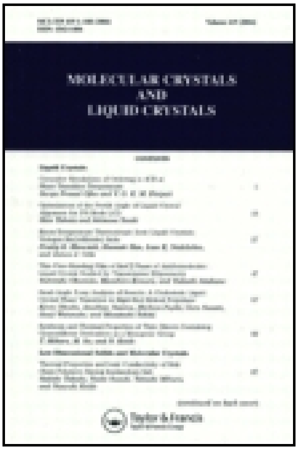

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McMillan Theory of Binary Smectic Mixtures

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McMillan Theory of Binary Smectic Mixtures

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The molecular field theory of the smectic A phase, developed by McMillan, is extended to binary smectic mixtures. Expressions for the orientation-dependent mean field potential of each component are derived. Besides the interaction terms of the pure components, two additional parameters appear. These mixed parameters describe the interaction forces between particles of different species. The composition dependences of the transition temperatures are determined from the free energies. The possible existence of a two-phase region is neglected. By suitable choices of the interaction parameter set, it is possible to predict induced phases. If all interaction parameters satisfy the geometric mean rule, the mixture will be an ideal one, exhibiting linear phase transition lines. Because of the coupling between the smectic order and the nematic order, the transition lines of both phases are correlated. By fitting an experimental phase diagram we are able to determine the unknown values of the mixed interaction parameters.

INTRODUCTION

In most cases of liquid crystal application one has to do with multicomponent systems of mesogenic and nonmesogenic materials. Until now, nearly all theories refer to pure substances or nematic mixtures.[1,2] In binary mixtures several authors have found nonideal phase diagrams. The most popular effects are the reentrant phases, discovered by Cladis,[3] and the induced phases.[4,5]

We extend the well-known McMillan theory[6] of the smectic A phase to investigate binary mixtures. For the sake of simplicity, we neglect the possible existence of a two-phase region in the case of a first order transition. We suppose the molecules of both components to have equal size. Therefore, the number density as well as the interaction parameters are independent of the composition of the mixture. There is no volume of mixing.

THEORY

The generalization of the McMillan theory to multicomponent systems is straightforward but is here not outlined in detail.

The mean field U_i acting on a particle of species (i) is a superposition of the interaction terms of the two components. Here we have a mole fraction weighing.

As in the simple McMillan theory, each species is described by two interaction constants a_{ii} and b_{ii} and by the corresponding order parameters η_i and σ_i

$$U_1 = (x_1 a_{11}\eta_1 + x_2 a_{12}\eta_2)P_2(\xi_1) + (x_1 b_{11}\sigma_1 + x_2 b_{12}\sigma_2)P_2(\xi_1)\cos(2\pi y_1/d)$$

$$U_2 = (x_1 a_{12}\eta_1 + x_2 a_{22}\eta_2)P_2(\xi_2) + (x_1 b_{12}\sigma_1 + x_2 b_{22}\sigma_2)P_2(\xi_2)\cos(2\pi y_2/d)$$

$$\eta_i = \langle P_2(\xi_i)\rangle, \qquad \sigma_i = \langle P_2(\xi_i)\cos(2\pi y_i/d)\rangle, \qquad \xi_i = \cos\theta_i \tag{1}$$

with

x_i = mole fraction ratio of species (i) in the mixture
d = average layer spacing of the smectic phase
η_i = nematic order parameter of species (i)
σ_i = mixed smectic order parameter

In Eq. 1 appear two additional parameters a_{12} and b_{12}, which describe the interactions between particles of different species. The interaction parameters a_{ij} and b_{ij} are averages over forces that cause the molecules to align parallel to each other and to form layers perpendicular to the director.

The ratio b_{ii}/a_{ii} is identical to McMillan's parameter α. McMillan has chosen specific forms of the interaction potentials which we can adopt to interpret the ratio $\alpha_i = b_{ii}/a_{ii}$ in terms of molecular parameters:

$$\alpha = 2\exp[-(\pi r_0/d)^2]$$

where r_0 measures the range of the interaction.

Several authors[7,8] introduce a purely translational interaction term c_{ij} and the corresponding order parameter $\tau_i = \langle\cos(2\pi y_i/d)\rangle$. This term reduces the strong smectic-nematic coupling of the above model and allows a better description of the smectic A phase. For simplicity we suppose $c_{ij} = 0$ throughout the paper. We remark that the translational order parameter τ_i doesn't vanish in that case but it yields no contribution to the free energy. Following McMillan, we can derive a set of self-consistent equations to determine the order parameters in dependence on the temperature and the mole fraction ratio. We get solutions describing the smectic, the nematic and the isotropic phase, respectively.

$$\eta_1 = d^{-1}Z_1^{-1}\iint P_2(\xi_1)\exp\{-1/(kT)$$

$$\cdot[x_1a_{11}\eta_1 + x_2a_{12}\eta_2 + (x_1b_{11}\sigma_1 + x_2b_{12}\sigma_2)\cos(2\pi y_1/d)]P_2(\xi_1)\}\,d\xi_1\,dy_1$$

$$\sigma_1 = d^{-1}Z_1^{-1}\iint P_2(\xi_1)\cos(2\pi y_1/d)\exp\{-1/(kT)$$

$$\cdot[x_1a_{11}\eta_1 + x_2a_{12}\eta_2 + (x_1b_{11}\sigma_1 + x_2b_{12}\sigma_2)\cos(2\pi y_1/d)]\cdot P_2(\xi_1)\}\,d\xi_1\,dy_1$$

$$Z_1 = d^{-1}\iint \exp\{-1/(kT)$$

$$\cdot[x_1a_{11}\eta_1 + x_2a_{12}\eta_2 + (x_1b_{11}\sigma_1 + x_2b_{12}\sigma_2)\cos(2\pi y_1/d)]P_2(\xi_1)\}\,d\xi_1\,dy_1$$

$$\eta_2 = d^{-1}Z_2^{-1}\iint P_2(\xi_2)\exp\{-1/(kT)$$

$$\cdot[x_1a_{12}\eta_1 + x_2a_{22}\eta_2 + (x_1b_{12}\sigma_1 + x_2b_{22}\sigma_2)\cos(2\pi y_2/d)]P_2(\xi_2)\}d\xi_2dy_2$$

$$\sigma_2 = d^{-1}Z_2^{-1}\iint P_2(\xi_2)\cos(2\pi y_2/d)\exp\{-1/(kT)$$

$$\cdot[x_1a_{12}\eta_1 + x_2a_{22}\eta_2 + (x_1b_{12}\sigma_1 + x_2b_{22}\sigma_2)\cos(2\pi y_2/d)]\cdot P_2(\xi_2)\}\,d\xi_2\,dy_2$$

$$Z_2 = d^{-1}\iint \exp\{-1/(kT)$$

$$\cdot[x_1a_{12}\eta_1 + x_2a_{22}\eta_2 + (x_1b_{12}\sigma_1 + x_2b_{22}\sigma_2)\cos(2\pi y_2/d)]P_2(\xi_2)\}\,d\xi_2\,dy_2 \tag{2}$$

Here Z_i is the partition function for particles of species (i). Using Eq. 3 we calculate the entropy and the free energy of the binary system.

$$S = N/T\{x_1^2(a_{11}\eta_1^2 + b_{11}\sigma_1^2) + 2x_1x_2(a_{12}\eta_1\eta_2 + b_{12}\sigma_1\sigma_2)$$

$$+ x_2^2(a_{22}\eta_2^2 + b_{22}\sigma_2^2)\} + Nk(x_1\ln Z_1 + x_2\ln Z_2)$$

$$F = -N/2\{x_1^2(a_{11}\eta_1^2 + b_{11}\sigma_1^2) + 2x_1x_2(a_{12}\eta_1\eta_2 + b_{12}\sigma_1\sigma_2)$$

$$+ x_2^2(a_{22}\eta_2^2 + b_{22}\sigma_2^2)\} - NkT(x_1\ln Z_1 + x_2\ln Z_2)$$

$N = N_0(n_1 + n_2)$
n_i = number of moles of species (i) in the mixture
N_0 = Avogadro constant

Now we can determine the transition temperatures in dependence on the mole fraction ratio.

RESULTS

We want to investigate the phase diagrams of binary mixtures for several sets of the interaction parameters. At first we investigate a mixture with both components having the same value of the McMillan parameter $\alpha = b_{11}/a_{11} = b_{22}/a_{22}$. Because the magnitudes of the interaction energies are different (see Figure 1), the pure components have unequal transition temperatures. We assume the mixed energy parameters to satisfy the geometric mean rule

$$a_{12} = (a_{11}a_{22})^{1/2} \qquad b_{12} = (b_{11}b_{22})^{1/2} \tag{4}$$

In that case the isotropic-nematic transition as well as the nematic-smectic A transition are represented by straight lines connecting the transition points of the pure substances. Such a behavior is already known from the theory of nematic mixtures.[1]

In Figure 1 we display the composition dependence of the order parameters at the nematic-smectic transition. In the insert the interaction parameters are to be seen in units of kT_0, where T_0 is the clearing point of the pure component (1). Whereas the upper lines represent the nematic order parameters, the lower ones represent the mixed smectic order parameters.

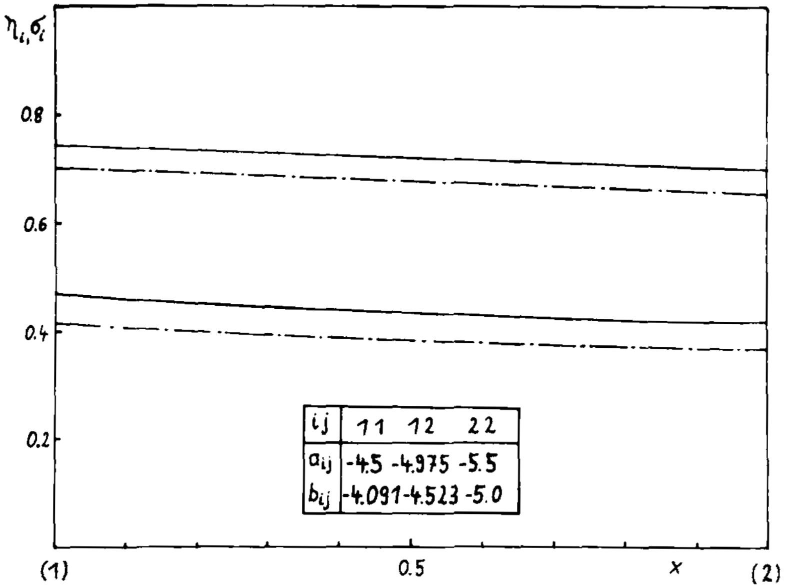


FIGURE 1 Nematic order parameters (upper lines) and smectic order parameters (lower lines) versus concentration at the phase transition of an ideal mixture.

The latter ones have nonvanishing values because the phase transition is of first order.

The composition dependence of the order parameters obeys nearly a linear relationship. From a linear least-square fit we get the correlation coefficients

$$r_\eta^2 = 0.994 \quad \text{and} \quad r_\sigma^2 = 0.987$$

These small deviations are well above the error limits of our calculation. The pure components have equal order parameters because they only depend on the McMillan parameter α. In the pure component (1) a single molecule of species (2) interacts via a_{12} and b_{12}. These values are of greater magnitude than the corresponding interaction terms of the component (1). Therefore, the order parameters of the species (2) are always higher than those of species (1). Because of the same reason, the order parameters rise with increasing amount of component (1). To a first approximation the ratios η_1/η_2 and σ_1/σ_2 are nearly independent of the mole fraction ratio. This behavior is similar to that of nematic mixtures.

Now we investigate a binary system with different ratios of the interaction parameters of the pure components

$$b_{11}/a_{11} = 0.7273 \qquad b_{22}/a_{22} = 0.6667$$

The mixed terms a_{12} and b_{12} again obey the geometric mean rule.

Whereas the component (1) must possess a first order nematic-smectic transition, it is of second order for the component (2). Despite such a different behavior of the pure components, we get linear phase transition lines for the mixture of Figure 2. A linear least-square fit gives a correlation coefficient of $r^2 = 0.99999$.

We also display the influence of small deviations from the geometric mean rule on the transition lines. Here only the nematic interaction parameter a_{12} is modified. Because of the strong smectic-nematic coupling also, the nematic-smectic A transition line deviates slightly from the ideal behavior. If the mixed interaction parameter a_{12} is greater or smaller than the geometric mean of a_{11} and a_{22}, the transition lines have a convex or concave shape, respectively.

The jump of the nematic order parameter η_1 at the nematic-smectic A transition is to be seen in Figure 3. The discontinuity vanishes near a mole fraction ratio of $x_1 = 0.55$, where the ratio of the transition temperatures is equal to $T_{SN}/T_{NI} = 0.866$. As known from the simple McMillan theory for such a temperature ratio the transition changes its order.

In Figure 4 we show the phase diagram for a mixture of two nematogenic substances. Despite vanishing smectic interaction terms in the pure compo-

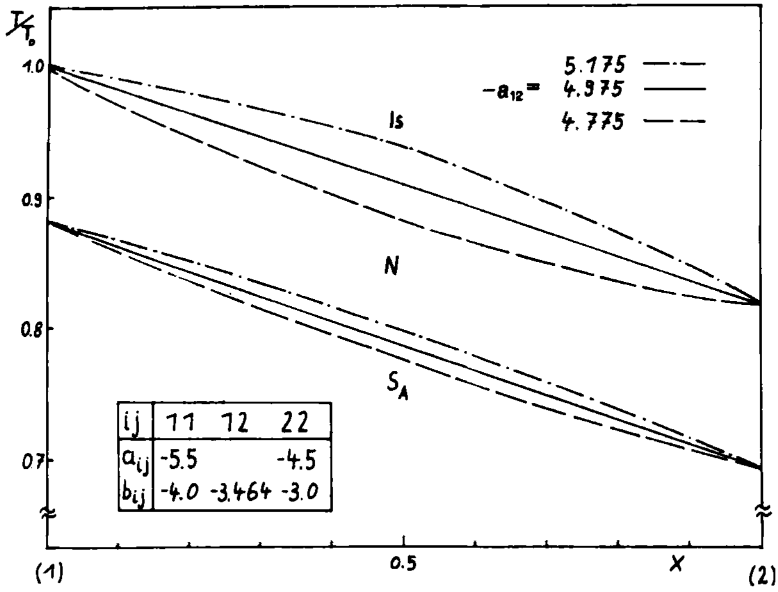


FIGURE 2 Transition temperatures versus composition of the mixture for different values of the mixed interaction parameter a_{12}.

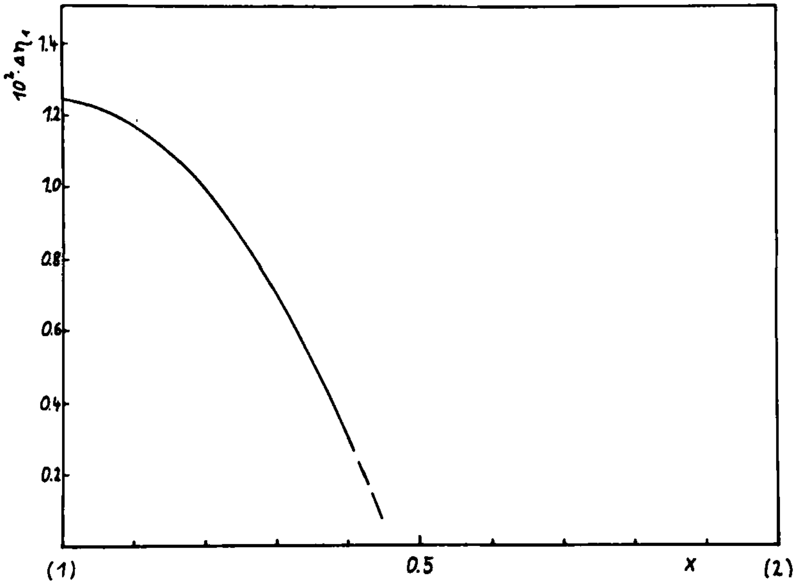
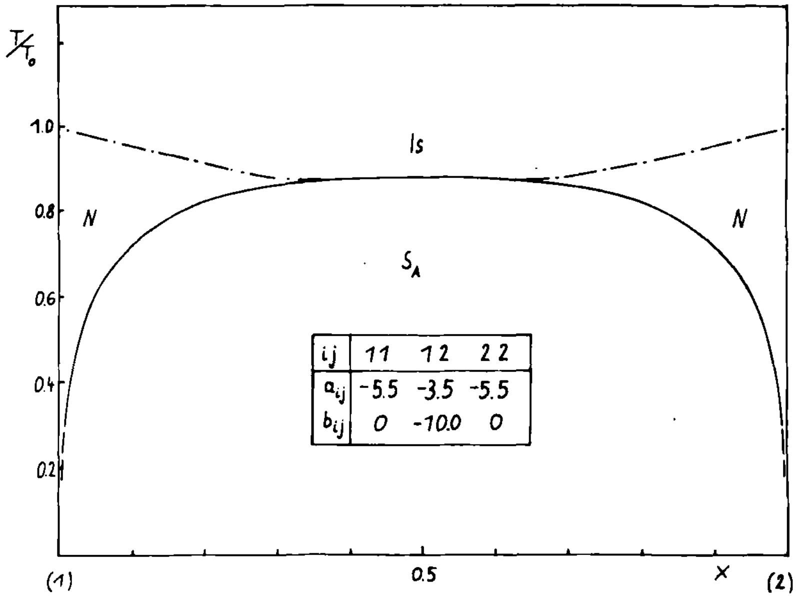


FIGURE 3 Jump of the nematic order parameter η_1 at the nematic-smectic A transition versus concentration.



ij	11	12	22
a_{ij}	-5.5	-3.5	-5.5
b_{ij}	0	-10.0	0

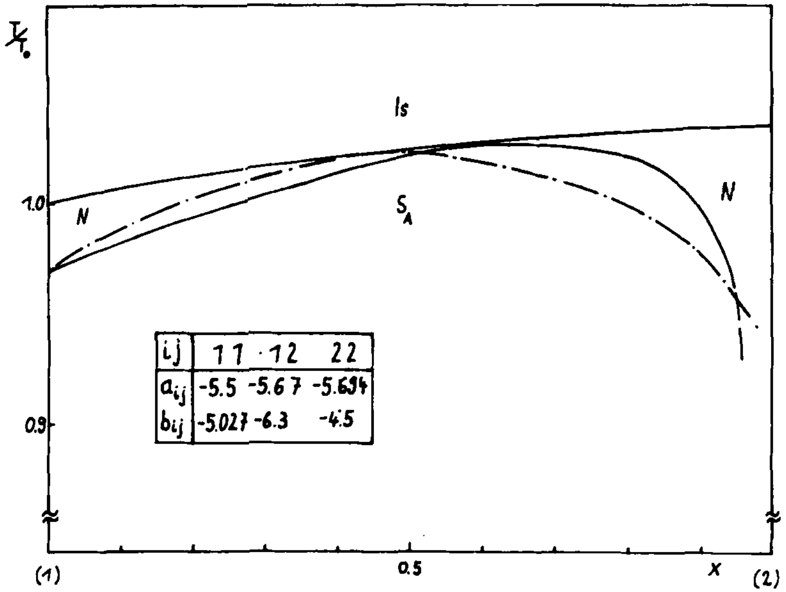
FIGURE 4 Concentration dependence of the transition temperatures for an induced smectic phase.

nents, we suppose a non-zero value of the mixed interaction parameter $b_{12} = -10.0$. This strong interaction between particles of different species induces the smectic phase of the mixture. In accordance to the experiment the induced phase appears in the medium concentration range.[9] Because the isotropic-nematic transition is of concave curvature the nematic region is narrowed and vanishes for medium concentrations if the mixed interaction is large enough. For simplicity, we assume equal values for the interaction parameters of both components; therefore, the phase diagram is symmetrical.

The non-vanishing smectic interaction between different species may be due to charge-transfer complexing. But in the framework of the present theory other interaction forces may also be responsible for the formation of the induced phase.

In Figure 5 we try to fit an experimental phase diagram (solid lines) of Pelzl *et al.*[10] The component (1) without a terminal-polar group possesses a nematic phase as well as a smectic phase. The component (2) with a terminal-polar group has only a nematic phase. For further details see Ref. 10.

The transition temperatures of the pure components are fitted by the pure interaction parameters a_{ii} and b_{ii}.



ij	11	12	22
a_{ij}	-5.5	-5.67	-5.634
b_{ij}	-5.027	-6.3	-4.5

FIGURE 5 Calculated fit of the phase diagram of Ref. 10.

To fit the composition dependence of the phase diagram, the mixed interaction parameters are modified. Here we must assume a metastable smectic phase for the component (2). The dot-dashed lines represent the theoretical results. The computed isotropic-nematic phase transition cannot be distinguished from the experimental curve. The experimental nematic-smectic transition line has its maximum on the right-hand side of the phase diagram in contrast to the theoretical curve. It was not possible to shift the maximum and to get a better fit.

The phase diagram of Pelzl *et al.*, possesses also a metastable reentrant nematic region (not displayed) which cannot be explained in the framework of the present theory.

CONCLUSIONS

Binary systems exhibit linear phase transition lines if the mixed interaction parameters satisfy the geometric mean rule. We suggest that this is also valid for nonvanishing translational interaction terms $c_{ij} \neq 0$.

Experimentally such a behavior is observed for components of similar chemical structure. Even for such ideal mixtures the concentration dependences of the order parameters show small, but distinct deviations from linearity.

All the non-linear effects discussed above are due to large deviations of the mixed interaction parameters from the geometric mean rule. If the smectic term b_{12} is large enough, a quenching of the nematic region is possible for medium concentrations. There is a critical value b_{12}^{+} for which the transition lines touch one another. This case is realized in Figure 5 where $b_{12} = -6.3$.

If the intermolecular forces in the pure components are not too disparate, we can derive an approximation for the critical value

$$0.98\,(a_{11} + a_{22} + 2a_{12}) = b_{11} + b_{22} + 2b_{12}^{+} \qquad (5)$$

Applying this condition to the data of Figure 5 we get $b_{12}^{+} = -6.3$ in complete accord with the above value. For the induced phase of Figure 4, Eq. 5 is exactly valid and yields $b_{12}^{+} = -8.8$.

Because of the strong coupling between the nematic order and the smectic order in the McMillan model the isotropic-nematic and the nematic-smectic transition lines are correlated. A non-linear behavior of the clearing points always causes a non-linear nematic-smectic transition line. Vice versa, a non-linear composition dependence of the nematic-smectic phase transition may occur in spite of a linear isotropic-nematic transition line.

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