the other hand, computer simulations of binary mixtures of hard-ellipsoidal molecules

with aspect ratios of $e_1 = 15$ and $e_2 = 1/15$, and $e_1 = 20$ and $e_2 = 1/20$ suggest that a biaxial nematic phase can be stabilized.[21]

The Onsager limit for the molecular aspect ratios is implemented in most theoretical approaches based on the second virial theory of Onsager, and hence the so-called end effects are neglected. However, it has recently been pointed out[5] that the end effects should not be neglected for aspect ratios less than 1000. When end effects are incorporated within the Onsager treatment the nematic–nematic demixing transition always turns out to be a more stable state than the mixed biaxial nematic phase for aspect ratios below 1000. It should be noted that, though the excluded volumes are accurately taken into account, in these calculations,[5] the free energy is not exact, since the Parsons–Lee scaling[19,20] is used to take account of higher body interactions. The delicate sensitivity of the phase transitions involving such phases does not allow confirmation of the stability of the demixing transition over the biaxial nematic phase at this stage. As was mentioned earlier, simulations involving mixtures of hard ellipsoids appear to suggest that there is a region in which biaxial nematic phases can be observed.

In a previous Monte Carlo computer simulation study,[22] we have shown that a mixture of rods and discs with short aspect ratios is seen to demix into two ordered phases as the density is increased; no sign of a stable biaxial nematic phase is observed. The interface of the demixed state was stabilized, and the molecular orientations across the interface were examined. In this work we examine the phase behavior of the system in more detail. As in the previous study, we consider a binary mixture of hard spherocylinders of aspect ratio $(L/D)_{HSC} = 5$ and hard cut-spheres of $(L/D)_{CS} = 0.12$, with a diameter ratio $D_{CS}/D_{HSC} = 3.62$ chosen so that the volumes of the two particles are equal. However, it is important to note that this mixture is not "symmetric," in the sense that the rod–rod and disc–disc excluded volumes are not equal. The relatively short molecular aspect ratios suggest that the model mixture corresponds to a thermotropic liquid crystal, and that the phase transitions occur at intermediate and high densities. We carry out canonical *NVT* Monte Carlo computer simulations, and compare the simulated phase boundaries with calculations performed with the Parsons–Lee scaling of the Onsager theory[19,20] scaling. In the theoretical calculations the rod–disc and disc–disc excluded volumes are evaluated numerically, and are essentially exact. The exact rod–rod excluded volume is known analytically.[23] In order to compare the findings with real systems, we report results of an experimental study of a binary mixture of two mesogenic molecules which exhibit the same phase behavior as the pure components in the simulation. We shall see that the phase behavior of this mixture is characterized by a marked nematic–columnar and smectic A-columnar (nematic–nematic in the case of the theory) demixing, and that biaxial nematic phases are not observed.

II. COMPUTER SIMULATION

Canonical *NVT* (constant number of particles *N*, volume *V*, and temperature *T*) Monte Carlo (MC-*NVT*) computer simulations are used to investigate the phase diagram of a
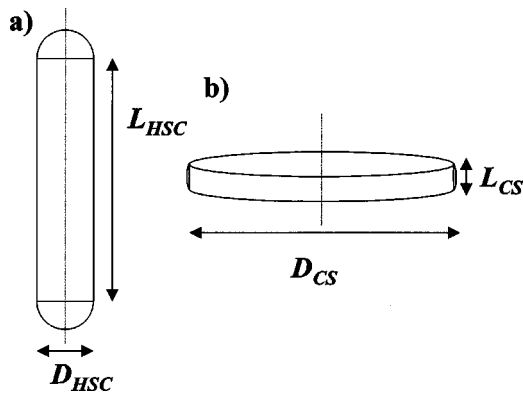
FIG. 1. (a) Rodlike molecules modeled as hard-spherocylinders of aspect ratio $L_{HSC}/D_{HSC}=5$. (b) Disclike molecules modeled as hard cut-spheres of aspect ratio $L_{HSC}/D_{HSC}=0.12$. The symmetry axes of the molecules are also indicated in the figure (dashed lines).

50:50 binary mixture of hard rodlike and disclike molecules. The rods are modeled as hard spherocylinders (HSC) of aspect ratio $(L/D)_{HSC}=5$, and the discs as hard cut-spheres (CS) of aspect ratio $(L/D)_{CS}=0.12$ (see Fig. 1). The diameter ratio is chosen to be $D_{CS}/D_{HSC}=3.62$, so that both particles have the same molecular volume to prevent any demixing due to size differences.[24] The packing fraction in the system is hence given by $\eta=\rho v_{CS}=\rho v_{HSC}$ where $\rho=N/V$ is the number density, and $v_{CS}=(\pi/12)D_{CS}^3(L_{CS}/D_{CS})[3-(L_{CS}/D_{CS})^2]$ and $v_{HSC}=(\pi/6)D_{HSC}^3+(\pi/4)L_{HSC}D_{HSC}^2$ are the molecular volumes of the cut-sphere and spherocylinder, respectively. While the Gibbs ensemble Monte Carlo (GEMC) technique[25] is very powerful for simulating two (or more) phases in coexistence, the relatively short aspect ratios of our molecules mean that the liquid crystalline phase transitions occur at very high densities. A GEMC cycle involves random particle displacements and reorientations, volume changes, and particle interchanges between the two simulation boxes, where this final step ensures the equality of the chemical potentials of the components in the phases. At high densities the probability of a successful particle insertion is extremely small, so that the simulation times are prohibitively long for these systems. In view of this, we use a direct Monte Carlo method to simulate coexisting phases in a single box, which has the added advantage of providing information about the interface. The simulation cell is prepared by arranging two half boxes side-by-side, one with $N_{HSC}=510$ rodlike particles and another with $N_{CS}=510$ disclike particles. The two sides are then allowed to mix by performing random particle displacements and orientation changes with an acceptance ratio of about 30%–40%. The liquid crystal phases are characterized using the nematic order parameter, which can be obtained from the ordering matrix

$$\mathbf{Q}=\frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha}\underline{\omega}_i^\alpha\underline{\omega}_i^\alpha, \tag{1}$$

where α indicates the type of component, and $\underline{\omega}_i$ corresponds to a vector coinciding with the molecular axis. On diagonalizing the tensor $\mathbf{Q}$, three eigenvalues can be obtained ($\lambda_+>\lambda_0>\lambda_-$), and the order parameter is then given by

$$S_\alpha=\tfrac{3}{2}\lambda_+-\tfrac{1}{2}. \tag{2}$$

A value of $S_\alpha=0$ corresponds to an isotropic phase, and $S_\alpha=1$ to a perfectly ordered phase. The director $\underline{\omega}_n$, which describes the principal orientation of the phase, is given by the corresponding eigenvector of λ_+. The difference Δ between the remaining eigenvalues[26]

$$\Delta_\alpha=\lambda_0-\lambda_-, \tag{3}$$

can be used to provide an indication of the biaxiality of the phase. We determine the density and order parameter profiles in order to characterize the state of the system.

TABLE I. Canonical *NVT* Monte Carlo simulation results for a binary mixture of $N_{HSC}=510$ $(L/D)_{HSC}=5$ hard spherocylinders and $N_{CS}=510$ $(L/D)_{CS}=0.12$ hard cut spheres. η_i is the starting total packing fraction, η the packing fraction of the equilibrated phases, x_{CS} the mole fraction of cut-spheres of the phase, and S_{CS} and S_{HSC} the order parameters of cut-spheres and spherocylinders in each phase. The asterisk indicates that the phases were obtained by expanding a system of higher density.

η_i	x_{CS}	η	S_{CS}	S_{HSC}	Single phase Phase
0.44	0.50	0.44	0.10	0.12	I
0.46	0.50	0.46	0.13	0.14	I

| | Two phase coexistence | | | | | | | | | |
| | Disc-rich | | | | | Rod-rich | | | | |
η_i	x_{CS}	η	S_{CS}	S_{HSC}	Phase	x_{CS}	η	S_{CS}	S_{HSC}	Phase
0.48	0.60	0.49	0.36	0.68	Col	0.36	0.47	0.35	0.71	N+
0.50	0.77	0.52	0.74	0.76	Col	0.13	0.46	0.35	0.82	N+
0.52	0.96	0.58	0.92	0.75	Col	0.04	0.49	0.25	0.90	SmA
0.48*	0.93	0.50	0.78	0.42	Col	0.20	0.45	0.33	0.78	N+
0.46*	0.93	0.49	0.76	0.25	Col	0.22	0.43	0.26	0.63	N+

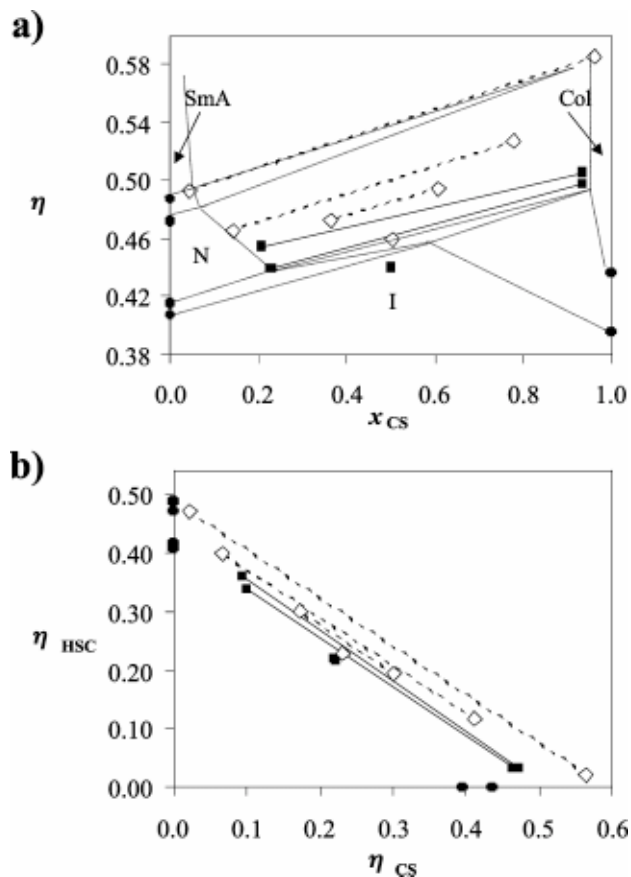| η_i	x_{CS}	η	S_{CS}	S_{HSC}	Single phase Phase
0.44*	0.50	0.44	0.12	0.15	I

FIG. 2. Phase diagram of a binary mixture of $L_{HSC}/D_{HSC}=5$ hard spherocylinder and $L_{HSC}/D_{HSC}=0.12$ hard cut-sphere molecules in the (a) packing fraction composition $\eta-x_{CS}$, and (b) rod-disc packing fraction $\eta_{HSC}-\eta_{CS}$ representations obtained by Monte Carlo NVT computer simulation. The filled circles indicate the transitions of the pure hard-spherocylinder fluid (Ref. 29), and cut-sphere fluid, the open diamonds states obtained by compression and the filled squares indicate states obtained by expansion (see text for more details).

At a packing fraction of $\eta=0.40$ a fully mixed isotropic state is equilibrated, and used as a starting configuration for a subsequent run of higher density. The density is increased in a number of steps, in each case starting from the previous equilibrated configuration. We have performed a set of compression simulations for packing fractions $\eta=0.44$, 0.46, 0.48, 0.50, and 0.52. A second set of expansion simulations have also been carried out for decreasing densities $\eta=0.48$, 0.46, and 0.44. The initial configuration for the case of $\eta=0.48$ was taken to be the equilibrated state of $\eta=0.50$, and the simulations at $\eta=0.46$ and 0.44 are started from the previous equilibrated configuration of higher density. The phases observed, order parameters, and densities of each of the coexisting phases are presented in Table I. The values presented are obtained by examining the density and order parameter profiles in each case. As a criterion to estimate the compositions of the phases we follow the density profile of the spherocylinders, as it is smoother than that of the cut-spheres, and define a phase where the profile is relatively flat. With this criterion it is possible to obtain the compositions of each of the phases and the corresponding order parameters. Though the estimates may be subject to large errors, at this stage we aim solely to give a qualitative indication of the

type of phase behavior exhibited by the system in terms of a phase diagram.

In Fig. 2 the phase diagram obtained from the MC-NVT computer simulations for the mixture of hard spherocylinders of aspect ratio $(L/D)_{HSC}=5$ and hard cut spheres with $(L/D)_{CS}=0.12$ is presented. A destabilization of the ordered phases upon mixing is noticeable in the phase diagram. In a fluid of pure hard spherocylinders of $(L/D)_{HSC}=5$ the isotropic–nematic transition is observed for packing fractions $\eta_I=0.407-\eta_N=0.415$, and the nematic–smectic A transition for packing fractions $\eta_N=0.472-\eta_{SmA}=0.487$.[27–30] Similarly, in a fluid of pure hard cut spheres of $(L/D_{CS}=0.12)$ an isotropic–columnar phase transition is observed for packing fractions $\eta_I=0.395-\eta_{Col}=0.436$.[31,32] However, the simulated equimolar mixture presents a stable mixed isotropic phase for packing fractions up to 0.44 at least. The findings of theoretical[3] and computer simulation[21] studies involving mixtures of hard molecules of large aspect ratios suggest a small stabilization of the ordered phases upon mixing, sometimes with the formation of biaxial nematic phases. The entropy of mixing always favors mixed states, whether ordered or disordered. A balance between the like and unlike excluded volumes of the components in the free volume entropy (which favors states that maximize the packing entropy, which are usually, but not always, ordered), and the orientational entropy (which favors disordered states) further determines the nature of the phases. The stabilization of the biaxial nematic phases appears to suggest that for systems with large molecular aspect ratios there is a gain in entropy due to ordering in a mixed phase, but the extra gain in packing entropy associated with demixing into two ordered phases does not compensate for the loss of entropy of mixing. In mixtures involving particles of smaller aspect ratios, the mixed phases are always found to be isotropic rather than biaxial nematic, indicating that the loss of orientational entropy does not compensate for the gain in packing entropy in this case. As we will see, however, the gain in packing entropy upon demixing at high densities is such that it compensates for both the loss of entropy of mixing and of orientational entropy; orientationally ordered demixed states are observed in this case. The detailed interplay of the free energy contributions in these systems has also been observed by Fraden and co-workers.[33,34] They have studied mixtures of aligned hard spherocylinderlike and hard spherical molecules, comparing experimental measurements, theoretical calculations and computer simulations. In their mixtures a stabilization of mixed lamellar phases is seen instead of the more intuitive rod-sphere separation.

In previous work[22] we reported that at a total packing fraction of $\eta=0.44$, the mixture is found to be in a fully mixed isotropic state, and that when the density is increased to $\eta=0.48$ coexistence between ordered rod-rich nematic and disc-rich columnar states is observed, both of which are found to be uniaxial. In the disc-rich columnar phase both the rods and the discs exhibit ordering, but the directors are parallel (uniaxial phase) instead of normal to each other (as would correspond to a biaxial phase). In the rod-rich nematic phase the symmetry axes of the discs lie in the plane normal
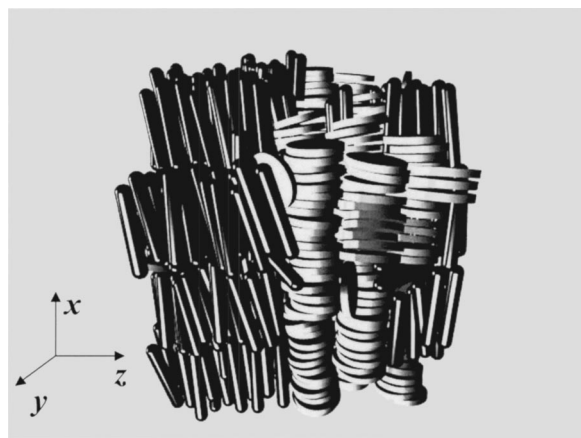
FIG. 3. Snapshot of a typical configuration for an equimolar mixture of $L_{HSC}/D_{HSC}=5$ hard spherocylinder and $L_{HSC}/D_{HSC}=0.12$ hard cut-sphere molecules at a total packing fraction of $\eta=0.52$. A rod-rich smectic A phase can be seen in coexistence with a disc-rich columnar phase.

FIG. 4. (a) Packing fraction η, (b) nematic order parameter S, and (c) biaxial order parameter Δ profiles along the z direction normal to the interface in an equimolar mixture of hard spherocylinders and cut spheres of total packing fraction $\eta=0.52$ obtained by compressing a state at $\eta=0.50$. The thick curves correspond to the profiles of cut-sphere molecules, and the thin curves to the profiles of the spherocylinders. The dashed curve in (a) corresponds to the total packing fraction profile.

to the nematic director of the rods, but are random within that plane, corresponding to a so-called random planar phase. We have further increased the density to $\eta=0.50$ and continue to observe a rod-rich nematic phase in coexistence with a disc-rich columnar phase with a wider phase separation in terms of the compositions. The coexistence compositions, densities and order parameters of rods and discs in each phase are presented in Table I. When the total density is further increased to $\eta=0.52$ a rod-rich smectic-A phase is found in coexistence with a disc-rich columnar phase (see Fig. 3). This is a rare example of computer simulations revealing the stable coexistence and interface between two ordered phases in a model mixture of liquid-crystal molecules. The coexistence is characterized by a marked phase separation in terms of the compositions; the rod-rich phase has mole fraction of cut spheres of $x_{CS}=0.04$ ($x_{HSC}=0.96$), and the disc-rich phase of $x_{CS}=0.96$ ($x_{HSC}=0.04$) (also see Table I). The density and order parameter profiles for the equilibrium configuration are presented in Fig. 4. The profiles have been averaged over 10^7 cycles with bin lengths $\Delta z \approx D_{HSC}$ in order to obtain reasonably smooth data. It should be noted that even though the bin length is chosen rather large to ensure that enough particles are taken into account in the calculation of the order parameters, the compositions of the coexisting phases are such that, in cases, very few particles of a given type are present. This is especially relevant to the calculation of the order parameters of the discs inside rod-rich phases. The densities of the phases are estimated to be $\eta=0.49$ in the rod-rich phase and $\eta=0.58$ in the disc-rich phase. A small destabilization with respect to the transition densities of the pure components is again seen; a pure fluid of hard-spherocylinders of $(L/D)_{HSC}=5$ exhibits a nematic–smectic A phase transition at packing fractions of $\eta_N=0.472$ and $\eta_{SmA}=0.487$.[29] In this configuration, the interface lies normal to the layers of the rod-rich smectic phase, so that the density profile of the rodlike molecules is homogeneous in the direction z normal to the interface. On the other hand, the columns of the disc-rich columnar phase lie parallel to the interface, and hence the density profile of the disclike molecules provides an indication of the structure of
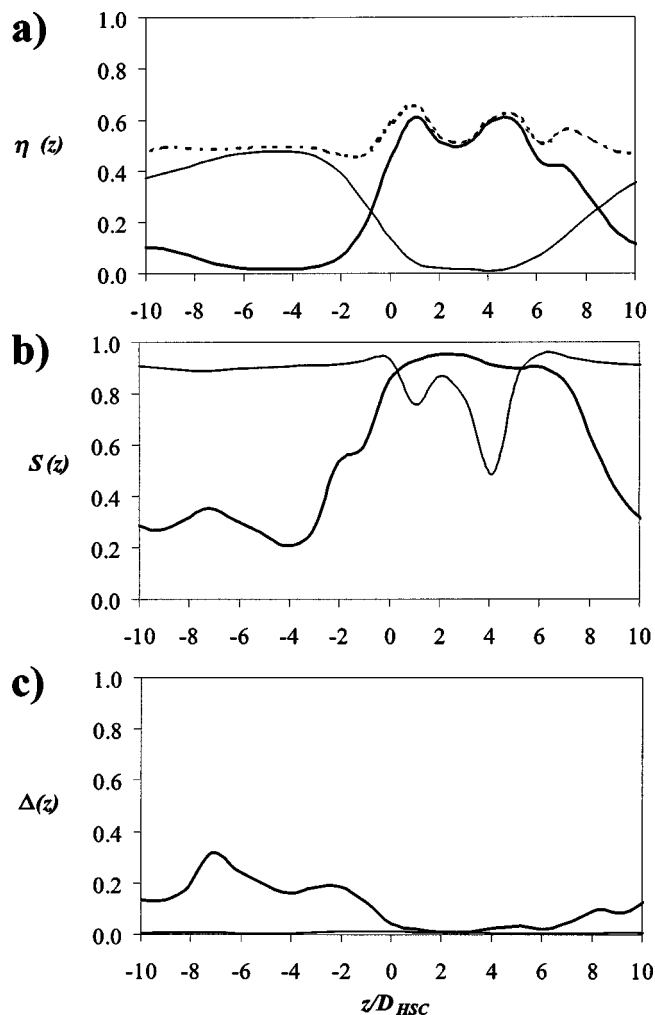
this phase [see Fig. 4(a)]. The width of the interface is of the order of $2D_{HSC}$ as can also be seen in the figure.

The nematic order parameter profiles are shown in Fig. 4(b). A large degree of order is seen in the phases. The cut-sphere and hard-spherocylinder order parameters are $S_{CS}=0.25$ and $S_{HSC}=0.90$ in the rod-rich smectic A phase, and $S_{CS}=0.92$ and $S_{HSC}=0.75$ in the disc-rich columnar phase. The order parameter of the smectic A phase is of a similar magnitude to that of the pure hard-spherocylinder fluid at the same density, as would be expected from the low mole fraction of cut spheres in the phase. In the disc-rich columnar phase, the rods are aligned parallel to the direction of the columns, and the biaxial order parameter Δ is found to be negligible. By contrast, in the case of the rod-rich phase, the symmetry axes of the discs are found to lie in a plane normal to the nematic director of the rods. This results in a value of Δ different from zero, but, as we have already mentioned in a previous paper,[22] the phase is not biaxial. The biaxial order parameter is not negligible due to the fact that,
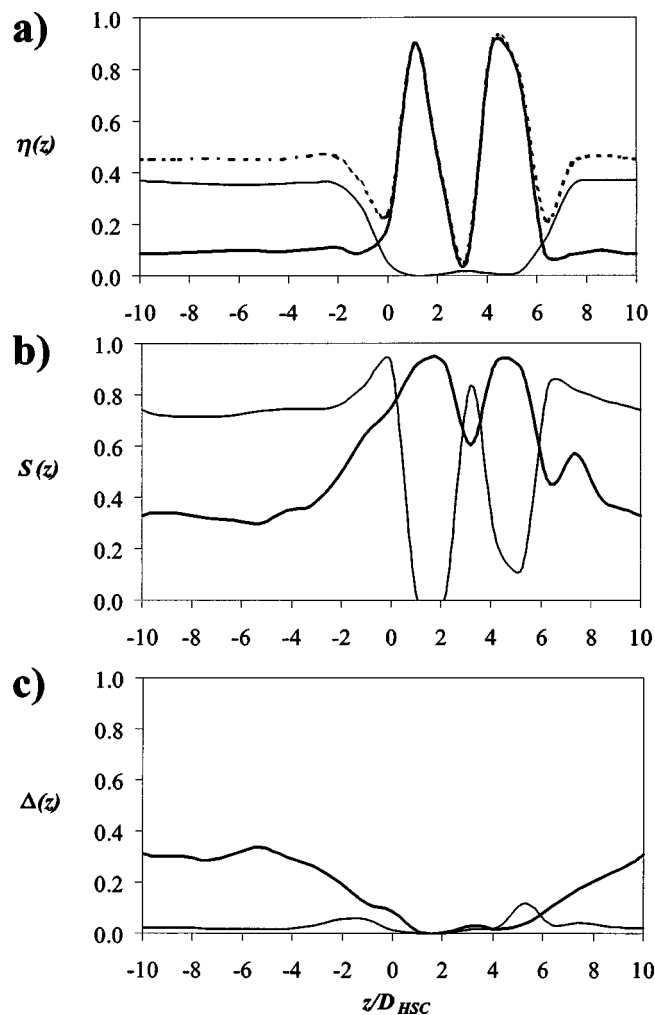
a)

b)

c)

FIG. 5. (a) Packing fraction η, (b) nematic order parameter S, and (c) biaxial order parameter Δ profiles along the z direction normal to the interface in an equimolar mixture of rods and discs of total packing fraction $\eta=0.48$ obtained by expanding a state at $\eta=0.50$. The thick curves correspond to the profiles of cut-sphere molecules, and the thin curves to the profiles of the spherocylinders. The dashed curve in (a) corresponds to the total packing fraction profile.
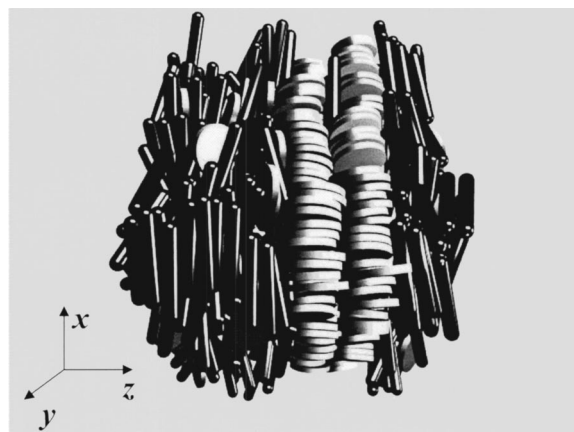

FIG. 6. Snapshot of a typical configuration for an equimolar mixture of $L_{HSC}/D_{HSC}=5$ hard spherocylinder and $L_{HSC}/D_{HSC}=0.12$ hard cut-sphere molecules at a total packing fraction of $\eta=0.48$. A rod-rich nematic phase can be seen in coexistence with a disc-rich columnar phase.

state. The corresponding density and order-parameter profiles are presented in Fig. 5, and a snapshot of the configuration is shown in Fig. 6. The stabilization of the interface between the rod-rich nematic phase and the disc-rich columnar phase is clearly seen in the figures. The director of the rod-rich nematic phase again lies parallel to the interface, and so does the director of the disc-rich columnar phase. It is interesting to note that a different configuration is possible in which the director of the disc-rich phase is normal to the director of the rod-rich nematic phase, and normal to the interface. As a mixed isotropic phase is used as the starting configuration, we have not biased the system, which suggests that we obtain the true equilibrium configuration. It is also noticeable from Fig. 5(b) that the order parameter of the spherocylinders increases at the interface. The order parameter of the rods inside the cut sphere-rich phase is also very high ($S_{HSC}=0.78$), but this phase is not biaxial, with the director of the rods parallel to the direction of the columns of cut spheres. In the rod-rich phase, however, the cut-spheres exhibit little order, suggesting that this phase is also uniaxial. The profile of the biaxial order parameter follows the trends observed previously, i.e., the parameter is found to be non-zero in the rod-rich phase, with the discs arranged in a random-planar configuration rather than being oriented in one preferential direction normal to the director of the rods (which would correspond to a biaxial nematic phase).

It is clear from the table and the phase diagrams of Fig. 2 that a wider phase separation is achieved when the system is expanded. The expansion allows the system to "anneal" into more stable states with a higher degree of order and fewer defects. However, in order to be confident that the phase separation is spontaneous it was necessary to compress a mixed isotropic phase rather than start with an ordered demixed state. In such a way we have been able to demonstrate the existence of nematic–columnar and smectic A–columnar phase separation, rather than the stability of biaxial nematic states. However, the expanded state at $\eta=0.48$ now exhibits an increased degree of phase separation, and a question arises about the lower-density states at $\eta=0.46$ and 0.44. Would these exhibit phase separation on expansion or

while we have defined a biaxial order parameter in three dimensions, the cut-disc molecules only access configurations in the plane normal to the director of the rods. It is important to mention also that in the transition from the nematic–columnar to the smectic A–columnar coexistence, a three-phase region must be present in the phase diagram. The size of our system is not big enough to allow for these three phases to be represented at the same time.

Before ending our examination of the computer simulation data we turn our attention back to the lower-density states. We have already mentioned that columnar–nematic coexistence is first observed for a total packing fraction $\eta=0.48$. A snapshot of a configuration exhibiting this phase behavior was presented in a previous work.[22] We have further stabilized this demixed state by carrying out small compression and expansion runs which have eliminated defects previously observable in the columnar phase. An increased order parameter and a sharper interface of width $2D_{HSC}$ (this run is labeled 0.48* in Table I) are now reported for this

would the mixed isotropic states be confirmed as stable configurations? As indicated in Table I, we find that when the density is lowered from $\eta=0.48$ to $\eta=0.46$ the nematic–columnar demixed state persists (a run of the order of 10^8 cycles was carried out to confirm this result). When the density is lowered to $\eta=0.44$ a mixed isotropic phase is readily obtained; the order parameters and coexisting compositions are presented in Table I. A three phase region must also exist mediating the transition between the mixed isotropic phase and the demixed nematic–columnar state.

In summary, the destabilization of the ordered phases on mixing for this mixture of rodlike and disclike molecules of short aspect ratios is confirmed. At high densities a marked demixing between disc-rich columnar phases and rod-rich nematic and smectic-A phases is observed instead of biaxial nematic states.

III. SCALED ONSAGER THEORY

Computer simulations can provide unequivocal answers concerning the stability, and the phase behavior, of a system. Unfortunately, such simulations can also be very time consuming. In the case of systems of hard particles, such as the one presented here, the difference in free energy and the interfacial tension between two phases in coexistence is extremely small. This results in very long computer times for the system to equilibrate. Investigation of global phase behavior in which the phase-space of the intermolecular parameters (e.g., aspect ratios and molecular volumes) are carried out are not viable by computer simulation. So far, we have been able to confirm that biaxial nematic phases are not present in the system of interest, but the question remains open for the case of mixtures involving other particle sizes or at different compositions. It is useful then to turn to theoretical models to carry out studies of global phase behavior. A number of such studies have recently been carried out using the theory of Onsager for isotropic–nematic ordering transitions in different approximations.[3–5] These studies have concentrated mainly on mixtures of particles with relatively large aspect ratios where the theories are more accurate. It is useful also, however, to consider here how such theoretical approaches compare with our computer simulation results.

In the original approach of Onsager[35] the free energy of the system is obtained as a functional of the single-particle orientational distribution function at the level of the second virial coefficient, in which the excluded volume of a pair of molecules is incorporated. The theory is exact in the limit of particles of infinite aspect ratios when the isotropic–nematic transition occurs at vanishingly low density. The scaling proposed independently by Parsons[19] and Lee[20] provides a more accurate approach for systems of molecules with smaller aspect ratios. In addition to the excluded volume between pairs of molecules, the residual free energy of the hard-sphere fluid is used as a scaling factor in order to take into account virial coefficients higher than the second. The Parsons–Lee theory has been found to provide an excellent description of hard-spherocylinder[29] and hard-ellipsoid[36] fluids, and more recently, mixtures of rodlike particles.[37] In this section we carry out calculations with the Parsons–Lee scaling in order to obtain a theoretical phase diagram for our system of interest. It is important to mention at this stage that these scaled Onsager theories can be used to describe isotropic–nematic phase transitions, but not transitions involving phases with translational order. The comparisons provided here are entirely qualitative. More sophisticated approaches, which take into account orientational and positional order have been developed to model smectic phases (see, for example, Ref. 38); unfortunately columnar phases have not yet been considered. Furthermore, the complexity of the approaches somewhat hinders their application at this stage to calculations of mixture phase behavior. As will become clear, our aim here is to indicate that demixing between orientationally ordered phases is seen in this system instead of a mixed biaxial nematic phase. In this sense a link between the computer simulations and the theoretical approach is made. Our simulations suggest that in mixtures of hard rodlike and disclike molecules of short aspect ratios, demixing is favored. This has also been discussed in a study of the global phase behavior of mixtures of hard rod and disc particles modeled as cylinders and using the scaled Onsager theory.[5] In this work we present only the main expressions of the Parsons–Lee theory and refer the reader to previous work[5,35] for more detail.

The Helmholtz free energy of a binary mixture in the Parsons–Lee approach is written as a functional of the orientational distribution functions (f_i, $i=1,2$) of the molecules in the mixture. We assume the one-fluid approximation[10,21,39] to generalize the original theory to model mixture phase behavior

$$\frac{\beta F}{N} = \sum_{i=1}^{2} x_i \left(\ln \rho - 1 + \ln \frac{\mathcal{V}_i}{4\pi} + \ln x_i + \sigma[f_i] \right) + \frac{4\eta - 3\eta^2}{(1-\eta^2)} \frac{\iint (x_1^2 v_{11}^{\text{exc}} f_1 f_1 + 2x_1 x_2 v_{12}^{\text{exc}} f_1 f_2 + x_2^2 v_{22}^{\text{exc}} f_2 f_2) d\underline{\omega}_1 d\underline{\omega}_2}{8(x_1 v_1 + x_2 v_2)}, \quad (4)$$

where $\beta=1/kT$ (k is Boltzmann's constant and T the temperature), $\rho=N/V$ is the total number density, $\mathcal{V}_i$ the de Broglie volume, and x_i the mole fraction of component i. The sum corresponds to the ideal translational and rotational contributions, the ideal entropy of mixing, and the ideal orientational entropy. The orientational entropy term $\sigma[f_i]$ is a function of the one-particle orientational distribution function $f_i(\underline{\omega})$, and can be written as
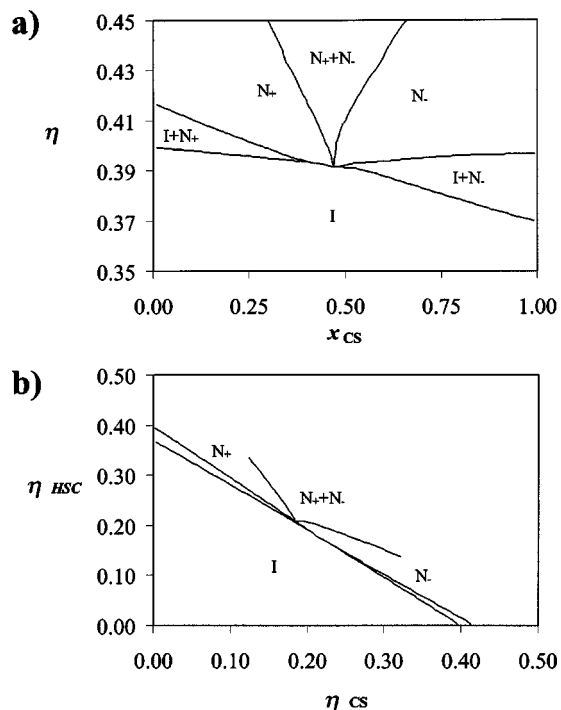
a)

b)

FIG. 7. Phase diagram of a binary mixture of $L_{HSC}/D_{HSC}=5$ hard sphero-cylinder and $L_{HSC}/D_{HSC}=0.12$ hard cut-sphere molecules in the (a) packing fraction-composition $\eta - x_{CS}$, and (b) rod-disc packing fraction $\eta_{HSC} - \eta_{CS}$ representation obtained using the theory of Onsager with the Parsons–Lee scaling. N_+ indicates a rod-rich nematic phase, N_- a disc-rich nematic phase, and I an isotropic phase. The curves indicate the phase boundaries predicted by the theory.

$$\sigma[f_i] = \int f_i(\underline{\omega}) \ln[4\pi f_i(\underline{\omega})] d(\underline{\omega}), \qquad (5)$$

where $\underline{\omega}$ is the orientational unit vector parallel to the molecular symmetry axis; it is determined by a polar angle $0 < \theta < \pi$ and an azimuthal angle $0 < \phi < 2\pi$. The second term takes into account the repulsive interactions, where $\eta = \rho(x_1 v_1 + x_2 v_2)$ is the packing fraction as before, and v_{ij}^{exc} is the excluded volume between particles i and j. For the sake of brevity, the orientational dependence of the excluded volumes and the orientational distribution functions are not shown in Eq. (4). The equilibrium orientational distribution functions and free energy are obtained by taking the functional minimum of Eq. (4) with respect to each orientational distribution function (f_i) while imposing the normalization constraints $(\int f_i(\underline{\omega}) d\underline{\omega} = 1)$. The numerical details of the minimization procedure can be found in Ref. 4. The nematic order parameter S_i of each component i is obtained as

$$S_i = \int P_2(\cos\theta) f_i(\underline{\omega}) d\underline{\omega}, \qquad (6)$$

where $P_2(\cos\theta) = \frac{3}{2}\cos^2\theta - \frac{1}{2}$ is the second Legendre polynomial, and $\theta = \arccos(\underline{\omega}_n \cdot \underline{\omega}_i)$ is the angle between the nematic director $\underline{\omega}_n$ and the symmetry axis $\underline{\omega}_i$ of molecule i. In this work the disc–disc and rod–disc excluded volumes are calculated numerically and are exact. Note that the exact rod–rod excluded volume is known analytically.[23]

The calculated phase diagram of a binary mixture of hard-spherocylinders of aspect ratio $(L/D)_{HSC}=5$ and hard

cut spheres of $(L/D)_{CS}=0.12$ (and $D_{CS}/D_{HSC}=3.62$) is presented in Fig. 7. The isotropic–nematic phase transition for the pure fluid of hard spherocylinders calculated with the Parsons–Lee approach is in very good agreement with the simulation data (see also Ref. 29). In the case of the hard cut-sphere fluid, the agreement is poorer; it is known that the original approximation of Onsager is not as accurate for oblate particles as for prolate particles.[35,40] In addition to this, the computer simulation results indicate that the fluid of hard cut spheres of aspect ratio $(L/D)_{CS}=0.12$ does not exhibit a stable nematic phase, and instead an isotropic–columnar phase transition is seen. In this sense, it is not possible to carry out a quantitative comparison between the theoretical and simulation results.

It is useful, nevertheless, to address two important points regarding the phase behavior of our mixture. Contrary to what is observed in mixtures of molecules of similar volume but with large aspect ratios, a stabilization of the isotropic phase relative to the ordered phases is seen in our mixture of molecules with short aspect ratios. The simulation results presented earlier clearly indicate a stabilization of the isotropic phase (see Fig. 2); although less marked, the theoretical calculations also predict a stabilization of the isotropic phase, especially for the disc-rich phases. In addition to this, a de-mixing transition is observed at the higher densities (see Figs. 2 and 7) both from the computer simulations and from the predictions of the Parsons–Lee approach. In previous work[5] calculations corresponding to symmetric mixtures of rodlike and disclike molecules have been presented using the same approach. It was demonstrated that biaxial nematic phases are not found to be stable, at least in the context of the theory of Onsager with the Parsons–Lee scaling. As a consequence, we did not consider the possibility of the existence of a nematic biaxial phase for our present system. At the higher densities nematic–nematic demixing is observed as suggested by the simulation study (note that in the case of the simulations the coexistence is between nematic and co-lumnar phases instead of between two nematic phases).

We now turn to an experimental investigation of an equivalent system in order to investigate further the stability of the biaxial nematic phase in liquid crystal fluids of molecules of short aspect ratios.

IV. EXPERIMENT

As we have already seen, the contrasting nature of rod-like and disclike molecules usually results in very different types of phase behavior. Rodlike molecules will form calamitic nematic and/or smectic phases, while disclike molecules will form discotic nematic and columnar phases under appropriate conditions. The so-called discotic nematic phases in which the symmetry axes of the molecules are aligned, but in which no positional order is observed, are relatively rare, and it is much more common to find disclike molecules forming columnar phases with two degrees of translational order. Though some theoretical studies have suggested that mixing a calamitic nematic with a discotic nematic would produce a biaxial nematic phase, we have not been able to confirm this in the case of molecules of short aspect ratios corresponding
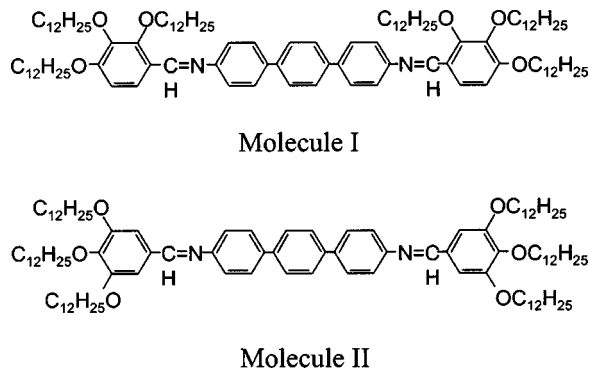
FIG. 8. 4,4″(p-terphenyl)-bis[2,3,4-tri) dodecyloxy) benzal]imine (molecule I) and 4,4″(p-terphenyl)-bis[3,4,5-tri) dodecyloxy) benzal]imine (molecule II).
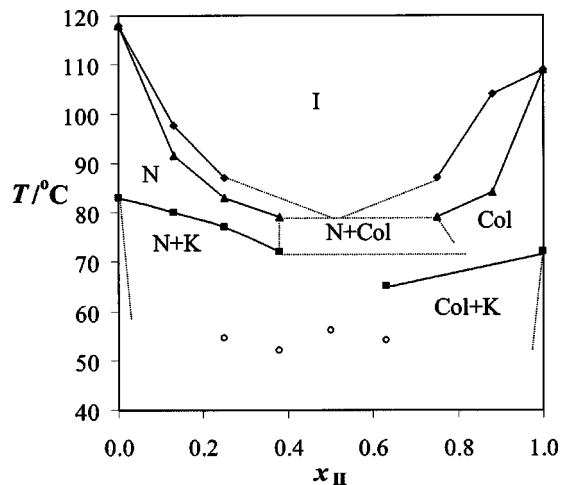

FIG. 9. Experimental phase diagram of a binary mixture of 4,4″(p-terphenyl)-bis[2,3,4-tri) dodecyloxy) benzal]imine (molecule I) and 4,4″(p-terphenyl)-bis[3,4,5-tri) dodecyloxy) benzal]imine (molecule II). Isotropic (I), nematic (N), columnar (Col), and crystal (K) phases are observed. The solid and dashed lines are provided to guide the eye.

to thermotropic liquid crystal phases. The chemical constitution of such systems is so different that they are usually immiscible, and so mixed phases are not observed. Note also that our repulsive model system studied theoretically demixes for purely entropic reasons.

In order to avoid the problem of immiscibility, it is desirable that the two components of the rod-disc mixture are as chemically similar as possible. Such a system is provided by the compounds 4,4″(p-terphenyl)-bis[2,3,4-tri)dodecyloxy)benzal]imine (molecule I) and 4,4″(p-terphenyl)-bis[3,4,5-tri)dodecyloxy)benzal]imine (molecule II) (see Fig. 8). These are simple chemical isomers, and as such would be expected to have a similar phase behavior and physical properties. The asymmetrically substituted species I has a nematic phase (an isotropic–nematic transition is seen at $T = 118\,°C$), while the symmetrically substituted molecule II exhibits a hexagonal columnar phase (an isotropic–columnar phase transition is seen at $T = 109\,°C$). It has been claimed that compound I does exhibit a biaxial nematic

phase,[41] but this has not been confirmed by structural studies or nuclear magnetic resonance (NMR) spectroscopy.[6] In our experimental study, we have constructed the binary phase diagram of the mixture of molecules I and II. This was done by making a range of mixtures of different compositions, and observing their behavior as a function of temperature using a Zeiss Universal polarizing microscope with a Linkam hot-stage. The experimental phase diagram is given in Fig. 9. As can be seen in the figure, a biaxial phase is not observed in the mixture. It is perhaps surprising that the symmetric species II forms a columnar phase, but the structure of the columns is presumed to be stacks of overlapping aromatic cores, around which the terminal alkyl chains form a cylin-
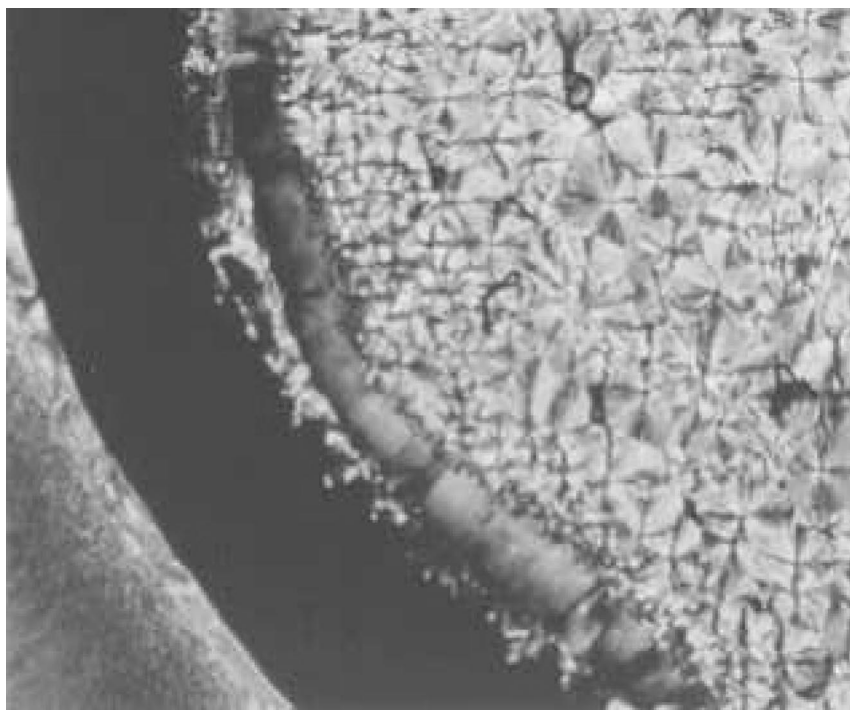

FIG. 10. Snapshot of a microscopic contact preparation for a mixture of 4,4″(p-terphenyl)-bis[2,3,4-tri) dodecyloxy) benzal]imine and 4,4″(p-terphenyl)-bis[3,4,5-tri) dodecyloxy) benzal]imine. From right to left, columnar, isotropic, and nematic phases are seen.

drical sheath. It is noticeable from the phase diagram that the ordered phases are destabilized on mixing. The region of miscibility can be conveniently observed using a microscopic contact preparation, which allows all compositions to be observed as the temperature is changed. In Fig. 10 we reproduce a snapshot of the contact preparation, which shows the coexisting hexagonal columnar phase, the isotropic phase, and the nematic phase. Also clearly visible is the wide two-phase region at the isotropic–columnar phase interface. No evidence of a new biaxial phase stabilized is observed in these mixtures. This is consistent with the predictions of the model systems studied in earlier sections.

V. CONCLUSIONS

Canonical MC computer simulations and theoretical calculations have been carried out for a binary mixture of rodlike and disclike model molecules of short aspect ratios (corresponding to the dimensions of real thermotropic mesogens). In both investigations a destabilization of the ordered phases on mixing is seen. When the ordered phases eventually become stable, demixing is observed instead of biaxiality. In the case of the computer simulations, we have been able to stabilize states exhibiting nematic–columnar and smectic A-columnar demixing, while only nematic–nematic separation was examined in the theoretical calculations. In this work we have used the theory of Onsager with the scaling of Parsons and Lee, which does not treat translationally ordered phases. The phase behavior of the model mixtures is compared with experimental results obtained for a mixture of two isomers, one of which exhibits an isotropic–nematic transition, and the other an isotropic–columnar transition. The reason for choosing two isomers is that the similar size of the molecules can promote mixing, while the different symmetry of the ordered phases may promote biaxiality. The results obtained in the experimental investigation do not, however, suggest the existence of a biaxial phase. Instead, phase separation between a nematic and a columnar phase is seen. The destabilization of the ordered phases suggested by the theoretical models is also confirmed.

Though the three approaches considered in this study cannot be compared quantitatively, they all suggest that demixed ordered phases are favored rather than biaxial nematic phases in mixtures of mesogens of short aspect ratios. The stabilization of this exciting new phase remains a challenge, both from an experimental and from a modeling point of view.

ACKNOWLEDGMENTS

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