

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

The influence of chirality and dielectric anisotropy on the voltage-temperature phase diagram of blue-phase systems

F. Porsch^a; H. Stegemeyer^a

^a Institute of Physical Chemistry, University of Paderborn, F. R. Germany

To cite this Article Porsch, F. and Stegemeyer, H.(1989) 'The influence of chirality and dielectric anisotropy on the voltage-temperature phase diagram of blue-phase systems', *Liquid Crystals*, 5: 3, 791 – 798

To link to this Article: DOI: 10.1080/02678298908026385

URL: <http://dx.doi.org/10.1080/02678298908026385>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The influence of chirality and dielectric anisotropy on the voltage-temperature phase diagram of blue-phase systems

by F. PORSCH and H. STEGEMEYER

Institute of Physical Chemistry, University of Paderborn, D-4790 Paderborn,
F.R. Germany

Voltage-temperature phase diagrams of liquid-crystalline blue-phase (BP) systems have been determined by means of polarizing microscopy and Bragg reflection spectroscopy. A three-component system composed of two non-chiral nematics with $\Delta\epsilon > 0$ and $\Delta\epsilon < 0$, and one chiral nematic with $\Delta\epsilon \approx 0$ has been studied, which allows the independent variation of chirality and dielectric anisotropy ($\Delta\epsilon$) over wide ranges. Mixtures of positive and negative resultant dielectric anisotropy have been investigated. They exhibit up to three zero-field BPs: BPI, BPII and BPIII (fog phase). Besides field-induced BP to cholesteric transitions, several field-induced BPs have been detected that are unstable in the field-off state. The effect of chirality and dielectric anisotropy on the transition temperature and the transition field strengths are evaluated, as well as the conditions for the occurrence of the field-induced BPs.

1. Introduction

In recent years the effect of electric fields on blue phases has been investigated by several groups [1-5]. Field-induced birefringence and lattice deformation have been detected [1] and field-induced phase transitions observed [2]. Even totally new blue phases, only stable in the presence of an electric field, have been discovered [3-5]. Theoretical voltage-temperature phase diagrams have been calculated by Hornreich and Shtrikman using an extension of the Landau theory [6]. As has been known for a long time, the helical pitch plays an important role in the stability of blue phases. For such electric-field investigations, the dielectric permittivity anisotropy is also important.

2. Experimental

A three-component mixed system has been investigated that allows an independent variation of both the chirality and the dielectric anisotropy (see figure 1). Two of the components, 3478 (Roche) and 1083 (Merck), are nematogenic wide-range mixtures with negative and positive dielectric anisotropy respectively. The third component, CE2 (BDH Chemicals), is a chiral nematogenic compound. The three components mix in any ratio at temperatures near the clearing point. Immediately below the clearing point there are always (chiral) nematic phases or blue phases. The clearing temperatures of the mixtures are given in figure 2. The phase-diagram contours represent the experimental data with a mean error of less than 1 K.

The pitch of the cholesteric phase has been determined by selective reflection measurements in a Cary 17 spectrophotometer 5 K below the clearing point (see figure 3). It decreases monotonically with increasing amounts of the chiral compound, and there is no helix inversion when going from 3478-rich mixtures to 1083-rich mixtures. In fact, the pitch is almost independent of the relative amount of 1083 and 3478, but depends only on the concentration of CE2.

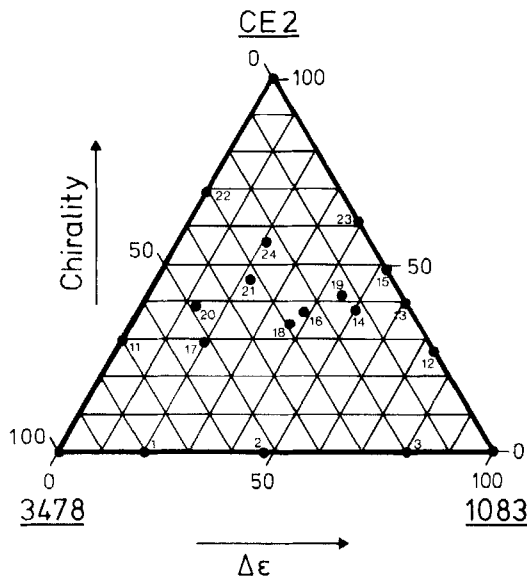


Figure 1. The three-component system studied: CE2 (BDH), 3478 (Roche) and 1083 (Merck). The numbered dots label the mixtures investigated. Concentrations are in weight per cent.

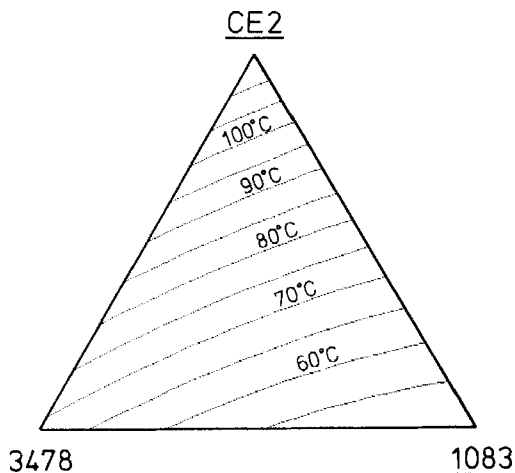


Figure 2. Contour map of the clearing temperatures of the mixtures.

As shown in figure 3, BPs appear in all mixtures with more than 20 per cent of CE2. Hence BPs occur in mixtures with positive, negative and zero dielectric anisotropy. The limiting concentration has been determined by Kofler's contact method [7]. Two mixtures, one from each side of the limiting concentration, are brought into contact. The contact zone contains the complete concentration range possible between the two mixtures. (Strictly, this is only true for binary mixtures, but it also holds for multi-component systems if the concentrations of the two mixtures brought into contact are not very different from each other.) The clearing point of the mixture with the lowest concentration of CE2 exhibiting a blue phase has been measured, and with the aid of the known clearing-point-composition function (see figure 2) the concentration of the mixture has been determined.

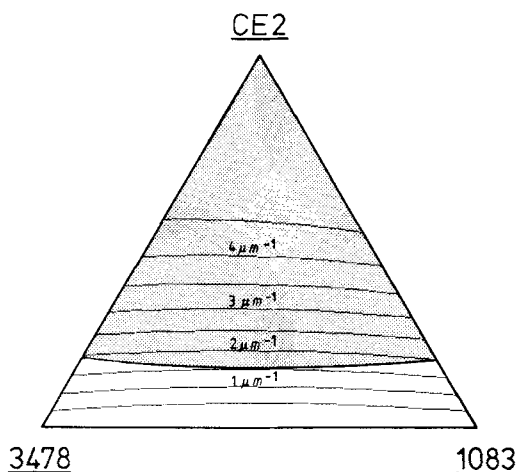


Figure 3. Contour map of the reciprocal pitch of the cholesteric phases of the mixtures 5 K below the clearing point. BPs appear in the shaded region.

The voltage-temperature phase diagrams were obtained by microscopic texture observation parallel to the field direction (polarizing microscope Leitz SM-Lux Pol). The cell thickness ($15\text{--}20\ \mu\text{m}$) was determined spectroscopically by using the empty cell as an interferometer. The frequency of the a.c. voltage applied to the cell was 4 kHz.

3. Voltage-temperature phase diagrams

3.1. Mixtures with low chirality and highly positive $\Delta\epsilon$

Figure 4 shows the voltage-temperature phase diagram of mixture 12 with 26.2 per cent CE2, 73.8 per cent 1083 and 0.0 per cent 3478. Because of the low concentration of the chiral compound, there is only one blue phase at zero field (BPI). In an

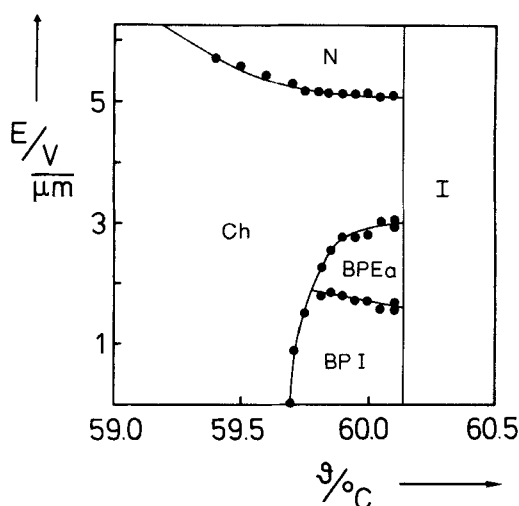


Figure 4. Electric-field-strength-temperature phase diagram of mixture 12 (26.2 per cent, 73.8 per cent 1083 and 0.0 per cent 3478).

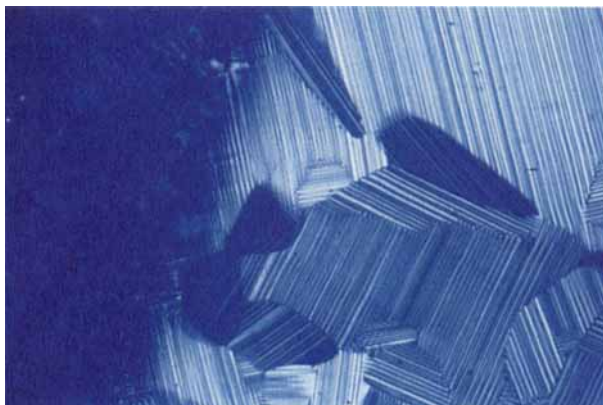


Figure 5. Microphotograph of mixture 18 showing the phase transition BPI to BPEa in an electric field. Magnification $200\times$, crossed polars.

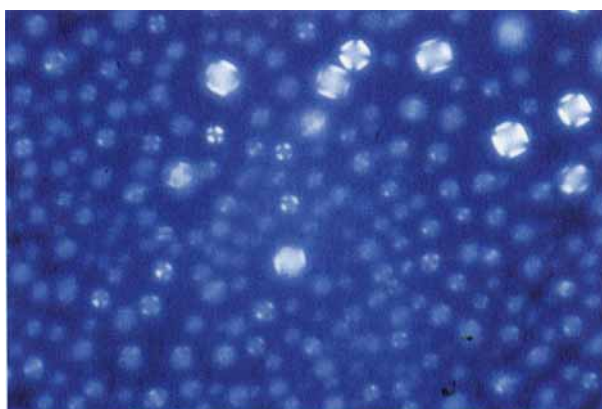


Figure 6. Microphotograph of BPEa single crystals grown in an electric field by cooling from the isotropic liquid, (43.5 per cent CB15, 56.5 per cent E9). Magnification $250\times$, crossed polars.

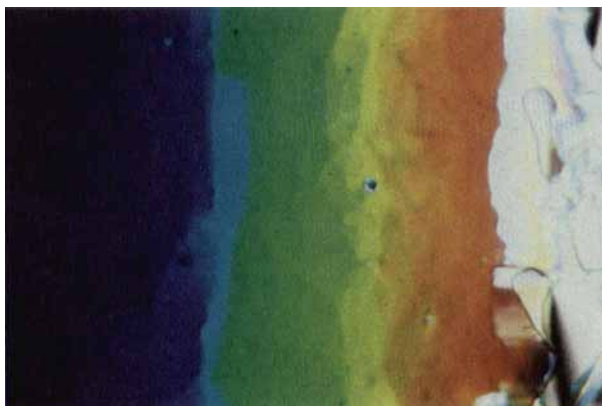


Figure 8. Microphotograph showing the phase sequence BPEa/BPEb/Ch (from left to right) in an electric field with a small gradient from the left to the right (mixture 18). Magnification $200\times$, crossed polars.

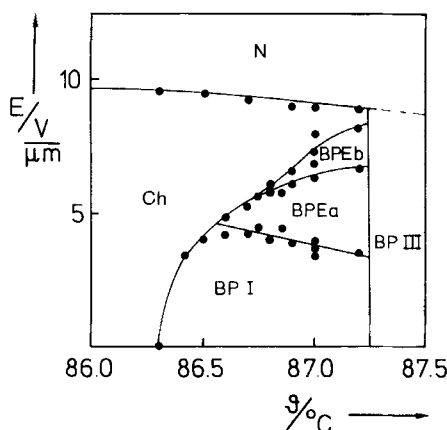


Figure 7. Electric-field-strength-temperature phase diagram of mixture 23 (61.9 per cent CE2, 38.1 per cent 1083 and 0.0 per cent 3478).

electric field a second BP, called BPEa, is induced, starting from BPI at constant temperature. This phase is identical with the BPE reported in [5], but now we add the suffix a, because we have found other field-induced blue phases. At the transition BPI to BPEa the well-known cross-hatched pattern of the BPI disappears (see figure 5), but the wavelength of the selective reflection parallel to the field direction does not show a discontinuity.

In mixtures where BPI coexists with the isotropic liquid it is possible to obtain single crystals of the BPEa. The crystals exhibit a fourfold symmetry. In figure 6 BPEa single crystals grown in the field from the isotropic liquid are shown. Each crystal is bordered by four birefringent domains. At the transition to the cholesteric phase these domains expand and form the cholesteric phase. The fourfold axis parallel to the field direction evidences a tetragonal structure of the BPEa.

A BPEa was found in all mixtures with positive dielectric anisotropy that exhibit a BPI. In mixtures with negative dielectric anisotropy this phase is not observed.

3.2. Mixtures with high chirality and lower positive $\Delta\epsilon$

In mixtures with higher concentrations of the chiral compound there is a second field-induced blue phase, called BPEb, induced by the field starting from the BPEa. As an example, the E/T diagram of mixture 23 with 61.9 per cent CE2, 38.1 per cent 1083 and 0.0 per cent 3478 is given in figure 7. At the transition from BPEa to BPEb the colour of the selectively reflected circularly polarized light changes (see figure 8). BPEb shows a remarkable colour shift with increasing field strength. By means of a microscope spectrometer, we have measured the selective reflection spectra of the BPEa and b (see figure 9). In the BPEa a moderate dependence of the wavelength λ_R on the field strength was observed. At the transition to the BPEb λ_R jumps to a higher value. This indicates a first-order phase transition from BPEa to BPEb. With increasing temperature, the jump of the reflection wavelength becomes smaller. In the BPEb there is a strong shift of the reflection wavelength with increasing field intensity. The wavelength assumes values more than twice as large as that of the cholesteric phase of this mixture, which is about 270 nm. According to the Bragg equation, the strong shift implies a considerable elongation of the lattice structure of BPEb.

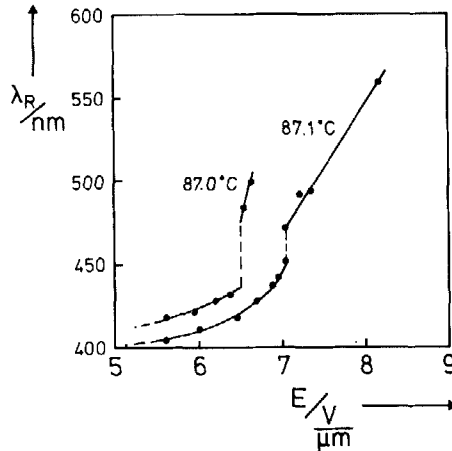


Figure 9. Field dependence of the circularly polarized Bragg reflection from planes perpendicular to the field direction at the transition BPEa to BPEb (mixture 23).

3.3. Mixtures with lower chirality and small positive $\Delta\epsilon$

As an example, the voltage–temperature of mixture 18 with 33.7 per cent CE2, 37.6 per cent 1083 and 28.7 per cent 3478 is given in figure 10. This mixture exhibits BPI and BPII at zero field. As in the previous mixture, there are the field-induced phases BPEa and BPEb. However, in this mixture the BPEb appears as a brownish texture with a selective reflection in the I.R. spectral region, which could not be measured with our microscope spectrometer. However, optical activity was observed. Unlike in previous mixture, BPEb transforms directly to the nematic phase without an intervening cholesteric phase.

In the temperature range of BPII we find a third field-induced blue phase, which we call BPEc. This uniaxial phase has a grey appearance, and we did not find any Bragg reflections in the direction parallel to the field. At the transition from BPII to

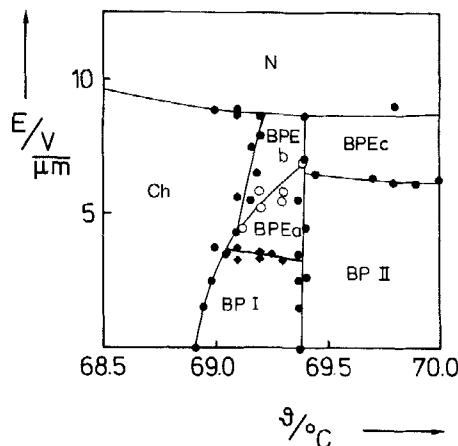


Figure 10. Electric-field-strength–temperature phase diagram of mixture 18 (33.7 per cent CE2, 37.6 per cent 1083 and 28.7 per cent 3478).

BPEc the reflection colour of BPII vanishes. The transition to the nematic phase was detected by conoscopy. At the transition strong birefringence of the nematic phase appears.

4. Discussion

We have observed three different field-induced blue phases in mixed systems with positive $\Delta\epsilon$. Because we did not determine their space group, we have named them BPEa, b and c. We now compare them with BPX, BPH^{2d} and BPH^{3d}, reported by Pieranski and Cladis [3, 4].

BPEa has a tetragonal symmetry and shows no discontinuity of the reflection wavelength at the transition to BPI, as observed for BPX. However, in contrast with BPX, we never found a BPEa in the temperature range of the BPII in all our mixtures. In fact, the transition temperature for BPEa to BPII turns out to be independent of field strength. According to the Kirkwood equation [8], this implies that the two phases have the same susceptibility. However, the field-induced transition BPII to BPX observed by Cladis *et al.* [4] shows that these two phases do have different susceptibilities. Because the two mixed systems have similar dielectric anisotropies, this should also be due to their field-induced BPs. So either BPX and BPEa are different or alternatively there are two different BPIIs. We suppose two alternative explanations. (i) BPX and BPEa are two distinct phases. Both exhibit tetragonal symmetry but belong to different space groups or possess different structures. (ii) The designation BPX is erroneously used for two different tetragonal phases: one induced from BPI (identical with BPEa) and the other from BPII (not present in our mixtures). Because Cladis and Pieranski [3, 4] investigated only phases coexisting with the isotropic liquid, they may have missed the fact that there are two different tetragonal phases. A voltage–temperature phase diagram of their mixture would clarify this question.

BPEc may be identical with BPH^{2d}, because both do not show Bragg reflections parallel to the field direction and both occur at the highest fields.

BPEb appears to be different from all of the phases reported hitherto. It has a very large lattice constant in the direction of the field, with a strong dependence on the field strength.

In summary, our results show that, together with the field-induced BPs observed previously [3–5], there are at least three different BPs that are stable only in the presence of an electric field. The high sensitivity of the BPs to external fields seems to be plausible because of their structural similarities and the small enthalpy differences between them. Further investigations are necessary to determine the structure of these field-induced BPs.

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The authors wish to thank E. Merck, Darmstadt, and Hoffmann–LaRoche, Basel, for providing them with liquid crystals.

References

- [1] PORSCH, F., STEGEMEYER, H., and HILTROP, K., 1984, *Z. Naturf.*, **39a**, 475. PORSCH, F., and STEGEMEYER, H., 1986, *Chem. Phys. Lett.*, **125**, 319. HEPPKE, G., KITZEROW, H.-S., and KRUMREY, M., 1985, *Molec. Crystals liq. Crystals Lett.*, **1**, 117; 1985, *Ibid.*, **2**, 59.

- [2] STEGEMEYER, H., and PORSCH, F., 1984, *Phys. Rev. A*, **30**, 3369.
- [3] PIERANSKI, P., CLADIS, P. E., and BARBET-MASSIN, R., 1985, *J. Phys. Lett. Paris*, **46**, L-973.
- [4] CLADIS, P. E., GAREL, T., and PIERANSKI, P., 1986, *Phys. Rev. Lett.*, **57**, 2841.
PIERANSKI, P., and CLADIS, P. E., 1987, *Phys. Rev. A*, **35**, 355.
- [5] PORSCH, F., and STEGEMEYER, H., 1987, *Liq. Crystals*, **2**, 395.
- [6] HORNREICH, R. M., KUGLER, M., and SHTRIKMAN, S., 1985, *J. Phys., Paris, Colloq.*, **46**, C3.
- [7] SACKMANN, H., and DEMUS, D., 1966, *Molec. Crystals*, **2**, 81. KOFLER, A., 1945, *Z. Elektrochem.*, **51**, 38.
- [8] KIRKWOOD, J. G., and OPPENHEIM, I., 1961, *Chemical Thermodynamics* (McGraw-Hill), p. 231 (see also [2]).