Consolute Critical Point for Two Smectic-*A* Phases

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This paper describes the first example of a consolute critical point associated with phase separation in a binary system of smectic liquid crystals. In particular, a homogeneous smectic-*A* mixture of a polar compound with an aliphatic tail and a nonpolar compound with a perfluoroalkyl tail separates on cooling into two coexisting smectic-*A* phases with different compositions. The characteristics of this system make it unique for the future investigation of the kinetics of spinodal decomposition in an anisotropic medium.

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The behavior of binary solutions which undergo liquid-liquid phase separation and exhibit a consolute point (see Fig. 1) has been extensively studied.[1] Nevertheless, the investigation of the universal properties of such systems near the critical point still remains an active field of research.[2] In classical cases, limited solubility between two isotropic liquid phases results from the mixing of unlike molecules that differ in polarity, chemical nature, or size.

Formally, there is nothing to prohibit the existence of consolute points in liquid-crystalline solutions. Practically, one must consider the severely limited conditions required to observe this type of critical point in a binary mixture: the stability of a liquid-crystalline phase with respect to crystallization or to any other phase change. Thus the problem is to combine unlike mesogens having sufficiently similar temperatures for mesophase formation and a sufficiently large range of mesophase stability over the concentration-temperature phase diagram. These experimental limitations explain why no miscibility gap has been reported for smectic liquid-crystalline mixtures even after many years of study.

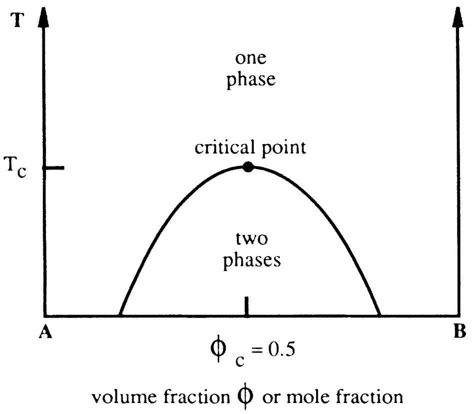
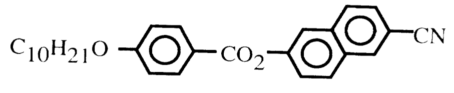


FIG. 1. Miscibility gap (coexistence curve) and critical point in a regular binary solution.

The synthesis of liquid-crystalline polymers and the study of their solubility in low-molecular-weight liquid-crystal solvents has led recently to the observation of phase separation between two nematic phases.[3] The two components differ greatly in size, which is usually a relevant parameter for phase separation, but their nematic-isotropic transition temperatures are quite similar owing to the chemical similarity between the mesogenic unit of the polymer and the liquid-crystalline solvent molecule. Furthermore, crystallization is significantly depressed owing to the noncrystalline character of the polymer. Recent work[4] extending to anisotropic systems the classic results of Flory[5] on macromolecular solutions shows the influence on phase separation of a coupling with the orientational order parameter.

In this Letter we report on a miscibility gap (coexistence curve) and critical point that occur in a smectic-*A* phase. Moreover, the unlike chemical constitutions of the components, not their dissimilar size, is responsible for the phase separation; we have introduced the use of a newly designed liquid crystal having a perfluorinated chain. Thus our new results can be considered as the extension of Hildebrand's classical investigations[6] performed thirty years ago on neutral solutions of hydrocarbons and fluorocarbons.

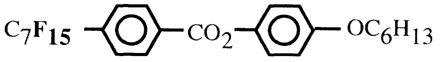
The first component in the mixture, denoted as compound *A*, exhibits a smectic-A_d (S_{A_d}) partial bilayer structure, as usual for this type of polar molecule:[7]



$d/l = 37.2/32.5 = 1.13$,

where d is the layer spacing and l is the molecular length. However, this kind of polar mesogen has never shown a miscibility gap in mixtures with usual nonpolar liquid crystals.

The original feature of the binary mixture studied in this work lies in the chemical nature of the second liquid-crystalline component, denoted compound *B*, which has one aliphatic and one perfluoroalkyl chain (instead of the usual two aliphatic chains). The properties of such compounds have been described only briefly in the literature[8,9] and are currently under investigation in our laboratories. However, it is clear that two characteristics of this perfluoro component are important: a much greater stiffness, owing to the steric hindrance of the fluorine atoms which produces a rigid helical tail, and the well-known incompatibility of perfluoro chains with aliphatic ones. Compound *B*,



$$d/l = 30.4/31 = 0.98\,.$$

Although some nonpolar compounds of this type have been reported to exhibit partial bimolecular smectic-A_d character,[9] it appears from our low-resolution x-ray experiments (Guinier camera, Co $K\alpha_1$ monochromatic beam) that the smectic phase of this compound is of the monolayer S_{A_1} type.[10]

The temperature–volume-fraction (T-ϕ_B) phase diagram obtained from polarizing-microscope observations is given in Fig. 2.[11] The photographs in Fig. 3 show the evolution of phase separation in a critical mixture at different times. The most interesting and obvious characteristic of this phase diagram is the large and quasisymmetric miscibility gap. The critical concentration and the critical temperature determined from this curve are

$$\phi_{B,c} = 0.44, \quad T_c = 95.2\,°\mathrm{C}\,,$$

where ϕ_B is the volume fraction of compound *B*. One notes that a log-log plot of the coexistence curve shows good linearity over about two decades (Fig. 4). However, the accuracy of the current data is not sufficient to discuss the value of the resulting exponent ($\beta = 0.41 \pm 0.07$).

Since the miscibility gap is not exactly centered on $\phi_B = 0.5$ as in regular solutions, one can first consider the size difference between the two components to explain this dissymmetry. Indeed, in the Flory-Huggins theory of binary solutions the critical concentration depends on the difference in the molar volumes of the compounds through their ratio u:[5]

$$\phi_{B,c} = 1/(1+\sqrt{u})\,.$$

From density data we find,[12] for compound *A*,

$$\rho = 1.0318\ \mathrm{g\,cm^{-3}}\ \text{at}\ 96\,°\mathrm{C}\,, \quad M_A = 429.6\ \mathrm{g\,mol^{-1}}\,,$$

and for compound *B*,

$$\rho = 1.3862\ \mathrm{g\,cm^{-3}}\ \text{at}\ 96\,°\mathrm{C}, \quad M_B = 666.4\ \mathrm{g\,mol^{-1}}\,.$$

Thus one obtains

$$u = v_B/v_A = 1.155 \rightarrow \phi_{B,c}^{\text{theory}} = 0.482 > \phi_{B,c}^{\text{expt}} = 0.44\,.$$

The theoretical value is shifted in the correct direction but remains significantly too large.

The evolution of the layer spacing as a function of

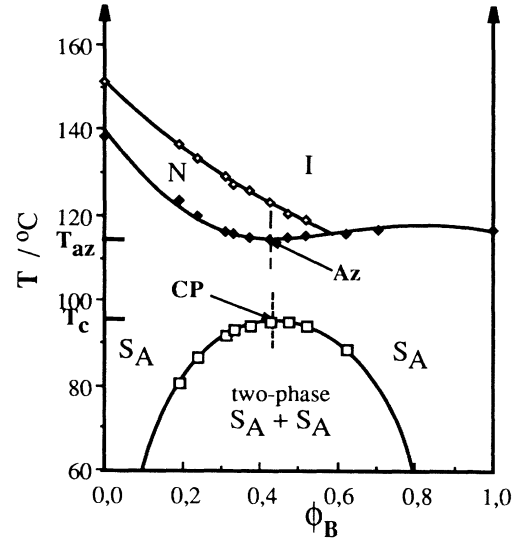


FIG. 2. Temperature–volume-fraction phase diagram. Note the coexistence region of two S_A liquid-crystal phases with consolute critical point (CP). The open squares mark the appearance of two phases when a homogeneous S_A phase is cooled; see Fig. 3 for further details. Az indicates an azeotrope on the nematic–smectic-A transition line; the narrow two-phase $N+S_A$ region along the N-S_A line is not shown. I denotes isotropic liquid; N, nematic; and S_A, smectic A.

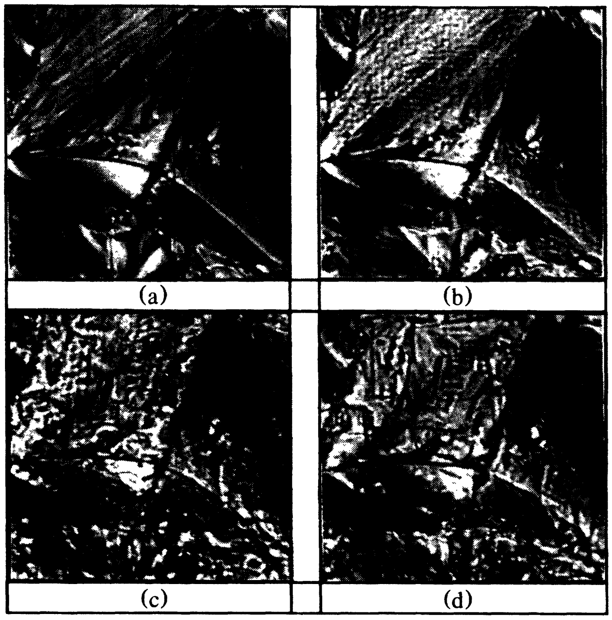


FIG. 3. Sequence of photographs from a critical mixture: (a) Focal-conic texture of the homogeneous S_A before quenching. (b)–(d) Same field after quenching 2° below T_c as time increases ($t = 5$ s, 10 s, and 10 min).

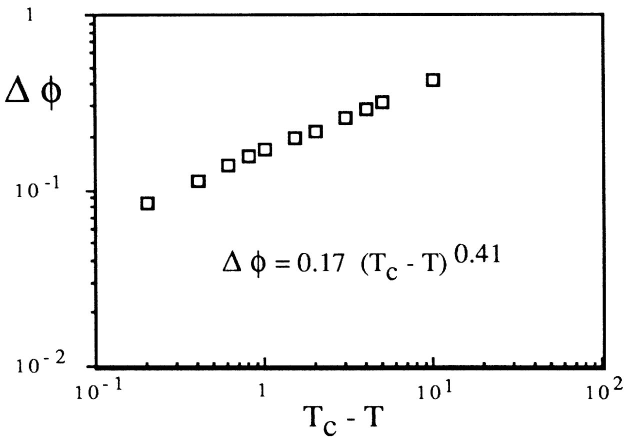


FIG. 4. A log-log plot of the S_A-S_A coexistence curve. $\Delta\phi$ is the difference in composition of the two coexisting S_A phases at $\Delta T = T_c - T$ below the critical temperature. Uncertainties are ± 0.02 ($\Delta\phi$) and $\pm 0.2\,^\circ\mathrm{C}$ ($T_c - T$). The equation results from a linear fit of this plot.

composition, shown in Fig. 5, is interesting and significant. Our preliminary x-ray investigations show that the thermal expansion of the layers of the mixtures in the homogeneous S_A phase is negligible below 105 °C. Thus the values of d for different mixtures along the coexistence curve should be essentially the same as those in Fig. 5. From the values corresponding to compositions away from $\phi_{B,c}$ we know that far from T_c (i.e., around 90 °C) the two phases at equilibrium are S_{A_d} and S_{A_1}. Then as the coexisting phases approach the consolute point along the curve, the values of $d/\bar{l}$, where $\bar{l}$ is the average of the molecular lengths, become identical in both phases and tend to 1 within experimental errors (see Fig. 5 at $\phi_{B,c}$).

Other details of the phase diagram in Fig. 2 are also of interest. The nematic–smectic-A transition line exhibits a minimum (i.e., a "negative azeotrope" at point Az) close to the critical volume fraction. This behavior confirms that the AB interactions are unfavorable to mixing in the smectic phase around this concentration. We stress that the reverse situation is usual in mixtures of a polar and a nonpolar compound where a maximum in the nematic–smectic-A curve is observed, i.e., a "positive azeotrope."[13] In this case, phase separation has little chance to occur. In our view, the location of the point Az almost directly above the consolute point is not a trivial accident. In nematic-nematic phase separation in polymeric liquid crystals, a negative azeotrope is observed on the equilibrium curve separating the high-temperature (isotropic liquid) and the low-temperature (nematic) phases close to the composition of the N-N critical point.[14] This proximity of the two special points does not appear to be fortuitous and must be thought of in terms of Brochard's theory of mesomorphic mixtures, in which the demixing between two nematic phases and the peculiar role of an azeotrope are analyzed.[15]

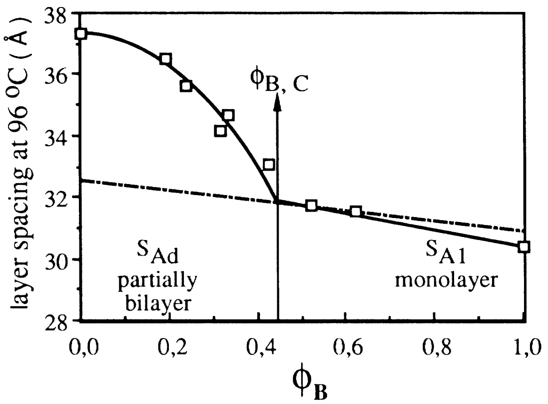


FIG. 5. Layer spacing in the homogeneous S_A phase as a function of composition at constant temperature (slightly above T_c). The dot-dashed line represents the average molecular length $\bar{l}$ as a function of composition.

A differential-scanning-calorimetry investigation confirms the optical observations: All phase changes and phase separations are detected thermally. Moreover, holding a near-critical mixture at 100 °C for two days does not modify the temperature of phase separation (within an uncertainty of 0.1 °C). This means that high-resolution experiments are feasible since the consolute temperature is rather low and the mixtures are stable over a long time period. Furthermore, the nematic phase exists for $\phi_B < 0.58$; this is an important advantage for the alignment of the samples in experiments requiring monodomains.

In conclusion, we have established a phase diagram in a smectic-A liquid-crystal mixture that exhibits most of the characteristic features of a liquid-liquid miscibility gap. Consequently, studies of the detailed characteristics of composition phase separation in a lamellar phase are now possible.

It should also be noted that a decoration of the texture is clearly seen microscopically (see Fig. 3) when mixtures close to the critical concentration are "quenched," indicating spinodal decomposition. The topology of this phase diagram rules out any ambiguity regarding the definition of the path of approach to the critical point.

A variety of basic investigations can be performed on this system. For example, the determination of critical exponents from high-resolution experiments should tell one whether the critical point belongs to the Ising universality class of usual binary mixtures (dominated by concentration fluctuations) or to the new universality class for smectic-A–smectic-A critical points defined by the theory of frustrated smectics (dominated by layer-spacing fluctuations at constant composition).[16] However, we stress that the system described here differs significantly from the frustrated-smectics approach since *the concentration and not the layer spacing* drives the phase separation between the two smectic-A phases. Finally, a study of the kinetics of phase separation in oriented samples seems very promising and is currently in progress.

The clarity of this paper has benefited from fruitful discussions with C. W. Garland and D. Roux.

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[10] The molecular lengths of both compounds were measured on stereomodels in their most extended conformations: $l_A = 32.5$ Å, $l_B = 31$ Å.

[11] Mixtures with known concentrations are observed on cooling from the homogeneous phase. The temperatures of phase separation give the coexistence curve.

[12] The measurement of the densities of the pure compounds has been achieved using a PAAR densitometer. It must be noted that the perfluoro compound has a much larger density than any usual liquid-crystalline compound. The temperature dependence of the densities is linear for both compounds and small.

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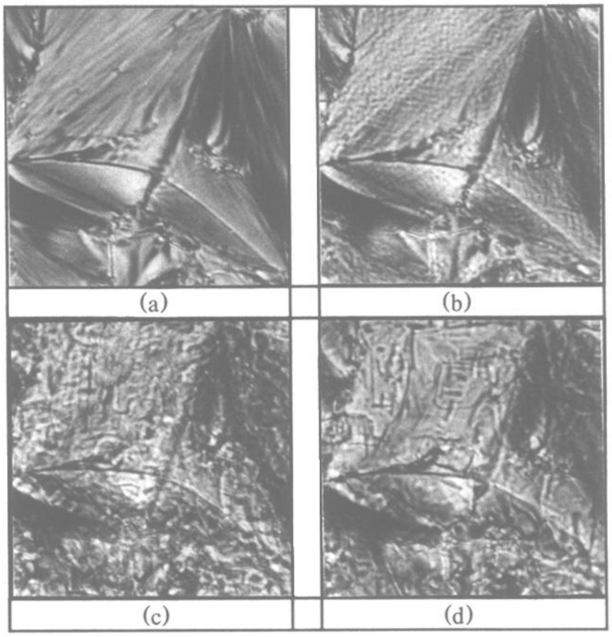

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