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Complete phase diagrams of mixtures of a nematic liquid crystal with n-alkanes

H. Orendi[a]; M. Ballauff[a]
[a] Max-Planck-Institut für Polymerforschung, Mainz, F. R. Germany

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PRELIMINARY COMMUNICATIONS

Complete phase diagrams of mixtures of a nematic liquid crystal with *n*-alkanes

by H. ORENDI and M. BALLAUFF
Max-Planck-Institut für Polymerforschung, Postfach 3148, 65 Mainz, F.R. Germany

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The full experimental phase diagrams of mixtures of the nematic liquid crystal 4,4′-azoxyanisole, (PAA), and *n*-tetracosane and of PAA and *n*-octadecane are given. Equilibria of a nematic phase with an isotropic phase, of two isotropic phases, and a reentrant isotropic phase could be observed directly. The experimental phase diagram is in qualitative agreement with the result derived from the Flory lattice model adopted for thermotropic systems.

Binary systems consisting of a nematic liquid crystal and a solute exhibit a biphasic region in which a nematic and an isotropic phase coexist. This effect has been studied with great care for a number of common nematogens mixed with various solutes, mainly to elucidate the role of the shape of the solute on phase stability [1–4]. Of particular interest are mixtures of nematic liquid crystals with flexible polymers. In this special case a strong incompatibility of the two components with increasing chain length of the macromolecular solute is predicted [5]. For mixtures of thermotropic nematogens with oligomers and polymers of varying chain length Kronberg *et al.* [6] gave clear experimental proof that the polymeric component is virtually excluded from the nematic phase if its chain length is sufficiently high; similar observations have been made by Dubault *et al.* [7]. This interesting effect leads to the fundamental question of how the coiled component influences the state of order in the nematic liquid crystal [7, 8]. Also, the interference of liquid–liquid demixing with the nematic–isotropic phase separation and the shape of the resulting phase diagrams are of general interest [4, 7, 9].

To elucidate these questions further the lattice model of nematic fluids [5, 10] has been extended to include mixtures of thermotropic nematogens with a polymeric species. Since the essential features of the theory have been discussed recently in detail [4, 9], a short summary will suffice here. As in [4] the rod-like solvent is characterized by its axial ratio x_r and the coiled component by its number of segments x_c. The anisotropic interaction between the molecules of the nematogen enters via a characteristic temperature [11] T^* which is related to the energy of anisotropic interaction ε_φ by

$$\varepsilon_\varphi = -(kT^*/\tilde{V})v_r S P_2(\cos\varphi),$$

$\tilde{V}$ denotes the reduced volume, i.e. the ratio of the volume of the system to the hard core volume of the components, v_r the volume fraction of the nematic component, S is the order parameter and P_2 $(\cos\varphi)$ is the second Legendre polynomial.

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Solvent–solute interactions are introduced through the familiar Flory–Huggins interaction parameter χ or a corresponding characteristic temperature T_i^* of isotropic interaction [9, 12] defined by,

$$\Delta H_M = n_c x_c v_r \chi = n_c x_c v_r (T_i^*/T),$$

where ΔH_M denotes the enthalpy of mixing and n_c the number of coiled molecules. It is assumed that nematic ordering does not change the solvent power of the solvent, i.e. χ remains unchanged upon formation of the nematic phase.

The phase diagram calculated [9] for a mixture of a typical nematogen 4-ethoxybenzylidene-4′-*n*-butylaniline (EBBA), with a short chain solute ($x_c = 27{\cdot}8$) is shown in figure 1. The interaction parameter expressed in terms of T_i^* is large enough to cause liquid–liquid demixing in the isotropic phase. At lower temperatures this effect, together with the nematic–isotropic demixing, leads to a triphasic line where either a nematic phase coexists with an isotropic phase or there are two isotropic phases in equilibrium. At still lower temperatures a reentrant isotropic phase [9] containing most of the coiled component is observed.

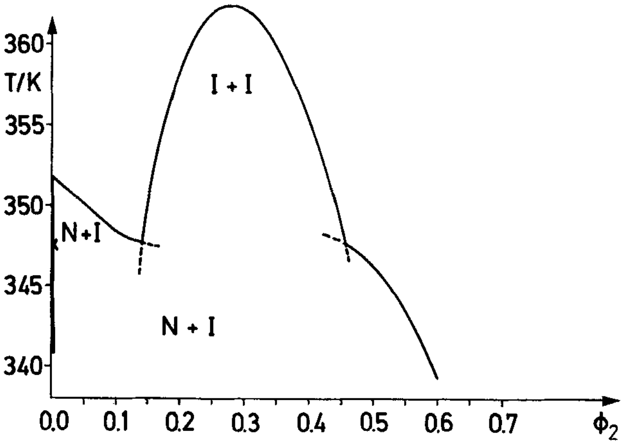
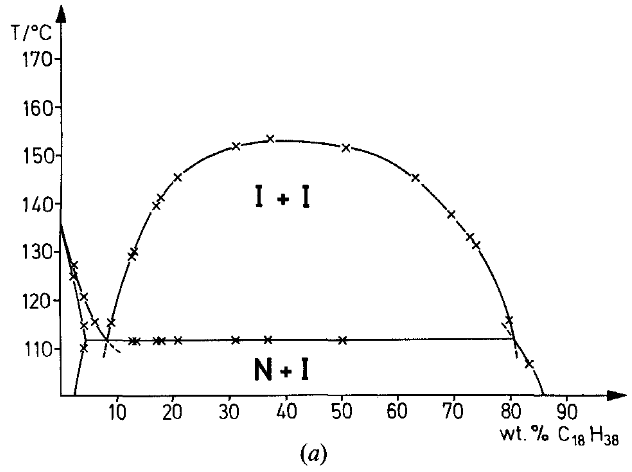


Figure 1. Theoretical phase diagram for a mixture of a thermotropic nematic liquid crystal and a coiled solute [9]. The quantity x_r denotes the axial ratio of the nematogen; x_c is the number of segments of the coiled component. The characteristic temperature T^* measures the strength of the anisotropic interaction between the solvent molecules, T_i^* refers to the strength of the isotropic interaction between solvent and solute. The quantities x_r and T^* refer to the nematic liquid crystal EBBA [9]. (For further details see [4, 9].) $x_r = 3{\cdot}7$, $x_c = 27{\cdot}8$, $T^* = 351{\cdot}2$ K and $T_i^* = 90$ K.

In this preliminary communication we report experimental data on phase diagrams which may serve as a test for this theory. Mixtures of the nematic liquid crystal PAA (4,4′-azoxyanisole, purchased from the Aldrich Chemical Company and recrystallized twice from ethanol) with octadecane or with *n*-tetracosane (Fluka (purum) used without further purification) were sealed in glass tubes and put into a well-thermostatted bath. The mixtures were stirred thoroughly at a given temperature to obtain equilibrium. Experiments approaching the final point from lower or higher temperatures lead to the same result in all cases. This shows that equilibrium can be attained for the systems under consideration. The resulting phase diagrams, which could be determined visually with good precision, are given in figures 2 (*a*), (*b*). It is apparent from a comparison of figure 1 with figures 2 (*a*), (*b*), that all the features



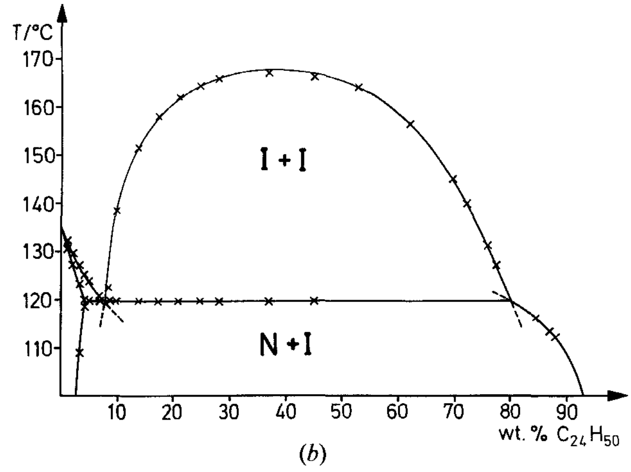


Figure 2. The experimental phase diagrams for the mixtures of the nematic liquid crystal PAA and *n*-alkanes; (*a*): with *n*-octadecane; (*b*): with *n*-tetracosane.

given theoretically in figure 1 are present in the experimental results. In the dilute regime, there is the nematic–isotropic equilibrium which has been studied for a large number of systems [1–4]. At higher concentrations, liquid–liquid demixing occurs in the isotropic phase, leading to the typical bell-shaped two-phase region. With increasing chain length x_c of the coiled component the critical point of isotropic demixing is shifted to higher temperatures (compare figures 2 (*a*) and (*b*)). At the concentrations indicated by crosses on the triphasic line, triphasic equilibria of a nematic and two isotropic phases can be observed. This indicates that due to small impurities and limitations in temperature control there is a triphasic region of finite width. The present experiments show, however, that the width of this region is less than 0·1 K. A visual determination of the transition range of pure PAA leads to values of comparable magnitude. Thus we have to conclude that due to minute impurities which cannot be avoided the triphasic line is changed to a very small triphasic region with a width of approximately 0·1 K. Lowering the temperature below this line reveals a reentrant isotropic phase as predicted by theory. The observation of this wide biphasic region is hampered somewhat by the onset of crystallization of PAA, especially in the case of the PAA/$C_{18}H_{38}$ mixture. However, the reentrant isotropic phase could be clearly observed within the accessible temperature ranges of both systems.

From this qualitative comparison of theory and experiment it is obvious that the simple model given in [4] describes the general features of the mixture of the nematogen PAA with octadecane and with tetracosane. However, theory and experiment are not in accord with regard to two points: first, the observed width of the miscibility gap is greater than theoretically predicted. This shortcoming of the theory is well known and can be remedied easily by the assumption of a concentration-dependent interaction parameter [12]. The second point is the width of the biphasic gap between the nematic and isotropic phase in the dilute regime. The calculation in [4] proceeds under the assumption that the solute does not take part in the ordering process. If the solute does takes part, the biphasic region is far smaller. This is obvious from experimental data as well as from theoretical arguments (see the discussion in [4]). We may conclude therefore that the dissolved *n*-alkanes do take part in the ordering process (cf. [13]). A more detailed analysis of this problem will be presented elsewhere.

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