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Phase diagrams of a binary smectic-A mixture

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A variety of smectic phase diagrams involving smectic-isotropic and smectic-nematic-isotropic transitions have been calculated based on a combination of Flory–Huggins (FH) theory for isotropic mixing and Maier–Saupe–McMillan (MSM) theory for smectic-A ordering of liquid crystals (LC). To describe the mesophase transitions, two nematic order parameters and two smectic order parameters have been coupled through the normalized orientation distribution and partition functions. Flory–Huggins interaction parameter (χ) for isotropic mixing and the coupling term involving the nematic interaction parameter (ν) and the McMillan smectic interaction parameter (α) for phase transitions of liquid crystals have been incorporated in the calculation. The predictive capability of the present combined FH/MSM model for determining the coexistence regions of a binary smectic-A mixture has been demonstrated by critically testing with a reported smectic phase diagram. © 1997 American Institute of Physics. [S0021-9606(97)51441-3]

I. INTRODUCTION

Understanding thermodynamic phase equilibria in mixtures of polymers and liquid crystals (LC) has become increasingly important for successful applications of flat panel displays, particularly in the areas of polymer dispersed liquid crystal (PDLC) and polymer stabilized liquid crystal (PSLC).^{1–3} In this connection, there is a growing interest on experimental determinations as well as theoretical predictions of phase diagrams of various nematic LC systems such as polymer/nematics,^{3–5} side-chain liquid crystalline polymer (SCLCP)/nematics,⁶ and concomitant kinetics of phase separation in those PDLC systems.⁷ Recently, we have developed a theory⁸ based on a combination of the Flory–Huggins (FH) theory for isotropic mixing⁹ and the Maier–Saupe–McMillan (MSM) theory^{10–14} for smectic-A ordering of liquid crystals (LC) to predict phase diagrams of the mixtures of polymer and smectic liquid crystals undergoing phase transitions from smectic-A (S_{mA}) directly to an isotropic phase or by passing through a nematic phase. During that time, it was recognized that the FH/MSM theory can be extended to elucidating the induced smectic phase diagram in a nematic mixture as well as to predicting the phase diagrams of binary smectic LC mixtures.

In this paper, a variety of smectic phase diagrams involving smectic-A–isotropic ($S_{mA}I$) as well as smectic-A–nematic–isotropic ($S_{mA}NI$) transitions have been calculated by coupling the nematic interaction parameters and the smectic interaction parameters. Further, two nematic order parameters and two smectic order parameters corresponding to the constituent smectic liquid crystals are also coupled via the normalized orientation distribution function and partition function. The predictive capability of the present combined FH/MSM model for determining the coexistence regions of the binary smectic-A mixture has been tested rigorously with the reported smectic phase diagram.^{15,16}

II. THEORETICAL SCHEME

The dimensionless total free energy density of mixing, g , for a binary smectic mixture may be represented by a simple addition of the free energy of mixing of isotropic liquids, g^i , and the free energy of anisotropic ordering of the smectic liquid crystals, g^s , i.e., $g = g^i + g^s$. In general, the free energy density of isotropic mixing of a binary polymer blend may be best described in terms of the Flory–Huggins theory⁸, viz.,

$$g^i = \frac{G^i}{nkT} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi \phi_1 \phi_2, \quad (1)$$

where k is Boltzmann constant and T is absolute temperature. r_1 is the number of sites occupied by one liquid crystal molecule (unity for a low molar mass liquid crystal), whereas r_2 represents the number of statistical segments or sites occupied by a single polymer chain. ϕ_1 and ϕ_2 represent the volume fractions of component 1 and 2, respectively, which may be given by $\phi_1 = n_1 r_1 / n$ and $\phi_2 = n_2 r_2 / n$, where, n_1 and n_2 are the numbers of liquid crystal and polymer molecules, respectively, and $n = n_1 r_1 + n_2 r_2$.⁹ χ is known as the Flory–Huggins interaction parameter which is generally assumed to be a function of reciprocal absolute temperature, viz., $\chi = A + B/T$, where A and B are constants.⁹

On the other hand, the free energy density of the anisotropic ordering of smectic liquid crystal mixtures may be expressed in terms of the Maier–Saupe–McMillan theory^{10–14} (please see Appendix for the detailed derivation) in what follows:

$$g^s = \frac{G^s}{nkT} = -\sum_1 \phi_1 - \sum_2 \phi_2 - \frac{1}{2} \nu_{11} (s_1^2 + \alpha_1 \sigma_1^2) \phi_1^2 - \frac{1}{2} \nu_{22} (s_2^2 + \alpha_2 \sigma_2^2) \phi_2^2 - \nu_{12} (s_1 s_2 + \alpha_{12} \sigma_1 \sigma_2) \phi_1 \phi_2, \quad (2)$$

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where Σ_1 and Σ_2 represents the decrease of entropy due to the alignment of the individual LC molecule of component 1 and the mesogenic group of component 2, respectively. ν_{11} and ν_{22} are the nematic interaction parameters of the pure components, whereas ν_{12} represents the cross-nematic interaction between the dissimilar mesogens. α_1 and α_2 are the dimensionless smectic interaction parameters introduced by McMillan¹² for the constituent smectic LCs, as follows:

$$\alpha_j = 2 \exp[-(\pi r_{0j}/d_j)^2], \quad (3)$$

where r_{0j} represents the molecular length of component j ($j=1$ or 2) (i.e., it is of the order of the length of the rigid portion of the LC molecule) and d_j represents the interlayer distance of the component j in the smectic phase. α_j is a parameter that characterizes the interaction strength of the smectic-A phase which determines whether phase transition occurs from a smectic directly to an isotropic phase when $\alpha > 0.98$ or the transition otherwise occurs via a nematic phase. The α_j value may vary from 0 to 2. The cross-interaction strength between two-dissimilar smectics, α_{12} , may be expressed by equating it to its geometric mean, i.e.,

$$\alpha_{12} = \sqrt{\alpha_1 \alpha_2}. \quad (4)$$

The nematic order parameters, s_1 and s_2 , and smectic order parameters, σ_1 and σ_2 , are further defined as^{11,12}

$$s_j = \frac{1}{2} \langle 3 \cos^2 \theta_j - 1 \rangle, \quad (5)$$

$$\sigma_j = \frac{1}{2} \langle \cos(2\pi z/d_j)(3 \cos^2 \theta_j - 1) \rangle, \quad (6)$$

in which the subscript $j=1,2$ and θ_j is the angle between the director of a liquid crystal molecule belonging to the component j and the reference axis, z . The angle bracket, $\langle \rangle$, denotes the ensemble average which is defined as

$$\langle \cos(2\pi z/d_j) \cos^2 \theta_j \rangle = \int \int \cos(2\pi z/d_j) \cos^2 \theta_j \cdot f(z, \cos \theta_j) dz d\Omega_j, \quad (7)$$

where Ω_j denotes the solid angle. $f(z, \cos \theta_j)$ represents the normalized orientation distribution function and is considered to be symmetric around the reference axis, which may be defined by coupling the nematic and smectic ordering as follows:

$$f(z, \cos \theta_j) = \frac{1}{4\pi Z_j} \exp \left[\frac{1}{2} m_{n,j} (3 \cos^2 \theta_j - 1) \right] \times \exp \left[\frac{1}{2} m_{s,j} \cos(2\pi z/d_j) (3 \cos^2 \theta_j - 1) \right], \quad (8)$$

where Z_j is the partition function given as

$$Z_j = \int \int \exp \left[\frac{1}{2} m_{n,j} (3 \cos^2 \theta_j - 1) \right] \times \exp \left[\frac{1}{2} m_{s,j} \cos(2\pi z/d_j) (3 \cos^2 \theta_j - 1) \right] dz d\Omega_j, \quad (9)$$

in which $m_{n,j}$ and $m_{s,j}$ are dimensionless nematic and smectic mean-field parameters, respectively, which characterize the strengths of the respective potential fields,¹³ $m_{n,j} = \nu_{jj} s_j \phi_j$ and $m_{s,j} = \nu_{jj} \alpha_j \sigma_j \phi_j$. The order parameters, s_j and σ_j , can then be related to Z_j through

$$s_j = \int \int f(z, \cos \theta_j) \cdot \frac{1}{2} (3 \cos^2 \theta_j - 1) dz d\Omega_j = \frac{1}{Z_j} \frac{dZ_j}{dm_{n,j}}, \quad (10)$$

$$\sigma_j = \int \int f(z, \cos \theta_j) \cdot \frac{1}{2} \cos(2\pi z/d_j) \times (3 \cos^2 \theta_j - 1) dz d\Omega_j = \frac{1}{Z_j} \frac{dZ_j}{dm_{s,j}}, \quad (11)$$

and the entropy, Σ_j , can be deduced as

$$\Sigma_j = - \int \int f(z, \cos \theta_j) \cdot \ln [4\pi f(z, \cos \theta_j)] dz d\Omega_j = \ln Z_j - m_{n,j} s_j - m_{s,j} \sigma_j. \quad (12)$$

It should be pointed out that the integration over z in Eqs. (7), (9)–(12) must be carried out in the limit of $[0, d_j]$ and then normalized by the distance, d_j . When phase transition occurs in a sequence of the smectic-nematic-isotropic phases, the order parameters ($s \neq 0, \sigma \neq 0$) in the smectic phase changes to $s \neq 0, \sigma = 0$ in the nematic phase, then to $s = 0, \sigma = 0$ in the isotropic phase. To describe the above transition phenomenon, it is necessary to know the temperature dependence of both nematic and smectic interaction parameters. The temperature dependence of the nematic interaction parameters, ν_{11} and ν_{22} , of the individual mesogenic component may be given on the basis of the nematic isotropic (NI) transition temperatures as before^{5,6}

$$\nu_{11} = 4.541 \frac{T_{NI,1}}{T}, \quad \nu_{22} = 4.541 \frac{T_{NI,2}}{T}, \quad (13)$$

where $T_{NI,j}$ is the nematic-isotropic transition temperatures of the component j . By choosing an appropriate α_j value the smectic-nematic (S_{mAN}) transition temperatures can be computed easily through the relationship for the α_j values and phase transition temperatures involving NI, S_{mAN} or smectic-isotropic (S_{mAI}) transitions established by McMillan.¹² The S_{mAN} transition is a first order for $0.7 < \alpha < 0.98$, but the transition becomes a second order when $\alpha < 0.7$. When the smectic directly transforms to an isotropic phase, i.e., $\alpha_j > 0.98$, ν_{11} and ν_{22} may be expressed by coupling with the smectic interaction parameters (α_j) as follows:

$$\nu_{11} \alpha_1 = 4.541 \frac{T_{SI,1}}{T}, \quad \nu_{22} \alpha_2 = 4.541 \frac{T_{SI,2}}{T}, \quad (14)$$

where $T_{SI,j}$ represents temperatures of the S_{mAI} transitions of the component j . The cross-nematic interaction parameter, ν_{12} , may be, to accommodate any departure from its geometric mean, defined as follow:⁶ i.e.,

$$\nu_{12} = c \sqrt{\nu_{11}\nu_{22}}, \quad (15)$$

where c is the proportionality constant characterizing the relative strength of the cross-interaction between the two dissimilar mesogens as compared to that in the same nematics.

Next, it is important to test the validity of Eq. (2) by reducing the free energy density to the limit of a single component smectic LC by letting $\phi_1 = 1$ and $\phi_2 = 0$. Then the free energy density becomes

$$g^s = \frac{G^s}{nkT} = -\Sigma_1 - \frac{1}{2} \nu_{11}(s_1^2 + \alpha_1 \sigma_1^2), \quad (16)$$

which is exactly the same as the original McMillan equation for describing isotropic, nematic and smectic-A phase transitions.¹¹⁻¹⁴ The prediction for the $S_{mA}N$ or $S_{mA}I$ transitions in the single component smectics by the McMillan theory¹² has been borne out experimentally.¹¹ In the absence of the smectic ordering, Eq. (2) will be deduced to the conventional free energy equation for the nematic mixtures.^{5,6} The recovery of the original McMillan free energy expression in the single component smectic limit along with the fact that the free energy equation of the nematic mixtures is recoverable in the absence of smectic ordering assures the validity of Eq. (2) for a binary smectic mixture.

The orientational order parameters, s_j and σ_j , may be evaluated by minimizing the free energy of anisotropic ordering with respect to the nematic and smectic order parameters, i.e.,

$$\frac{\partial g^s}{\partial s_j} = 0 \quad \text{and} \quad \frac{\partial g^s}{\partial \sigma_j} = 0 \quad (17)$$

which yields the equations, viz.;

$$\frac{\partial g^s}{\partial s_1} = m_{n,1} - \nu_{11}s_1\phi_1 - \nu_{12}s_2\phi_2 = 0, \quad (18)$$

$$\frac{\partial g^s}{\partial s_2} = m_{n,2} - \nu_{22}s_2\phi_2 - \nu_{12}s_1\phi_1 = 0, \quad (19)$$

$$\frac{\partial g^s}{\partial \sigma_1} = m_{s,1} - \nu_{11}\alpha_1\sigma_1\phi_1 - \nu_{12}\alpha_{12}\sigma_2\phi_2 = 0, \quad (20)$$

$$\frac{\partial g^s}{\partial \sigma_2} = m_{s,2} - \nu_{22}\alpha_2\sigma_2\phi_2 - \nu_{12}\alpha_{12}\sigma_1\phi_1 = 0. \quad (21)$$

From Eqs. (18)–(21), it is obvious that the orientational order parameters (s_j and σ_j) are composition-dependent. Moreover, the coupling terms comprised of the smectic interaction parameters (α_1 , α_2 , and α_{12}) and the nematic interaction parameters (ν_{11} , ν_{22} , and ν_{12}) themselves are temperature-dependent [e.g., Eq. (14)]. For a given c value, the s_j and σ_j can be evaluated numerically as functions of temperature (T) and composition (ϕ_1) using Eqs. (18)–(21). Once the order parameters have been determined, the free energy density of anisotropic ordering can be calculated accordingly. The equilibrium coexistence points of the phase diagram may then be computed by equating the chemical potentials of each component in two equilibrium phases (α and β), viz.,

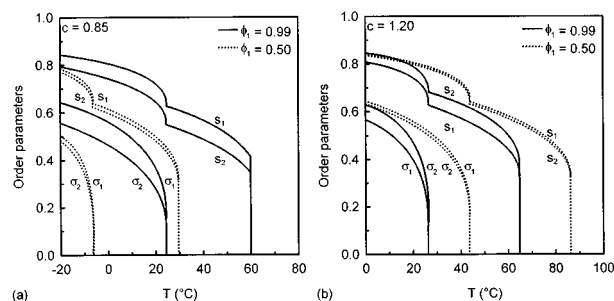


FIG. 1. Nematic and smectic order parameters as functions of temperature and composition for a mixture of two smectic liquid crystals having smectic-nematic-isotropic transitions at $T_{NI,1} = 60$, $T_{SN,1} = 25$, $T_{NI,2} = 40$, and $T_{SN,2} = 5$ °C for (a) $c = 0.85$ and (b) $c = 1.20$. The solid lines and dashed lines correspond to $\phi_1 = 0.99$ and $\phi_1 = 0.50$, respectively.

$$\mu_1^\alpha = \mu_1^\beta \quad \text{and} \quad \mu_2^\alpha = \mu_2^\beta. \quad (22)$$

Alternatively, the binodal points at a given temperature may be determined by a double tangent method where the equilibrium volume fractions of the individual phase (ϕ^α and ϕ^β) fall on the same tangent line of the free energy curve. The first derivatives of the total free energy with respect to volume fraction are equivalent at these two compositions and also equal to the slope connecting these two points, i.e.,

$$\frac{g^\alpha - g^\beta}{\phi^\alpha - \phi^\beta} = \left(\frac{\partial g}{\partial \phi} \right)^\alpha, \quad (23)$$

$$\frac{g^\alpha - g^\beta}{\phi^\alpha - \phi^\beta} = \left(\frac{\partial g}{\partial \phi} \right)^\beta. \quad (24)$$

The first derivative of total free energy of the system with the volume fraction of the component 1 can be deduced to give

$$\begin{aligned} \frac{\partial g}{\partial \phi_1} = & \frac{1}{r_1} \ln \phi_1 - \frac{1}{r_2} \ln \phi_2 + \frac{1}{r_1} - \frac{1}{r_2} + \chi(1 - 2\phi_1) \\ & + \ln \frac{Z_2}{Z_1}. \end{aligned} \quad (25)$$

A similar calculation can be performed for the component 2. For the detailed calculations, the interested readers are referred to our previous paper.⁶

III. RESULTS AND DISCUSSION

Figure 1 illustrates the relationships between the two nematic order parameters and two smectic order parameters of a binary smectic mixture having two different smectic-nematic transitions as well as two different nematic-isotropic transitions. In the case (a) where $c < 1$, the cross interaction of the dissimilar mesogens is weak relative to that in the same mesogens. It can be noticed that the smectic-nematic transition as well as the nematic-isotropic transition temperatures are lower for the mixture (e.g., $\phi = 0.5$) relative to that for the pure LC state (e.g., $\phi = 0.99$) suggesting that both nematic and smectic phases in the mixtures are less stable than that in the constituents, that is to say, the mesophases are favored to form in the pure constituents as compared to that in the LC mixtures. On the contrary where $c > 1$, i.e.,

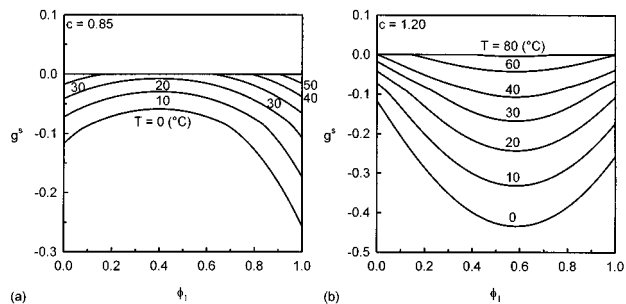


FIG. 2. Temperature dependence of free energy density of anisotropic ordering as a function of volume fraction for a mixture of two smectic liquid crystals having smectic-nematic-isotropic transitions at $T_{NI,1}=60$, $T_{SN,1}=25$, $T_{NI,2}=40$, and $T_{SN,2}=5$ °C for (a) 0.85 and (b) $c=1.20$.

case (b), both the smectic-nematic as well as the nematic-isotropic transition temperatures are higher for the middle compositions relative to the constituents. Hence, the nematic and smectic phases in the mixtures are more stable than that in the pure states which is just opposite to the case (a).

Figures 2(a) and 2(b) exhibit the free energy density of the anisotropic ordering of the smectic mixtures as a function of temperature and volume fraction for the two corresponding cases. When $c < 1$, the free energy curves are convex downward, indicating that the free energy is the lowest in the constituents. This implies that both nematics and smectics are more stable in the pure states than in their mixtures. On the other hand, the free energy curves of the case (b) show the concave upward trend, suggesting that the nematics as well as the smectics in the intermediate compositions are more stable relative to those in the pure LC phases. These stable nematics and smectics are induced by the strong cross-interactions of the dissimilar mesogens, thus they may be regarded as induced nematics and induced smectics, respectively.

Once the total free energy of the binary smectic mixture has been determined, the coexistence curves of smectic phase diagrams can be obtained by a double tangent method according to Eqs. (23)–(25). Figures 3(a)–3(c) depict the influence of the c parameter from (a) weak to (c) strong

cross-interactions by setting, $T_{NI,1}=60$ °C, $T_{NI,2}=40$ °C, $T_{SN,1}=25$ °C, and $T_{SN,2}=5$ °C (corresponding to $\alpha_1=0.755$ and $\alpha_2=0.742$). When the cross-mesogenic interaction is weaker than those in the constituents, nematics are favored to form among the same mesogens as manifested by the large neat state (N_1 or N_2) at high compositions of either constituent. A similar trend has been observed for the large pure smectic regions ($S_{mA,1}$ or $S_{mA,2}$). In the descending order of temperature, phase transition occurs from the isotropic to the nematic phase via an extremely narrow coexistence region of the L_j+N_j phase at high concentrations of either LC component ($j=1$ or 2). Upon further cooling, phase transition takes place from the pure nematic to the pure smectic by passing through the N_j+S_{mAj} coexistence region. At some intermediate compositions, a liquid+liquid (L_1+L_2) coexistence region is evident, but it changes to various coexistence phases in the following order with decreasing temperature: N_1+L_2 , N_1+N_2 , $S_{mA,1}+N_2$, and $S_{mA,1}+S_{mA,2}$.

As for the ideal case of $c=1$, the $I+N$ coexistence region and the $N+S_{mA}$ coexistence region are extremely narrow as though the coexistence curves are almost overlapped, suggesting that the nematic and smectic interactions do follow a simple geometric mean. It should be pointed out that the determination of these coexistence lines is technically feasible only if the nematic and smectic transition temperatures are sufficiently far apart. Figure 3(b) exhibits phase transitions from the isotropic (I), the $I+N$ coexistence region, the single nematic phase (N), the $N+S_{mA}$ coexistence region and the single smectic phase (S_{mA}) in the descending order of temperature.

When the cross-interaction gets stronger ($c=1.2$), the coexistence ($I+N$ and $N+S_{mA}$) curves show convex curvature although the sequence of isotropic, coexistence of $I+N$, the pure N , the $N+S_{mA}$ and the pure smectic-A phases in the descending order of temperature remains the same as that in the case for $c=1$ [Fig. 3(b)]. The convexity of the coexistence curves strong suggests that the pure smectic-A can be induced in some middle compositions for the small values of α_1 and $\alpha_2 < 0.98$. At high compositions of either constituent, the induced nematic phase tends to be more

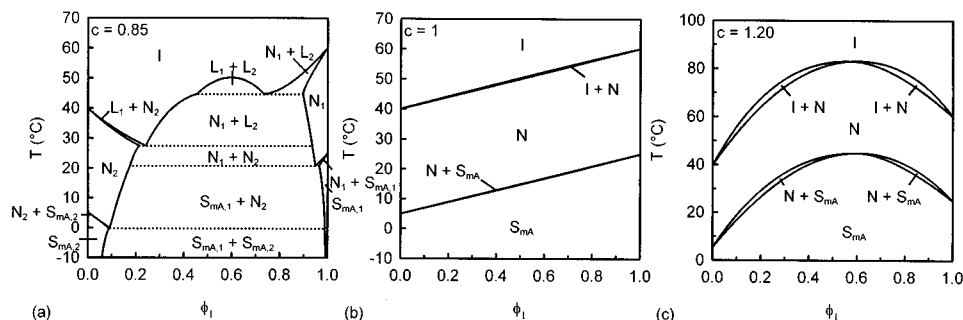


FIG. 3. The effect of “ c ” parameter on phase diagrams of two smectic mixtures undergoing smectic-nematic-isotropic transitions at $T_{NI,1}=60$, $T_{SN,1}=25$, $T_{NI,2}=40$, and $T_{SN,2}=5$ °C along with the corresponding α_1 and α_2 values of $\alpha_1=0.755$ and $\alpha_2=0.742$. The other parameters are set to $r_2/r_1=2.25/1$, $\chi = -1 + 969/T$ for case (a), and $\chi = -1 + 605/T$ for (b) and (c). The c value signifies the relative strength of cross-interaction changing from (a) weak to (c) strong.

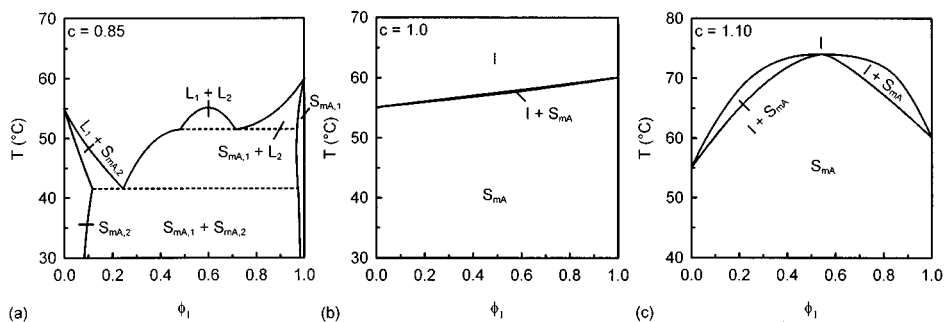


FIG. 4. The effect of “ c ” parameter on phase diagrams of two smectic mixtures undergoing smectic-isotropic transitions at $T_{SI,1}=60$ and $T_{SI,2}=55$ °C along with $\alpha_1=1.0317$, $\alpha_2=1.0323$, $r_2/r_1=2.25/1$, and $\chi=-1+784/T$. The c value signifies the relative strength of cross-interaction changing from (a) weak to (c) strong.

stable as compared to the constituent nematics [Fig. 3(c)]. On the same token, the induced smectic phase is more stable than the pure smectics.

In the case of two smectic mixtures undergoing the smectic-isotropic phase transitions, the phase diagrams are reminiscent of those of two nematic mixtures, thereby appreciably simpler [Figs. 4(a)–4(c)]. When the cross-interaction is relatively weak, e.g., $c=0.85$, the L_1+L_2 coexistence region appears in the intermediate compositions while the pure $S_{mA,i}$ phase can be discerned in the high compositions of either constituent. The $L_1+S_{mA,2}$ and $S_{mA,1}+L_2$ regions can be predicted between the isotropic and pure smectic phases. Below the lower peritectic line, there is the coexistence of two separate smectic phases ($S_{mA,1}+S_{mA,2}$). In the case of $c=1.0$, the binary smectic mixture simply follows the geometric mean, exhibiting the isotropic, isotropic+smectic and pure smectic regions [Fig. 4(b)]. When $c=1.1$, the cross-mesogenic interactions gets stronger which in turn induces a smectic-A phase in their mixtures [Fig. 4(c)]. The convexity of the $I+S_{mA}$ coexistence curves suggests that the induced smectic LCs are more stable in the mixtures than in the constituent pure smectics. Moreover, the azeotropic point can be discerned clearly in the coexistence curves.

In Fig. 5(a), one can immediately notice the intermediate case of two smectic mixtures where the first component un-

dergoes the smectic-isotropic transition ($T_{SI,1}=55$ °C and $\alpha_1=1.0323$), whereas the second component undergoes the smectic-nematic-isotropic transitions ($T_{NI,2}=55$ °C, $T_{SN,2}=52$ °C, and $\alpha_2=0.956$). In the region where the component 1 is rich, a coexistence region of $S_{mA,1}+L_2$ appears between the isotropic and the pure smectic-A region. In the other region where the component 2 is rich, the coexistence regions of L_1+N_2 , the pure nematic (N_2), $N_2+S_{mA,2}$ and the pure $S_{mA,2}$ are observed in the descending order of temperature. In the middle compositions, liquid–liquid phase separation (L_1+L_2) and two-separate smectic ($S_{mA,2}+S_{mA,1}$) phases have been predicted by the present theory.

When $c=1.1$, the coexistence region of $I+S_{mA}$ along with the azeotropic point can be discerned in the compositions rich in the component 1, which is accompanied by the induced smectic-A resulting from the strong cross-interaction of the dissimilar mesogens [Fig. 5(b)]. In the compositions where component 2 is rich, the theory predicts the coexistence of the $I+N_2$, the pure N_2 , the N_2+S_{mA} and the pure S_{mA} in the descending order of temperature.

To evaluate the predictive capability of the present theory, it is imperative to test with the experimental phase diagrams of two-smectic mixtures although they are extremely rare to come by in open literature. Figure 6 shows

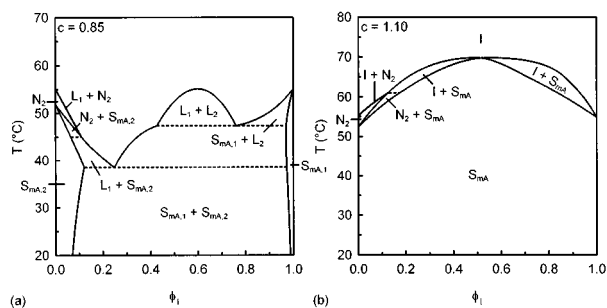


FIG. 5. The effect of “ c ” parameter on phase diagrams of two smectic mixtures undergoing smectic-isotropic and smectic-nematic-isotropic transitions at $T_{SI,1}=55$, $T_{NI,2}=55$, and $T_{SN,2}=52$ °C along with $\alpha_1=1.0323$ and $\alpha_2=0.956$. The values of r_2/r_1 and χ are the same as in Fig. 4. The c value signifies the relative strength of cross-interaction changing from (a) weak to (b) strong.

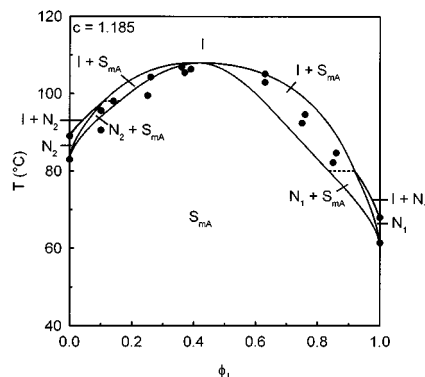


FIG. 6. Temperature vs composition phase diagram (filled circles) for a mixture of two low molar mass liquid crystals (4-nitropentyl-4'-octyloxybenzoate and 4-*n*-hexyloxyphenyl-4'-*n*-decyloxybenzoate) from Ref. 15 in comparison with the calculated coexistence curves for nematic and induced smectic coexistence phase boundaries (solid lines).

a temperature vs composition phase diagram for a mixture of two low molar mass liquid crystals (4-nitropentyl-4'-octyloxybenzoate and 4-*n*-hexyloxyphenyl-4'-*n*-decyloxybenzoate)^{15,16} in comparison with the calculated coexistence curves for the nematic and induced smectic coexistence phase boundaries. The closed circles are the experimental data points^{15,16} and the solid lines represent the calculated coexistence curves using $T_{SN,1}=61$ °C and $T_{NI,1}=68$ °C and $T_{SN,2}=83$ °C and $T_{NI,2}=89$ °C of the constituents from the experiment.¹⁶ The α_1 and α_2 values were computed to be $\alpha_1=0.943$ and $\alpha_2=0.953$, respectively. The composition of the azeotrope was estimated to be $\phi_1^{AZ}=0.42$ from the experimental phase diagram that in turn gives $c=1.185$, and thus the c parameter is no longer an adjustable parameter in the present case. Since there existed no liquid–liquid coexistence region, the Flory–Huggins interaction parameter was taken as $\chi=-1+969/T$ which should be inconsequential for the induced nematic or smectic phase diagrams.

It is striking to notice that the pure smectic-A can be induced in some middle compositions for the small values of α_1 and $\alpha_2 < 0.98$. Hence, this phase transition of the induced smectic-A directly to isotropic phase is contrary to the McMillan criterion which states that α must be greater than 0.98 in order to see the smectic-isotropic transition in the constituent smectic LC. We believe that this induced smectic phase is due to significantly strong cross-mesogenic interaction in the mixtures as compared to that in the same species, suggesting the need for taking into consideration the important role of the “ c ” cross-interaction parameter of the mesogens. As can be seen in Fig. 6, our theoretical calculation shows qualitative agreement with the experimental phase diagrams or at least captures the experimental trends, attesting to the rigor of its predictive capability.

IV. CONCLUSIONS

We have demonstrated that a variety of smectic phase diagrams involving two nematic order parameters and two smectic order parameters have been predicted based on the combination of the Flory–Huggins (FH) theory for isotropic mixing and the Maier–Saupe–McMillan (MSM) theory for smectic ordering of liquid crystals (LC). The calculated phase diagrams of binary smectic mixture involving the smectic-nematic-isotropic transitions have revealed the L_1+L_2 , N_1+L_2 , N_1+N_2 , $S_{mA,1}+N_2$, and $S_{mA,1}+S_{mA,2}$ coexistence regions in the descending order of temperature. In the compositions rich in either component, the N_1+L_2 and N_2+L_1 coexistence regions exist between the isotropic and pure nematic (N_j) phase. Similarly, the coexistence of the N_j+S_{mAj} phases has been predicted to exist between the pure N_j and the pure S_{mAj} regions. In the case of two-smectic mixtures undergoing the smectic-isotropic transition, the phase diagrams are similar to those of the two-nematic mixtures and show strong dependence on the cross-mesogenic parameter, c . Our combined FH/MSM model for determining the coexistence regions of the binary smectic mixture has shown to capture the experimental smectic phase diagrams, confirming the reasonably good predictive capability

of our theory. We also demonstrated that in the single component smectic limit, the original McMillan's equation can be recovered. During the review process, it came to our attention that a new theory¹⁷ based on Landau model for phase transitions of the pure smectics could be equally useful, if not more, for elucidating phase diagrams of a binary smectic mixture. There is no doubt that it should be of interest to compare the predictive capability of that theory with our theoretical predictions of a binary smectic mixture, but we did not pursue this aspect as it is obviously beyond the scope of the present work.

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APPENDIX: EXTENSION OF MCMILLAN'S THEORY TO A BINARY SMECTIC MIXTURE

In the original McMillan's derivation,¹² the self-consistent one particle potential, u , for a single component liquid crystal undergoing nematic-smectic phase transitions, consists of the nematic field potential, u^n , and the smectic field potential, u^s , which is expressed as

$$\begin{aligned} \frac{u(z, \cos \theta)}{kT} &= \frac{u^n(z, \cos \theta)}{kT} + \frac{u^s(z, \cos \theta)}{kT} \\ &= -\nu s \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) - \nu \alpha \sigma \cos(2\pi z/d) \\ &\quad \times \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right), \end{aligned} \quad (\text{A1})$$

where s and σ are the nematic and smectic order parameters, respectively, given as

$$s = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \quad (\text{A2})$$

$$\sigma = \frac{1}{2} \langle \cos(2\pi z/d) (3 \cos^2 \theta - 1) \rangle. \quad (\text{A3})$$

The normalized orientation distribution function $f(z, \cos \theta)$ is defined as

$$f(z, \cos \theta) = \frac{1}{4\pi Z} \exp[-u(z, \cos \theta)/kT], \quad (\text{A4})$$

where Z is the partition function given by

$$Z = \int \int \exp[-u(z, \cos \theta)/kT] dz d\Omega. \quad (\text{A5})$$

The order parameters, s and σ , are coupled through $f(z, \cos \theta)$,

$$s = \int \int f(z, \cos \theta) \cdot \frac{1}{2} (3 \cos^2 \theta - 1) dz d\Omega, \quad (\text{A6})$$

$$\sigma = \int \int f(z, \cos \theta) \cdot \frac{1}{2} \cos(2\pi z/d) \times (3 \cos^2 \theta - 1) dz d\Omega. \quad (A7)$$

The internal energy of the system is the thermodynamic average of the two-particle interaction, viz.,

$$\begin{aligned} U &= \frac{n}{2} \langle u \rangle = \frac{n}{2} \langle u^n \rangle + \frac{n}{2} \langle u^s \rangle \\ &= -\frac{nkT}{2} \int \int -\nu_s \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \cdot f(z, \cos \theta) dz d\Omega + \frac{nkT}{2} \\ &\quad \times \int \int -\nu \alpha \sigma \cos(2\pi z/d) \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \cdot f(z, \cos \theta) dz d\Omega \\ &= -\frac{1}{2} nkT (\nu s^2 + \nu \alpha \sigma^2). \end{aligned} \quad (A8)$$

The entropy, S , of n molecules in the one-particle potential [Eq. (A1)] can be described as

$$S = nk\Sigma, \quad (A9)$$

where

$$\begin{aligned} \Sigma &= - \int \int f(z, \cos \theta) \cdot \ln[4\pi f(z, \cos \theta)] dz d\Omega \\ &= \ln Z - (\nu s^2 + \nu \alpha \sigma^2) \end{aligned} \quad (A10)$$

and the free energy density of the system due to the anisotropic ordering of the LC is

$$g = \frac{G}{nkT} = \frac{U-TS}{nkT} = -\Sigma - \frac{1}{2} (\nu s^2 + \nu \alpha \sigma^2). \quad (A11)$$

In order to extend the McMillan's theory¹² of the pure smectics to a binary smectic mixture, the volume fraction of each constituent must be incorporated into the field potential [Eq. (A1)] such that

$$\begin{aligned} \frac{u_{jj}(z, \cos \theta_j)}{kT} &= \frac{u_{jj}^n(z, \cos \theta_j)}{kT} + \frac{u_{jj}^s(z, \cos \theta_j)}{kT} \\ &= -\nu_{jj} s_j \left(\frac{3}{2} \cos^2 \theta_j - \frac{1}{2} \right) \phi_j \\ &\quad - \nu_{jj} \alpha_j \sigma_j \cos(2\pi z/d_j) \\ &\quad \times \left(\frac{3}{2} \cos^2 \theta_j - \frac{1}{2} \right) \phi_j, \end{aligned} \quad (A12)$$

where $j=1,2$ and u_{jj} represents the field potential due to the interaction within the same mesogens. As defined in a previous section, the volume fraction of component j is given as $\phi_j = n_j r_j / n$, where $n = n_1 r_1 + n_2 r_2$. The internal energy

density, U_{jj}^n/nkT , for component j arising from the nematic field potential of the interaction between the same mesogens is then given by

$$\begin{aligned} \frac{U_{jj}^n}{nkT} &= \frac{n_j r_j}{2n} \left\langle \frac{u_{jj}^n}{kT} \right\rangle = \frac{\phi_j}{2} \left\langle \frac{u_{jj}^n}{kT} \right\rangle \\ &= \frac{\phi_j}{2} \int \int -\nu_{jj} s_j \left(\frac{3}{2} \cos^2 \theta_j - \frac{1}{2} \right) \\ &\quad \times \phi_j \cdot f_j(z, \cos \theta_j) dz d\Omega_j = -\frac{1}{2} \nu_{jj} s_j^2 \phi_j^2, \end{aligned} \quad (A13)$$

whereas the internal energy density for component j due to the smectic field potential is

$$\begin{aligned} \frac{U_{jj}^s}{nkT} &= \frac{n_j r_j}{2n} \left\langle \frac{u_{jj}^s}{kT} \right\rangle = \frac{\phi_j}{2} \left\langle \frac{u_{jj}^s}{kT} \right\rangle \\ &= \frac{\phi_j}{2} \int \int -\nu_{jj} \alpha_j \sigma_j \cos(2\pi z/d_j) \\ &\quad \times \left(\frac{3}{2} \cos^2 \theta_j - \frac{1}{2} \right) \phi_j \\ &\quad \cdot f_j(z, \cos \theta_j) dz d\Omega_j \\ &= -\frac{1}{2} \nu_{jj} \alpha_j \sigma_j^2 \phi_j^2. \end{aligned} \quad (A14)$$

The internal energy density due to the cross-nematic interaction may be defined in terms of relative strength of the nematic energy densities of the dissimilar mesogens with that of the pure mesogens, c , to accommodate any deviation from their geometric mean. Assuming $U_{12}^n = U_{21}^n$, it may be expressed as

$$\begin{aligned} \frac{U_{12}^n}{nkT} = \frac{U_{21}^n}{nkT} &= -c \sqrt{\frac{U_{11}^n}{nkT} \frac{U_{22}^n}{nkT}} \\ &= -\frac{1}{2} c \sqrt{\nu_{11} \nu_{22}} s_1 s_2 \phi_1 \phi_2 \\ &= -\frac{1}{2} \nu_{12} s_1 s_2 \phi_1 \phi_2, \end{aligned} \quad (A15)$$

where $\nu_{12} = c \sqrt{\nu_{11} \nu_{22}}$. Likewise, the internal energy density due to the cross-smectic interaction is given by

$$\begin{aligned} \frac{U_{12}^s}{nkT} = \frac{U_{21}^s}{nkT} &= -c \sqrt{\frac{U_{11}^s}{nkT} \frac{U_{22}^s}{nkT}} \\ &= -\frac{1}{2} c \sqrt{\nu_{11} \nu_{22}} \sqrt{\alpha_1 \alpha_2} \sigma_1 \sigma_2 \phi_1 \phi_2 \\ &= -\frac{1}{2} \nu_{12} \alpha_{12} \sigma_1 \sigma_2 \phi_1 \phi_2, \end{aligned} \quad (A16)$$

where $\alpha_{12} = \sqrt{\alpha_1 \alpha_2}$. Finally, the total internal energy density of the system due to the mesogenic interactions can be described as follows:

$$\begin{aligned} \frac{U}{nkT} &= \frac{1}{nkT} (U_{11}^n + U_{11}^s + U_{22}^n + U_{22}^s + U_{12}^n + U_{21}^n + U_{12}^s + U_{21}^s) \\ &= -\frac{1}{2} \nu_{11}(s_1^2 + \alpha_1 \sigma_1^2) \phi_1^2 - \frac{1}{2} \nu_{22}(s_2^2 + \alpha_2 \sigma_2^2) \phi_2^2 \\ &\quad - \nu_{12}(s_1 s_2 + \alpha_{12} \sigma_1 \sigma_2) \phi_1 \phi_2. \end{aligned} \quad (\text{A17})$$

Further, the decrease of entropy associated with the anisotropic ordering of component j is given by

$$S_j = n_j r_j k \Sigma_j. \quad (\text{A18})$$

Combining Eqs. (A17) and (A18), the anisotropic part of the total free energy density of the system can be deduced to Eq. (2) in what follows:

$$\begin{aligned} g &= \frac{G}{nkT} = \frac{U - T(S_1 + S_2)}{nkT} \\ &= -\Sigma_1 \phi_1 - \Sigma_2 \phi_2 - \frac{1}{2} \nu_{11}(s_1^2 + \alpha_1 \sigma_1^2) \phi_1^2 \\ &\quad - \frac{1}{2} \nu_{22}(s_2^2 + \alpha_2 \sigma_2^2) \phi_2^2 - \nu_{12}(s_1 s_2 \\ &\quad + \alpha_{12} \sigma_1 \sigma_2) \phi_1 \phi_2. \end{aligned} \quad (\text{A19})$$

In the limit of a single component smectic LC, i.e., letting $\phi_1=1$ and $\phi_2=0$, the free energy density of the original McMillan equation¹² for the pure smectic-A can be recovered, viz.,

$$g = \frac{G}{nkT} = -\Sigma_1 - \frac{1}{2} \nu_{11}(s_1^2 + \alpha_1 \sigma_1^2). \quad (\text{A20})$$

Thus, the derivation of Eq. (A19) can be justified in extending the Maier–Saupe–McMillan theory of the pure smectic-A to the smectic-A mixtures.

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