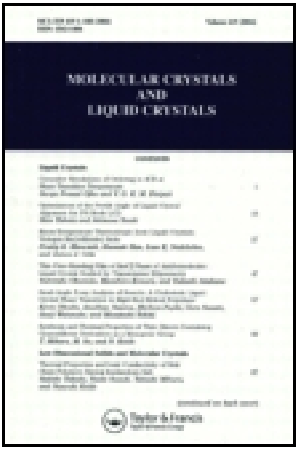

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phase Equilibria in Mixtures of Thermotropic Liquid Crystals and Flexible Polymers

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Version of record first published: 20 Apr 2011.

To cite this article: M. Ballauff (1986): Phase Equilibria in Mixtures of Thermotropic Liquid Crystals and Flexible Polymers, Molecular Crystals and Liquid Crystals, 136:2-4, 175-195

To link to this article: http://dx.doi.org/10.1080/00268948608074726

Mol. Cryst. Liq. Cryst., 1986, Vol. 136, pp. 175–195
0026-8941/86/1364-0175/$25.00/0

Printed in the United States of America

Phase Equilibria in Mixtures of Thermotropic Liquid Crystals and Flexible Polymers

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(*Received December 27, 1985*)

A theory of the nematic isotropic phase equilibrium in mixtures of thermotropic nematogens and flexible coils is presented. The steric part of the partition function is evaluated along the lines given earlier by Flory for phase equilibria of rods and coils in lyotropic systems. The soft anisotropic forces between the molecules of the nematogenic component are treated by an additional factor in the partition function. From these premises the respective phase diagrams may be calculated using the characteristic parameters of the pure components (nematogen: axial ratio, characteristic temperature, thermal expansion coefficient; coiled solute: contour length, thermal expansion coefficient) without resort to adjustable parameters. The biphasic region where a nematic and an isotropic phase coexist is predicted to increase markedly with increasing chain length of the coiled component; in case of a polymeric solute there is a virtually complete exclusion of the coils from the nematic phase. Experimental phase diagrams obtained on mixtures of low molecular weight nematogens and flexible solutes are in semiquantitative agreement with theory, for increasing chain length of the flexible compound nearly full agreement is achieved.

Keywords: lattice model, phase equilibrium, statistical mechanics

INTRODUCTION

It is now well understood that the stability of a nematic phase is mainly determined by the steric forces stemming from the anisometry of shape exhibited by typical nematogens.[1] As has been set forth by Flory in 1956[2] and later by Flory and Ronca[3] the steric forces may be dealt with by use of a lattice model. The soft anisotropic interactions which have been treated first in the theory of Maier and Saupe[4] then may be introduced by an additional factor in the partition function.[5] The treatment of lyotropic systems consisting of rods differing in length and a solvent using the lattice model[6,7] has been shown to account for all experimental facts at least in a semi-quantitative manner.[8] A similar treatment of a mixture consisting of rods, coils and a solvent[9] met with gratifying success in a comparison with experimental data.[10,11] The present work extends the latter considerations to a mixture of a thermotropic nematogen and a coiled species consisting of isodiametric segments linked together flexibly. The free volume which has been shown to be of utmost importance in describing thermotropic systems is introduced by the methods devised previously.[12,13] It has to be recalled that within the frame of this mean-field approach isotropic dispersion forces do not promote directly the ordering transition. Hence, in the model presented herein there is no coupling between the ordering process and the isotropic interaction of the coil and the nematogen as discussed recently by Brochard[14] and by de Gennes and Veyssie.[15] Thus, the nematogen is solely described by its axial ratio x_r and its characteristic temperature T^* measuring the strength of the anisotropic dispersion forces. The coiled species is fully characterized by its number of segments denoted as x_c thus disregarding the small contribution from anisotropic interactions with the nematogen. This rendition gains support from previous neutron scattering data by Dubault, Ober, Veyssie and Cabane[16] showing the ordering effect of the "nematic field" on the random coil to be very small. Furthermore, the anisotropy of the polarizability along the chain of the coiled polymers under consideration here is comparatively small and may be disregarded. In first approximation, additivity of the molar volumes can be adopted owing to the small concentration of the coiled component in the nematic matrix. The partition function of the respective mixtures may be derived from these premises in a straightforward manner. All theoretical deductions obtained herein are compared with recent experimental results on mixtures of low molecular weight nematogens and typical polymers.[17-20]

THEORY

Consider a binary system consisting of a rodlike nematogen and a random-coil polymer. The diameters of the components are assumed to be equal to the size of the lattice cell. The axial ratio of the rodlike particle is x_r and the contour length of the random coil is x_c. The free volume present in the system is introduced by allowing a corresponding fraction of the lattice sites to remain vacant. The shortcoming of this device is well-known[21] and has been discussed in more detail recently.[12,13] Inasmuch as the assignment of the free volume to the lattice cells is restricted to the treatment of the dependence of the partition function on orientation it does not affect the representation of the other properties of the liquid which may be dealt with by well-established methods.[22] The excellent agreement of theory and experiment when applied to suitable model systems[23,24] furthermore demonstrates the validity of this treatment.

The combinatorial analysis along the lines given by Flory in Ref. 9 may be readily adapted for the system under consideration. As usually,[3,12,13] the mixing partition function Z_M is subdivided into the combinatorial part Z_{comb}, the orientational part Z_{orient} and the intramolecular or conformational part Z_{conf}:

$$Z_M = Z_{\text{comb}} \cdot Z_{\text{orient}} \cdot Z_{\text{conf}} \tag{1}$$

Since the configuration of the random coil is assumed to be independent of the order present in the respective phase, Z_{conf} is a constant and may be dismissed in the subsequent treatment. Let n_0 denote the total number of lattice sites, n_x the number of rodlike molecules and n_c the number of random coils. As in Ref. 2 the quantity y specifies the disorientation of the rodlike particle. For a molecule with the long axis at an angle ψ with respect to the domain axis:[3]

$$y = \frac{4}{\pi} x_r \sin\psi \tag{2}$$

With the orientational distribution function for the rodlike component being given by the ratio n_{xy}/n_x of the number of molecules with disorientation y to the total number n_x, the mean value $\bar{y}$ follows as:

$$\bar{y} = \sum_y \frac{n_{xy}}{n_x} y \tag{3}$$

As shown in Ref. 9 Z_M then is given by:

$$Z_M = \frac{(n_0 - n_x(x_r - \bar{y}))!}{(n_0 - n_x x_r)!\, n_x!\, n_0^{n_x(\bar{y}-1)}} Z_{\text{orient}} *$$

$$\frac{(n_0 - n_x x_r)!}{(n_0 - n_x x_r - n_c x_c)!\, n_c!\, n_0^{n_c(x_c - 1)}} \tag{4}$$

The first factor in braces in Eq. (4) expresses the expected number of configurations for the rodlike species in the empty lattice.[3] The last term takes into account the configurations accessible to the n_c coiled molecules which have been added to the lattice subsequently (cf. Ref. 9). Thus:

$$Z_M = \frac{(n_0 - n_x(x_r - \bar{y}))!\, Z_{\text{orient}}}{(n_0 - n_x x_r - n_c x_c)!\, n_x!\, n_c!} n_0^{-n_x(\bar{y}-1) - n_c(x_c - 1)} \tag{5}$$

The orientational partition function Z_{orient} may be expressed as:[3,12]

$$Z_{\text{orient}} = \prod_y \left[\left(\frac{\omega_y n_x}{n_{xy}} \right) \exp(-x_r \epsilon_y / 2 k_B T) \right]^{n_{xy}} \tag{6}$$

where[5]

$$\omega_y = \sin\psi \tag{7}$$

is the a priori probability of disorientation y for a rodlike solute, and ϵ_y is the orientation-dependent energy of one segment in the mean field of its neighbors when its disorientation is y; k_B and T are the Boltzmann constant and the temperature, respectively. Inasmuch as we assume the conformation of the random coil to be independent of the order in the coexisting phases, Z_{orient} only depends on the distribution function n_{xy}/n_x of the rodlike species. The orientation-dependent interaction energy may be expressed by:[5,12,13]

$$\epsilon_y = -(k_B T^* / \tilde{V})\, s \left(1 - \frac{3}{2} \sin^2\psi \right) \tag{8}$$

with the characteristic temperature T^* measuring the strength of the orientation-dependent dispersion forces; $\tilde{V}$ is the reduced volume, i.e., the ratio of the volume V of the system to the occupied volume V^*

$$\tilde{V} = V / V^* \tag{9}$$

and s is the usual order parameter:[5]

$$s = 1 - \frac{3}{2} \langle \sin^2\psi \rangle \tag{10}$$

The reduced orientation-dependent energy of the whole system follows as:[5]

$$E_{\text{orient}}/k_B T = -\frac{n_x x_r}{2\tilde{V}\theta}s^2 \tag{11}$$

with the reduced temperature θ being defined by:

$$\theta = T/T^* \tag{12}$$

Combining Eqs. (4), (6), and (18) and introducing Stirling's approximation for the factorials, one obtains for the reduced free energy (cf. Ref. 9)

$$\begin{aligned} -\ln Z_M = & -(n_0 - n_x x_r + n_x \bar{y}) \ln\left[1 - \frac{n_x x_r}{n_0}\left(1 - \frac{\bar{y}}{x_r}\right)\right] \\ & + n_x \ln\frac{n_x}{n_0} + n_c \ln\frac{n_c}{n_0} + n_x(\bar{y} - 1) + n_c(x_c - 1) \\ & + (n_0 - n_x x_r - n_c x_c) \ln[(n_0 - n_x x_r - n_c x_c)/n_0] \\ & - n_x \sum_y \frac{n_{xy}}{n_x} \ln\frac{n_{xy}}{n_x \omega_y} - \frac{n_x x_r}{2\tilde{V}\theta}s^2 \end{aligned} \tag{13}$$

Note that this expression holds for any disorientation y.

Let V_1^* denote the volume of one segment. Then it follows that

$$n_0 V_1^* = V = (n_x x_r + n_c x_c)\tilde{V} V_1^* \tag{14}$$

Thus

$$n_0 = (n_x x_r + n_c x_c)\tilde{V} \tag{15}$$

Also, we have

$$\tilde{V} = (\tilde{V}_r n_x x_r + \tilde{V}_c n_c x_c)/(n_x x_r + n_c x_c) \tag{16}$$

with $\tilde{V}_r$ and $\tilde{V}_c$ being the reduced volume of the nematogen and the coiled solute, respectively.

Hence, the volume fractions v_r and v_c of the rodlike and the coiled species follow as:

$$v_r = \tilde{V}_r n_x x_r / [(n_x x_r + n_c x_c)\tilde{V}] \tag{17}$$

$$v_c = \tilde{V}_c n_c x_c / [(n_x x_r + n_c x_c)\tilde{V}] \tag{18}$$

Thus:

$$\tilde{V}^{-1} = \frac{v_r}{\tilde{V}_R} + \frac{v_c}{\tilde{V}_c} \tag{19}$$

The orientational distribution function n_{xy}/n_x for the rodlike species can be derived by taking the variation of $-\ln Z_M$ with respect to n_{xy}/n_x[5] resulting to

$$n_{xy}/n_x = \omega_y/f_1 \exp\left[-\frac{4}{\pi} a x_r \sin\psi - \frac{3x_r s}{2\tilde{V}\theta}\sin^2\psi\right] \tag{20}$$

where the quantity a is defined by[5]

$$a = -\ln\left[1 - \frac{n_x x_r}{n_0}\left(1 - \frac{\bar{y}}{x_r}\right)\right] \tag{21}$$

or, by virtue of Eq. (17) (cf. Refs. 12 and 13):

$$a = -\ln\left[1 - \frac{v_r}{\tilde{V}_r}\left(1 - \frac{\bar{y}}{x_r}\right)\right] \tag{22}$$

As in Ref. 5 the family of integrals f_p can be expressed as

$$f_p = \int_0^{\pi/2} \sin^p\psi \exp\left[-\frac{4}{\pi} a \sin\psi - \frac{3x_r s}{2\tilde{V}\theta}\sin^2\psi\right] \tag{23}$$

leading to the self-consistency relations

$$\bar{y} = \frac{4}{\pi} x_r f_2/f_1 \tag{24}$$

$$s = 1 - (3/2) f_3/f_1 \tag{25}$$

The chemical potentials of the two components are conveniently obtained by partial differentiation of Eq. (13) subject to the stipulation that the ratios n_{xy}/n_x shall be assigned the equilibrium values that minimize $-\ln Z_M$. Therefore, these ratios are exempt from differentiation. Substitution from Eq. (15) for n_0, partial differentiation with respect to n_r or n_c and subsequent replacement of the n_{xy}/n_x by Eq. (20) then leads to

$$\begin{aligned}\Delta\mu_x/RT = {} & \ln\frac{v'_r}{x_r\tilde{V}_r} + v'_r(\bar{y}-1) + v'_c x_r\left(1-\frac{\tilde{V}_r}{\tilde{V}_c x_c}\right)\\ & + x_r\left(\frac{\tilde{V}_r}{\tilde{V}'}-1\right) + x_r(\tilde{V}_r-1)\left[a+\ln\left(1-\frac{1}{\tilde{V}'}\right)\right]\\ & -\ln f_1 - \frac{x_r s}{\tilde{V}\theta}\left[1-\frac{1}{2}s-\frac{1}{2}s\,v'_r\left(1-\frac{\tilde{V}'}{\tilde{V}_r}\right)\right] \qquad (26)\end{aligned}$$

and

$$\begin{aligned}\Delta\mu_c/RT = {} & \ln\frac{v'_c}{x\tilde{V}_c} + v'_r\frac{\tilde{V}_c x_c}{\tilde{V}_r x_r}(\bar{y}-1) + v'_c\left(\frac{\tilde{V}_c}{\tilde{V}_r}x_c-1\right)\\ & + x_c\tilde{V}_c\left(\frac{1}{\tilde{V}'}-\frac{1}{\tilde{V}_r}\right) + \tilde{V}_c x_c a + x_c(\tilde{V}_c-1)\ln\left(1-\frac{1}{\tilde{V}'}\right)\\ & + \frac{s^2 x_c}{2\tilde{V}\theta}\frac{v'_r}{\tilde{V}_r}(\tilde{V}_c-\tilde{V}) \qquad (27)\end{aligned}$$

for the reduced chemical potentials of the respective compounds at orientational equilibrium. Here, primes are appended to all quantities which may differ in the coexisting phases. As usually[12,13] the small difference of the reduced volumes of the components in the isotropic and the anisotropic phases is neglected, i.e., $\tilde{V}_r = \tilde{V}'_r$, and $\tilde{V}_c = \tilde{V}'_c$. However, $\tilde{V} \neq \tilde{V}'$ since the composition in the coexisting phases is different. Note that in case of $\tilde{V}_r = \tilde{V}_c = 1$ and $\theta \rightarrow \infty$ Eq. (26) reduces to Eq. (10) of Ref. 9 when f_1 is expressed in the terms of the "1956" approximation.[2,3] Correspondingly, Eq. (27) becomes identical with Eq. (11) of Ref. 9 upon equating the reduced volumes $\tilde{V}_r$, $\tilde{V}_c$ and $\tilde{V}$ to unity.

The chemical potentials for the isotropic phase obtained by setting $y = x_r$, $s = 0$ and $f_1 = 1$ are:

$$\Delta\mu_x/RT = \ln\frac{v_r}{x_r\tilde{V}_r} + v_r(x_r - 1) + v_c x_r\left(1 - \frac{\tilde{V}_r}{\tilde{V}_c x_c}\right) + x_r\left(\frac{\tilde{V}_r}{\tilde{V}} - 1\right) + x_r(\tilde{V}_r - 1)[\ln(1 - \tilde{V}^{-1})] \quad (28)$$

and

$$\Delta\mu_c/RT = \ln\frac{v_c}{x_c\tilde{V}_c} + v_r\frac{\tilde{V}_c x_c}{\tilde{V}_r}\left(1 - \frac{1}{x_r}\right) + v_c\left(\frac{\tilde{V}_c}{\tilde{V}_r}x_c - 1\right) + x_c\tilde{V}_c\left(\frac{1}{\tilde{V}} - \frac{1}{\tilde{V}_r}\right) + x_c(\tilde{V}_c - 1)\ln(1 - \tilde{V}^{-1}) \quad (29)$$

(cf. Eqs. (13) and (14) of Ref. 9).

Biphasic Equilibria

For calculating the characteristic temperature T^* of the neat nematogen we first consider the equilibrium condition for a one-component system. Upon equating the molar free energies given by Eqs. (26) and (27) for the case of a single component we obtain (cf. Refs. 12 and 13):

$$x_r(\tilde{V}_r - 1)a - \ln f_1 - (x_r - \bar{y}) - \frac{x_r s}{\tilde{V}_r\theta}\left(1 - \frac{s}{2}\right) = 0 \quad (30)$$

The reduced volumes of the pure compounds are accessible through the relation:[25]

$$\tilde{V}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \quad (31)$$

where α denotes the thermal expansion coefficient of the respective component at a given temperature T. As stated above, the reduced volumes of the anisotropic phase $\tilde{V}'$ may be set equal to its corresponding value in the isotropic phase with negligible error. Given x_r and $\tilde{V}_r$, Eq. (30) can be solved numerically to yield the reduced temperature θ. With the temperature T_{ni} of the nematic-isotropic transition being known one may obtain the characteristic temperature T^* via Eq. (12).

BINARY MIXTURES

Biphasic equilibria

Biphasic equilibrium between the nematic and the isotropic phase requires $\Delta\mu_i = \Delta\mu_i'$ for all components present in the system the respective chemical potentials being given by Eq. (26)–(29). If x_r, x_c, $\tilde{V}_r$, $\tilde{V}_c$ and T^* are known, the equilibrium conditions may be solved numerically as follows: Provisional values of v_r', $\bar{y}$ and s serve for the numerical evaluation of the f_p (Eq. (23)) which subsequently yield improved values of $\bar{y}$ and s via Eqs. (24) and (25). The calculation is repeated until self-consistency is achieved. Upon setting $\tilde{V} = \tilde{V}'$ the latter quantity being accessed through (19), the condition $\Delta\mu_r = \Delta\mu_r'$ may be solved for v_r which in turn leads to an improved value of $\tilde{V}$. Finally, the starting value of v_r' is compared to the value calculated from the condition $\Delta\mu_c = \Delta\mu_c'$ and the entire process is repeated until all conditions for equilibrium are satisfied.

RESULTS AND DISCUSSION

It has been predicted by Flory[9] that a mixture of rods and coils immersed in a solvent will separate into an anisotropic phase containing nearly exclusively the rodlike particles and an isotropic phase which consists mainly of a solution of the coiled polymer. The experimental confirmation of this prediction[10,11] demonstrates clearly the validity of the lattice treatment of the nematic state. As is evident from Figure (1) where the reduced temperature T/T_{ni} is plotted versus the segment fraction φ_2 given by:

$$\varphi_2 = v_c/\tilde{V}_c \cdot (v_c/\tilde{V}_c + v_r/\tilde{V}_r)^{-1}$$

the partitioning of the rodlike and the coiled species is predicted to occur also in mixtures of a thermotropic nematogen and a flexible solute. In the example presented in the following three figures T^* has been chosen to locate the nematic-isotropic transition temperature T_{ni} at 100°C; the magnitude of the expansion coefficients is of

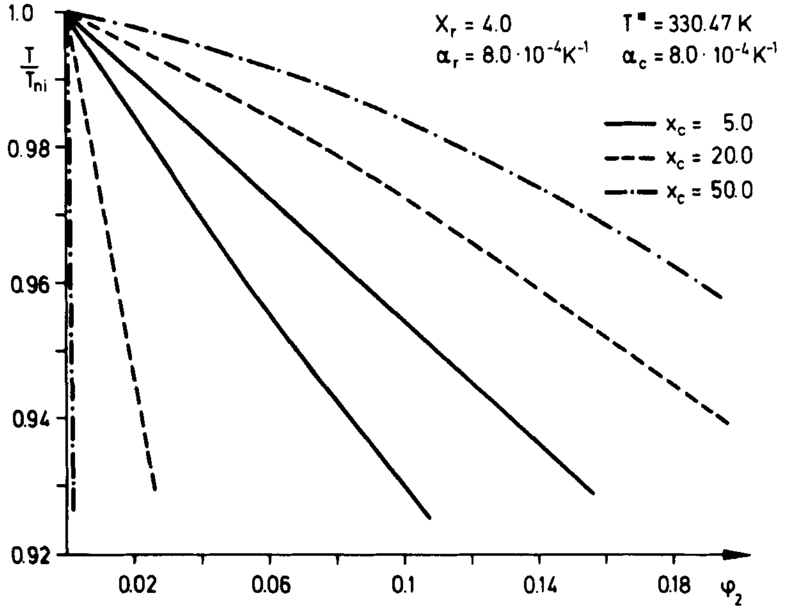


FIGURE 1 Calculated phase diagrams of a mixture consisting of a thermotropic nematogen and a coiled species differing in number of segments denoted by x_c. The quantity x_r is the axial ratio of the rodlike component; T^* its characteristic temperature measuring the strength of the anisotropic dispersion forces and T_{ni} is the nematic-isotropic transition temperature of the pure nematogen. The thermal expansion coefficients of the rodlike and the coiled component are denoted by α_r and α_c, respectively. The segment fraction φ_2 of the flexible species has been chosen as the independent variable.

the order found in typical low molecular weight liquids. In all calculations presented herein the thermal expansion coefficients are assumed to be constant in the comparatively narrow range of temperature. In view of the fact that additivity of molar volumes has been inferred through Eq. (16) this approximation may be justified in the course of the present calculation. As in the case of lyotropic systems[9] the compatibility of the two components decreases with increasing length of the coiled molecule. When x_c is greater than 50 the flexible species is excluded nearly totally from the isotropic phase thus rendering the "nematicus" line identical with the ordinate. Owing to the fact that in the model presented here the coiled species has no thermotropic transition, the upper curve indicating the temperature where the first nematic droplet is formed has a slight downward curvature.

The phase diagram in Figure 2 underscores the importance of the equation-of-state parameters. Changing the thermal expansion coef-

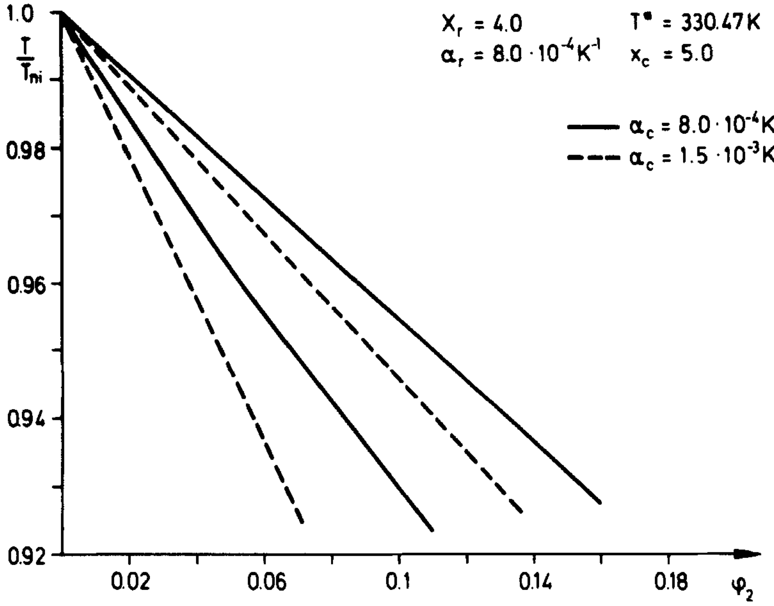


FIGURE 2 Calculated phase diagrams of a mixture of a thermotropic nematogen and a coiled species characterized by a different coefficient of thermal expansion α_c. The quantity x_r denotes the axial ratio of the rodlike compounds, T^* its characteristic temperature and T_{ni} its nematic-isotropic transition temperature, and x_c is the number of segments of the coiled species. As the independent variable the segment fraction φ_2 of the solute has been chosen.

ficients of the coiled component from 8.0 10^{-4} to 1.5 10^{-4} shifts the biphasic region to considerably lower temperatures. This finding clearly is related to the fact that a higher α_c leads to an increase of the reduced volume. As shown in Ref. 12 the stability of the nematic phase is very sensitive towards the free volume present in the system; the transition temperature is predicted to decrease rapidly with increase of $\tilde{V}$. The same reasoning applies to the system considered here, of course. Figure 3 finally demonstrates the influence of the axial ratio x_r of the nematogen when the nematic-isotropic transition temperature is kept constant. Thus the characteristic temperature T^* is going down considerably when changing x_r from 4.0 to 5.0 which is followed by a lowering of the range of temperature where the two phases coexist.

An additional point of interest is the dependence of the order parameter s on temperature along the "nematicus" line. Earlier measurements on mixtures of a nematogenic liquid crystal and a low molecular weight solute[18,26] showed s to be nearly constant along that

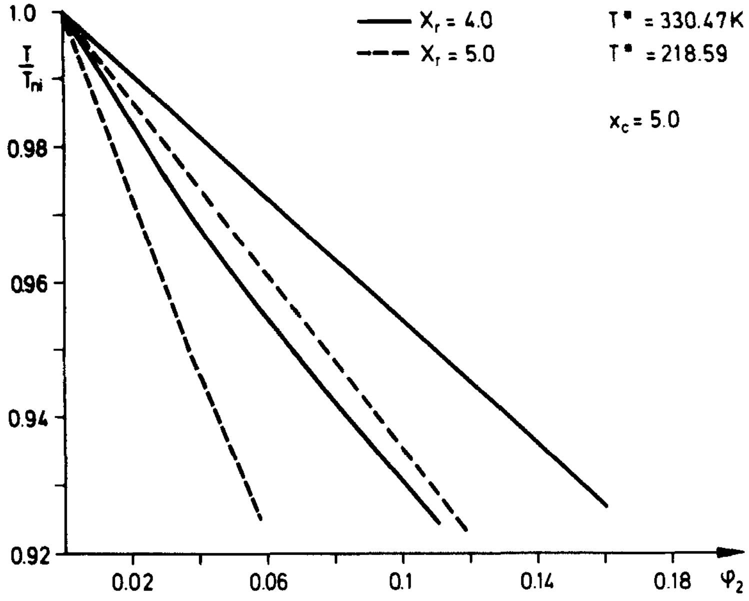


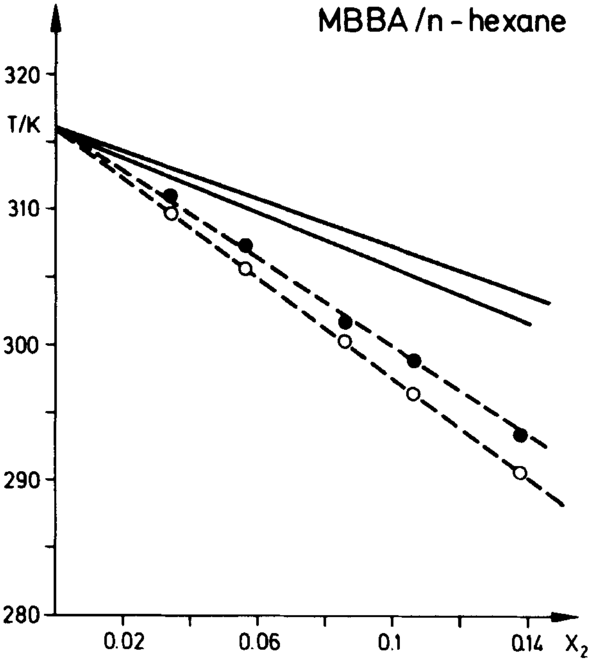
FIGURE 3 Calculated phase diagrams of a mixture of a thermotropic nematogen and a coiled species. The quantity x_r denotes the axial ratio of the rodlike compounds, T^* its characteristic temperature which has been adjusted to yield a nematic-isotropic transition temperature of 100°C for both axial ratios. The number of segments of the coiled species is denoted by x_c; α_r and α_c are the thermal expansion coefficients of the rodlike and the coiled species, respectively. As the independent variable the segment fraction φ_2 of the solute has been chosen.

line. However, a recent investigation of this point by Dubault et al.[19] using a mixture of EBBA and a polystyrene of molecular weight 2100 demonstrates that s changes considerably upon lowering the temperature. This fact has been discussed by the authors in terms of the concept of a pseudo clearing temperature introduced by F. Brochard[14,27] (see also the discussion of the problem by de Gennes and Veyssie).[15] Due to the neglect of higher order terms in the expansion Eq. (8) the treatment of the orientational distribution function within the frame of the present model is not suitable for an extensive discussion of the order parameter. However, the present calculation suffices to demonstrate the general feature of the dependence of s on temperature. In case of $x_r = 4$ and $x_c = 5$ where the magnitude of the latter quantity corresponds to a typical low molecular weight solute the calculation shows the order parameter to be nearly constant (ca. 0.64) along the nematicus line (cf. Figure 1). This is in accord with the above mentioned measurements[18,26] on systems characterized by similar values of x_r and x_c. In these experiments the nematic phase contains a considerable amount of the randomly oriented species. Hence, the order parameter under these circumstances results from a cancellation of the increase of s due to the lowering of the temperature and the decreasing concentration of the nematogen in the ordered phase favoring disorder. When x_c is much larger than x_r, i.e., in a mixture of a low molecular weight nematogen and a polymer the concentration of the coiled species in the ordered phase is very much diminished (see Figure 1). As a consequence, the order parameter is less influenced by the solute. Its calculated dependence on temperature resembles more the behavior found in the neat nematogen; s is increasing upon lowering the temperature. Hence, the present model can explain the temperature dependence of the order parameter without additional assumptions.

We now turn to a comparison of the calculated phase diagrams with experimental data. In doing so, one should bear in mind that all nematogenic liquid crystals used in these investigations are not ideally rodlike molecules as assumed by theory but contain flexible tails like *n*-butyl groups. The error thus introduced is very difficult to estimate at present. Furthermore, the model assumes a strictly binary solution but real polymers always exhibit a finite width of the molecular weight distribution. Since theory shows the breadth of the biphasic gap to be strongly dependent on the length of the coiled species as expressed by x_c, the error inferred by neglecting the nonuniformity may be of appreciable magnitude (cf. Figure 1). Finally, a comparison of the theory developed herein and experiments is as well a test of the mixing relation Eq. (16) and the underlying equation-of-state data obtained by Eq. (31).

Figure (4a–d) shows the phase diagrams calculated for mixtures of MBBA with *n*-alkane liquids studied by Kronberg, Gilson and Patterson.[18] For a direct comparison with the Ref. 18 the mole fraction of the solute is used as the independent variable. The parameters of the respective compounds used in the calculation are summarized in Table I.

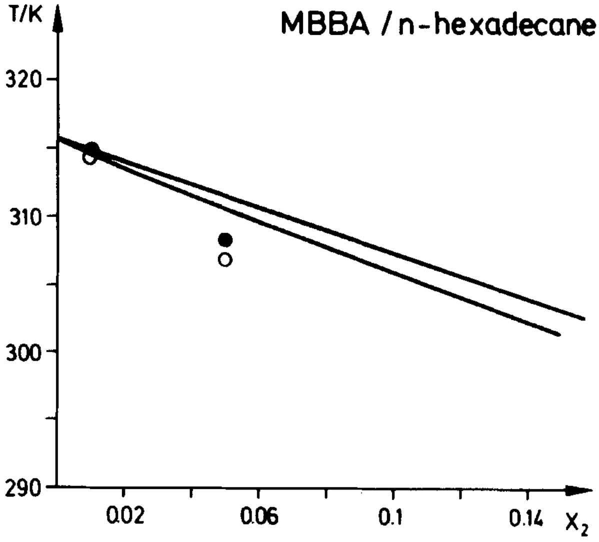
The density and the thermal expansion coefficient of MBBA were obtained by the data given by Kuss.[28] Its axial ratio x_r was deduced from the molar hard core volume and the main diameter of the molecule the latter quantity being estimated to 4.7Å from the mean diameter of the benzene ring in related compounds.[24] Since MBBA contains flexible end groups thus departing considerably from a rodlike structure this method seems to be the only appropriate way for a reasonable estimate of x_r. A comparison of the x_r obtained from



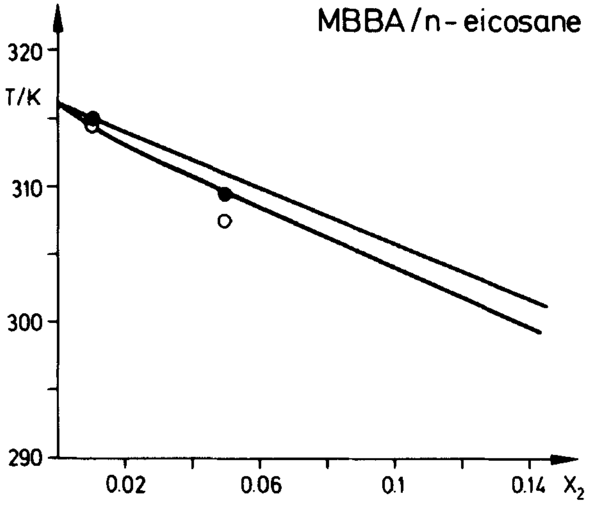
(a)

FIGURE (4a–d) Comparison of calculated phase diagrams with experimental data obtained from mixtures from MBBA with *n*-alkane liquids studied by Kronberg, Gilson and Patterson.[18] The characteristic parameters of the respective components are summarized in Table I. As the independent variable the mole fraction of the solute has been chosen. Bold lines: theory; filled circles: boundary of the isotropic region and the two-phase region; empty circles: boundary of the two-phase region and the nematic region; in Figure (4a) the data have been taken from Figure (3) of reference 18; in Figure (4b–d) the data have been calculated using the respective β^I and β^N values of reference 18. (See text for explanation).

this method with the values deduced from structural data by Flory and Ronca[5] furthermore reconfirmed the validity of the present way of access to this quantity. Equation-of-state data of the *n*-alkanes have been taken from the work of Flory, Orwoll, and Vrij[25] and from the density data given by Templin.[29] The number of segments of these components results from the ratio of their respective hard core volumes and the hard core volumes of one segment of the rodlike species. Trial calculations demonstrates that the error of the axial ratio which may be inferred by this method of determining x_r and x_c is nearly inconsequential for the resulting phase diagrams. In Figure 4a, experimental points were taken from the corresponding graph in Ref. 18; the points in Figure 4b and 4c at low concentration (mole

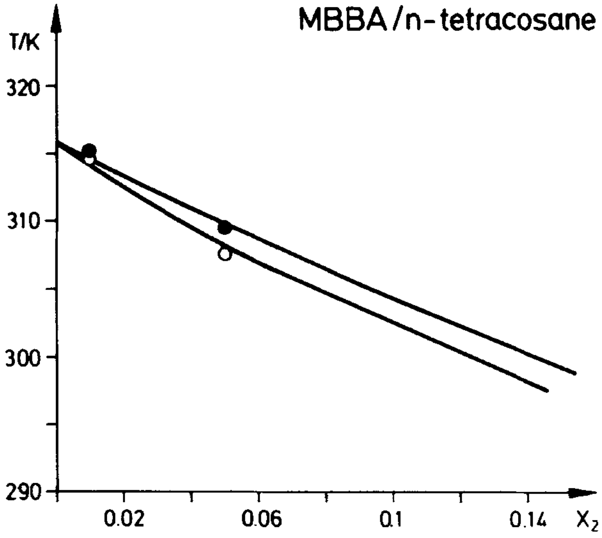


(b)



(c)

FIGURE 4 *(continued)*



(d)

FIGURE 4 *(continued)*

TABLE I

Equation-of-state data for the system MBBA/*n*-alkane

MBBA (*p*-Methoxybenzylidine-*p*-*n*-butylaniline)

$\rho(40°C) = 1.0332$ g/cm^3 [28]
$T_{ni} = 43.4°C$
$x_r = 3.4$
$\alpha = 8.5\ 10^{-4}K^{-1}$
$\tilde{V}$ at $T_{ni} = 1.225$
$V^* = 211.2$ cm^3/Mol
$T^* = 351.74K$

n-Alkanes

n	V^*/cm^3 Mol^{-1}	x_c	$\alpha \cdot 10^3K^{-1}$	Reference
6	99.9	1.6	1.51	25
16	241.1	3.9	0.92	25
20	297.8	4.8	0.86	25
24	354.2	5.7	0.82	29

α: thermal expansion coefficient in the respective range of temperature; V^*: molar hard core volume; T_{ni}: nematic-isotropic transition temperature; V: reduced volume; T^*: characteristic temperature of the nematogen; x_r: axial ratio of the nematogen; x_c: number of segments of the coiled component.

fraction of solute = 0.01) have been calculated using the $\beta^{N\infty}$ and the $\beta^{I\infty}$ values given in Table I of Ref. 18, for the higher mole fraction 0.05 the corresponding β^N and β^I were used (see discussion of these quantities in Ref. 18). The comparison of the theoretical phase diagrams and the experimental data shows that the present model approximates the width of the biphasic gap very well. But in case of the short-chain solute the range of temperature where the two phases coexist is overestimated. However, this error is very much diminished when going from *n*-hexane to *n*-eicosane; in case of a mixture of MBBA and *n*-tetracosane nearly full agreement of theory and experiment is achieved. It has to be noted that no adjustable parameter has been used in the course of the calculation presented in Figure 4a–d. The discrepancy of theoretical and measured phase diagrams, especially in case of shorter chains may be originated in the neglect of the change of volume when mixing the two components. As already mentioned in the Introduction this effect is expected to be of minor importance in the regime of concentration under consideration here. Also it could be argued that the relatively stiff *n*-alkane molecules take part in the ordering process. This clearly would lead to an increased stability of the nematic phase. Consequently, the biphasic gap should be located at higher temperatures as compared to theory. This is contrary to the experimental results presented in Figure 4a–d. However, the above statement does not exclude an alignment of the hydrocarbon molecules in the immediate neighborhood of the rodlike nematogens. The present results only indicate that this short-range order does not change considerably when going from the isotropic to the nematic phase. Another feature not taken into account in the present approach is the enthalpy of mixing due to isotropic equation of state contributions. In the present model of the nematic state, isotropic forces do not promote directly the ordering transition. However, in case of a binary mixture the coexisting phases may differ considerably in composition. Consequently, the enthalpy of mixing alters the free energy of mixing when going from the nematic to the isotropic state, especially in case of two chemically disparate components. The results shown here indicate that this contribution to the free energy is important when x_c is small, i.e., when a low molecular weight compound is dissolved in a liquid crystalline solvent. The enthalpy of mixing becomes less important with increase of the chain length of the flexible component. When the flexible solute is long enough, i.e., with increasing x_c the phase diagram is expected to be fully governed by the entropic part of the free energy.

The foregoing considerations suggest that the present model should work best in case of a polymeric solute where $x_r << x_c$. Unfortunately, the experimental determination of the phase boundaries becomes more and more difficult with increasing x_c, for high polymer a virtually complete demixing occurs ((cf. Ref. 17) for a discussion of this point). Since the theory given herein only addresses the case of a molecularly uniform solute, the polymer used in the respective experiments should exhibit a very narrow molecular weight distribution. Only anionically prepared samples with sufficient degree of polymerization may match this requirement. Figure 5a and 5b show the comparison of measured and calculated phase diagrams for polystyrene dissolved in EBBA. The respective data of the pure components are gathered in Table II.

In Figure 5a, data were taken from the work of Kronberg, Bassignana and Patterson,[17] and from the work of Dubault, Casagrande, Veyssie and Deloche.[20] The respective data for polystyrene are avail-

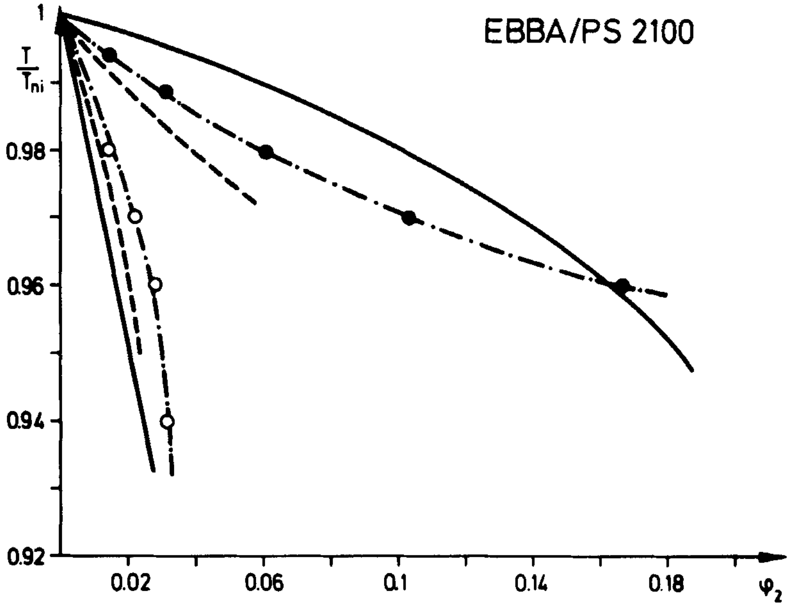


FIGURE (5a) Comparison of calculated phase diagrams with data obtained from the system EBBA/polystyrene 2.100. The data used in the calculation are summarized in Table II; as the independent variable the segment fraction of the solute has been chosen. Points: data taken from the work of Kronberg, Bassignana and Patterson;[17] dashed line: data taken from Figure (1) from the work of Dubault, Casagrande, Veyssie and Deloche.[20]

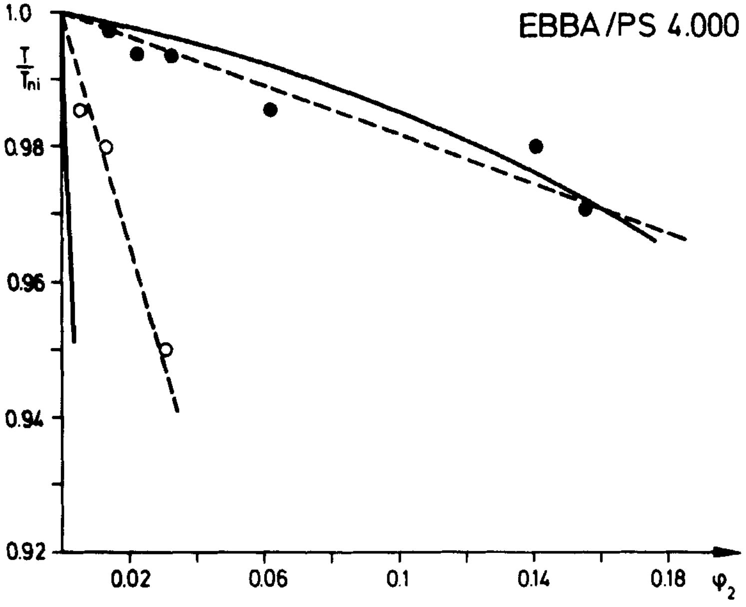


FIGURE (5b) Comparison of calculated phase diagrams with data obtained from the system EBBA/polystyrene 4.000. The data used in the calculation are summarized in Table II; as the independent variable the segment fraction of the solute has been chosen. Points: data taken from the work of Kronberg, Bassignana and Patterson.[17]

TABLE II

Equation-of-state data for the system EBBA/polystyrene

EBBA (*p*-Ethoxybenzylidine-*p*-*n*-butylaniline)

$\rho(80°C) = 0.9881\ g/cm^3$ [28] $\alpha = 8.22\ 10^{-4}K^{-1}$ [28] $V^* = 229.3\ cm^3/Mol$

$T_{ni} = 79.1°C$[17] $\tilde{V}$ at $T_{ni} = 1.242$ $T^* = 351.2K$

$x_r = 3.7$

Polystyrene $v\ (100°C) = 0.9746\ cm^3/g$ $v^* = 0.8205\ cm^3/g$[30]

M_w	x_c	$\alpha \cdot 10^3K^{-1}$	Reference
2.100	27.8	0.577	30
4.000	52.9	0.577	30

α: thermal expansion coefficient in the respective range of temperature; V^*: molar hard core volume; v^*: specific hard core volume; $\tilde{V}$: reduced volume; T^*: characteristic temperature of the nematogen; x_r: axial ratio of the nematogen; x_c: number of segments of the coiled component; T_{ni}: nematic-isotropic transition temperature.

able from the work of Höcker, Blake and Flory.[30] As is obvious from Figure 5a the agreement is sufficient for the nematicus line, but the upper phase boundary where the scattering of experimental data seems to be more severe the curvature exhibited by the experimental line is not reproduced. Here the effect of the residual nonuniformity of the polymer sample may cause this discrepancy. When the chain length of the solute component is increasing further (cf. Figure 5b), nearly full agreement of the calculated and measured isotropic phase boundary is achieved whereas the nematicus line seems to be reproduced at least in a semiquantitative fashion. In case of still higher chain length of the polymer, theory predicts nearly complete demixing of the two components in good agreement with the data of Kronberg et al. (cf. Figure 1 of Ref. 17). This corroborates the above statement that for increasing x_c the free energy is mainly determined by its entropic part. Hence, from these results it appears to be questionable that the Flory-Huggins theory with an adjustable interaction parameter[31,32] is suitable to describe the thermodynamics of the systems under consideration here. This deduction gains further support from the experimental finding of the demixing of rods and coils even under athermal conditions[10] an observation which obviously cannot be described by the Flory-Huggins theory.

CONCLUSION

A theory of the phase behavior of mixtures of thermotropic nematogens and flexible coils has been developed on the base of the Flory lattice model. Using the equation of state data of the respective components the phase diagrams may be derived without adjustable parameters. The most prominent feature predicted by the present model is the widening of the biphasic gap with increasing chain length of the polymeric compound. Despite the simplicity of the treatment semi-quantitative agreement is found in a comparison with data obtained on mixtures of low molecular weight nematogens with *n*-alkanes and polystyrenes.

Acknowledgment

Financial Support by the Bundesministerium für Forschung und Technologie (Projekt "Steife Makromoleküle") is gratefully acknowledged.

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