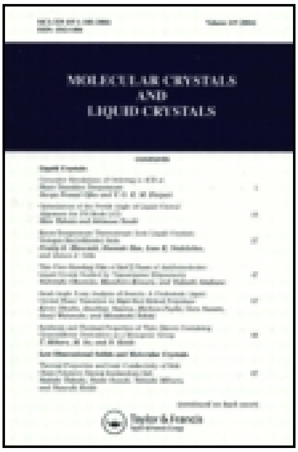

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Krystyna Szumilin & Jacek J. Milczarex (1992): Tricritical Points in Mixtures of Polar Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 212:1, 305-311

To link to this article: http://dx.doi.org/10.1080/10587259208037271

Mol. Cryst. Liq. Cryst. 1992, Vol. 212, pp. 305–311
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Printed in the United States of America

TRICRITICAL POINTS IN MIXTURES OF POLAR LIQUID CRYSTALS

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(Received March 12, 1991)

Abstract A general molecular theory of liquid crystal mixtures is presented. The phase transitions between polar and nonpolar smectic phases are discussed. The tricritical point occurence is shown.

Keywords: phase transitions, tricritical points

INTRODUCTION

The phenomena occuring in the liquid crystals mixtures containing the polar component have attracted many theoretical and experimental attentions lately.[1-4]

Our previously presented model of polar liquid crystal [5,6] allowed for discussion of the phase diagrams in the density-temperature plane. One of the interesting results of that model was the prediction of tricritical points (TCP) occurence on the phase transition lines separating polar from nonpolar phases.

Since the variation of the polar molecules density can be easily realized in the binary mixtures, it seems worthwhile to develop a molecular theory of liquid crystalline mixtures with the polar component present. To describe the experimentally studied liquid crystalline mixtures we consider the system composed of three types of molecules with different symmetries:

P - polar uniaxial molecules with the dipole moment parallel to the long molecule's axis;

N - nonpolar uniaxial molecules;

I - spherical molecules.

We propose the interaction potential between molecules of μ and ν types (μ,ν = P,N,I) in the simple form:

$$U_{\mu\nu}(1,2) = \sum_{\ell=012} W^{\ell}_{\mu\nu}(|\underline{r}_1 - \underline{r}_2|)\, P_\ell(\cos \vartheta_{12}) \qquad (1)$$

Note that this formula does not reflect properly the true symmetry of the molecular interaction in the $(\underline{r},\Omega)$ - space. Here $W^{\ell}_{\mu\nu}(r)$ depend only on the distance between the centers of masses of the molecules and are the parameters of the model.

The symmetry of the molecules constituting the system induces the following properties of the $W^{\ell}_{\mu\nu}(r)$:

$$\begin{aligned} &W^{\ell}_{I\nu} \equiv 0 \quad \text{for } \ell = 1,2, \text{ and any } \nu; \\ &W^{1}_{NN} \equiv 0; \\ &W^{1}_{NP} \equiv 0. \end{aligned} \qquad (2)$$

Those $W^{\ell}_{\mu\nu}$ functions which do not vanish for every r, determine the thermodynamical properties of the system.

THEORETICAL FRAMEWORK

The free energy F of the multicomponent system with the interaction potential defined by Eq.(1) is now calculated within the Morita and Hiroike diagram expansion method [7] in terms of the component one-particle distribution functions $\rho_\nu(\underline{r},\Omega)$ (ν=P,N,I), following the previously developed general method.[8] The total one-particle distribution function $\rho(\underline{r},\Omega)$ of the system is the sum of the component ones

$$\rho(\underline{r},\Omega) = \sum_{\nu=PNI} \rho_\nu(\underline{r},\Omega) \qquad (3)$$

According to the approximations introduced in [8] the functions ρ_ν are the only quantities which describe the possible orderings of the system. Note that the free energy F becomes now the functional of every separate ρ_ν but not of the total ρ defined by Eq.(3).

Our theory is based on the minimization of the free energy F with respect to the expansion coefficients $\alpha^\nu_{\ell m}(\underline{q})$ of the deviations of the one-particle distribution functions $\delta\rho_\nu$ from the isotropic liquid state in the generalized Fourier type series:

$$\delta\rho_\nu(\underline{r},\Omega) = n_\nu\ V^{-1/2} \sum_{\ell,m,\underline{q}} \alpha^\nu_{\ell m}(\underline{q})\ Y^m_\ell(\vartheta,\varphi)\ e^{i\underline{q}\underline{r}} \tag{4}$$

n_ν is the number density of the molecules of the ν-th type in the system of volume V.

Generalizing our previous calculations [5,8] for the one-component system to the multicomponent one we expand the free energy F in the power series in the coefficients $\alpha^\nu_{\ell m}(q)$. The second order terms can be expressed in the form:

$$F^{[2]} = \sum_{\substack{\mu,\nu \\ \ell,m,\underline{q}}} \mathscr{A}^{\mu\nu}_{\ell m}(\underline{q})\ \alpha^\nu_{\ell m}(\underline{q})\ \{\alpha^\mu_{\ell m}(\underline{q})\}^* \tag{5}$$

where

$$\mathscr{A}^{\mu\nu}_{\ell m}(\underline{q}) = \delta_{\mu\nu}\ a\ n_\nu\ \left[T - T^{\nu *}_{\ell m}(\underline{q})\right] + (1 - \delta_{\mu\nu})\ b\ n_\mu n_\nu\ \tilde{W}^\ell_{\mu\nu}(\underline{q}) \tag{6}$$

and

$$T^{\nu *}_{\ell m}(\underline{q}) = -\ n_\nu\ d_\ell\ \tilde{W}^\ell_{\nu\nu}(\underline{q}) + \text{higher order terms in } n_\nu \tag{7}$$

a,b,d_ℓ - numerical constants.

$\tilde{W}^\ell_{\mu\nu}(q)$ is the Fourier transform of the $W^\ell_{\mu\nu}(r)$ interaction function.

According to the Eq.(3) the possible orderings of the system should be described by the linear combinations of the coefficients $\alpha^\nu_{\ell m}(\underline{q})$

$$\alpha^{m}_{\ell}(\underline{q}) = \sum_{\nu} c_{\nu}\, \alpha^{\nu}_{\ell m}(\underline{q}) \qquad (8)$$

$c_{\nu} = n_{\nu}/n \; ; \; n = \sum n_{\nu}, \quad (\nu = P,N,I).$

For the $\tilde{W}^{\ell}_{\mu\nu}(q) \not\equiv 0$ case, the appearance of the second order term in Eq.(6) makes impossible the application of the previously used scheme [8] of choosing the order parameters $\alpha^{N}_{LM}(Q)$ as those $\alpha^{\nu}_{\ell m}(q)$ for which $T^{\nu *}_{\ell m}(q)$ reaches maximum. For instance this is the case of the orientational order parameter $\alpha^{0}_{2}(Q) \sim \langle Y^{0}_{2} e^{iQr} \rangle$ for the system with nonpolar uniaxial molecules present. However, these difficulties do not arise in the discussion of the polar order parameter $\alpha^{0}_{1}(Q) \sim \langle Y^{0}_{1}\, e^{iQr} \rangle$ because $W^{1}_{NN} = W^{1}_{NP} = W^{1}_{NI} \equiv 0$, then $\alpha^{0}_{1}(Q) \equiv \alpha^{P}_{10}(Q)$. For similar reasons the smectic order parameter $\alpha^{0}_{2}(Q)$ becomes $\alpha^{P}_{20}(Q)$ when we consider the binary mixture of polar and spherical molecules.

POLAR - NONPOLAR PHASE TRANSITION

To calculate the free energy F of the system we have considered the ring diagrams up to sixth order [7] and the more than double connected square diagram [5].

Our calculations show that the part of the free energy dependent on the polar order parameter $\alpha_{1} \equiv \alpha^{P}_{10}(Q)$ can be written in the standard form

$$F_{polar} = \mathcal{A}\,(T - T^{*})\,\alpha_{1}^{\,2} + \mathcal{B}\,\alpha_{1}^{\,4} + \mathcal{C}\,\alpha_{1}^{\,6} \qquad (9)$$

The α^{3}_{1} term vanishes because of the properties of the Clebsch-Gordan coefficients[5]. The non-zero critical wavevector Q, which determines the polarization smectic wave in the ordered polar phase is given by the minimum of the $\tilde{W}^{1}_{PP}(q)$. The T^{*}, $\mathcal{A}$, $\mathcal{B}$ and $\mathcal{C}$ are expressed in terms of the density n_{P} of the polar molecules and depend on the interaction functions $W^{\ell}_{P\nu}$ as well as their convolution integrals.

For the discussion of the tricritical point location on the phase transition line separating polar ($\alpha_1 \neq 0$) from nonpolar ($\alpha_1 = 0$) phase region in the density-temperature plane, the dependence of the $\mathcal{B}$ coefficient on the density n_p of the polar molecules is important. Limiting our cosiderations to the case of binary mixture of polar and nonpolar molecules we find

$$\mathcal{B} \sim n_p \left[a + n_p \beta \, (b - d\,\beta^2) + c\, n_p^4 \beta^5 \right] \tag{10}$$

where a, b, c, d are constants given by the appropriate convolution integrals of the interaction functions; ($\beta = 1/k_B T$). Eq.(10) is analogous to the one obtained for the one-component system [5,6] with $n_p = n$. One can find the region in the (n_p, T) plane where $\mathcal{B} > 0$, allowing for the continuous (2nd order) phase transitions and region with $\mathcal{B} < 0$, allowing for discontinuous (1st order) phase transitions. The points separating the phase transition lines of 1st and 2nd order are the tricritical points.

Since the sixth order term in α_1 in Eq.(9) is positive, the solutions of the $\mathcal{B}(T, n_p) = 0$ equation determine the locations of the tricritical points on the phase transition line $T = T^*(n_p)$ in the polar molecules density-temperature plane.

The numerical analysis of this model yields various possibilities for TCP existence. The interesting case of the TCP location is shown in Fig.1.

The choice of the numerical parameters in Eq.(10) allowed to obtain the results comparable to the experimental phase diagram of Shashidhar et al. [4] for C_7 - 7OPDOB mixture.

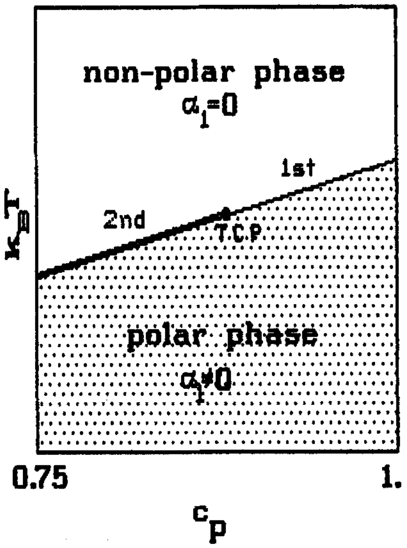

FIGURE 1 The example of the tricritical point location for the binary mixture of polar and nonpolar molecules ($c_p = n_p/n$).

DISCUSSION

Development of the previously detailed method [5,6,8] allowed to discuss the polar - nonpolar phase transitions in mixtures containing the polar uniaxial molecules with the comparatively simple model potential Eq.(1).

By consideration of higher order diagrams contributions to free energy, including the more than double-connected ones the prediction of tricritical point occurence was possible.

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