Electric field effect on phase transitions in liquid-crystalline blue-phase systems

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The influence of an electric field on the phase-transition temperatures of cholesterogenic mixtures CB 15/M 18 exhibiting blue phases (BP) has been investigated. From temperature-voltage phase diagrams it can be seen that the transition temperature BP I/cholesteric depends on the field strength E, whereas that of BP II/cholesteric does not. The effect $\Delta T(E)$ can be understood by means of the Kirkwood-Helfrich equation considering the nonlinear field dependence of the BP I permittivity.

Blue phases (BP) are thermodynamically stable liquid-crystalline phases which exist in a very small temperature range (< 1 K) close below the clearing point.[1,2] They only occur in cholesterogenic systems with a sufficiently small helical pitch ($p \lesssim 700$ nm).[3] Because of their optical isotropy and several other physical properties[2] as well as from theoretical considerations[4] it is accepted that BP possess a molecular axis distribution function of cubic symmetry.

Bearing in mind that the helical pitch in cholesteric liquid crystals can be changed by the application of external fields[5] we studied the phase behavior of BP systems under the influence of an electric field. We used mixtures of the BDH p-R-p'-cyanobiphenyls M 18 [$R = C_6H_{13}O)$] and CB 15 [$R = C_2H_5CH(CH_3)CH_2$] similar to those of former investigations.[6] The mixtures were prepared in tin dioxide coated glass cells with 12-μm Mylar spacers driven by a square-wave ac voltage source (200 Hz) in a Mettler heating stage FP 52. The phase transitions have been observed parallel to the field direction by a polarizing microscope Leitz SM-Lux Pol. As an example the temperature-voltage diagram of a mixture CB 15/M 18 with 47 mol% CB 15 is given in Fig. 1. On increasing temperature at zero field we observed *two* BP's above the cholesteric region and a rather broad two-phase region BP II + iso below the clearing temperature. On increasing field strength E the well-known cholesteric-to-nematic transition has been observed at slightly temperature dependent threshold fields $E_c(T)$ (Ref. 5) which deserves no further discussion in this paper. From Fig. 1 one can see that BP I as well as BP II will be transformed

into the cholesteric phase by application of an electric field at field strengths $E_{BP/ch} < E_c$. For the BP II it was found in all mixtures under investigation that $E_{BP/ch}$ was temperature independent (cf. Fig. 1) but linearly dependent on the inverse cholesteric pitch. The phase transitions BP I/BP II and BP II/isotropic are independent on the applied field strength within the limit of experimental error. From this result it follows that a phase transition BP II/BP I cannot be induced by an electric field contrarily to the conclusion of Heppke.[7] The temperature of the BP I/cholesteric transition, however, has been found to *increase* on increasing field strength. Consequently, the BP I range of existence decreases with increasing field strength.

In an earlier paper Helfrich[8] has reported the effect of an electric field on the nematic-isotropic phase transition temperature which has been discussed in terms of a relation first mentioned by Kirkwood.[9] We give the Kirkwood-Helfrich equation in a slightly modified form using the molar phase transition enthalpy ΔH as well as SI units:

$$\Delta T = \frac{1}{2}\frac{T_0 M}{\rho \Delta H}(\epsilon_2 - \epsilon_1)\epsilon_0 E^2 \; . \tag{1}$$

ΔT is the temperature shift at a field strength E with respect to the transition temperature T_0 at zero field, M is the molar mass, ρ is the density, ϵ_0 the field constant, and ϵ_1, ϵ_2 are the permittivities of the two phases under discussion.

From Eq. (1) it follows immediately that the temperature shift ΔT at a given field will be the larger the lower ΔH and the larger $\epsilon_2 - \epsilon_1$ is. In the case of the cholesteric/BP I transition a value of $\Delta H \approx 50$ J mol^{-1} has been measured[10] which is only about one tenth of the value in Helfrich's system.[8]

According to Eq. (1) the value of $\Delta \epsilon = \epsilon_{ch, \perp} - \epsilon_{BP}$ must be estimated from the cholesteric permittivity perpendicular to the helical axes ($\epsilon_{ch, \perp}$) and that of the BP I (ϵ_{BP}) which must be isotropic because of the cubic phase structure.

These values have been obtained as follows: For the nematogenic compounds M 15, M 21, and K 15 (BDH designations) which are very similar in molecular structure to M 18 and CB 15, the permittivities $\epsilon_1 = 18$ and $\epsilon_2 = 6$ are known parallel and perpendicular to the nematic director, respectively.[11] If we use $\epsilon_{ch, \perp} = \frac{1}{2}(\epsilon_1 + \epsilon_2)$ and $\epsilon_{BP} = \frac{1}{3}(\epsilon_1 + 2\epsilon_2)$ according to the Vuks relation[12] we obtain $\Delta \epsilon = \frac{1}{6}(\epsilon_1 - \epsilon_2) \approx 2$. Inserting this value, a density $\rho \approx 1$, an average molar mass $\overline{M} = 214$ and a field strength of $E = 4 \times 10^4$ V cm^{-1} in Eq. (1) results in $\Delta T \approx 0.2$ K. This temperature shift has been observed approximately in all the systems under investigation (cf. Fig. 1). It should be
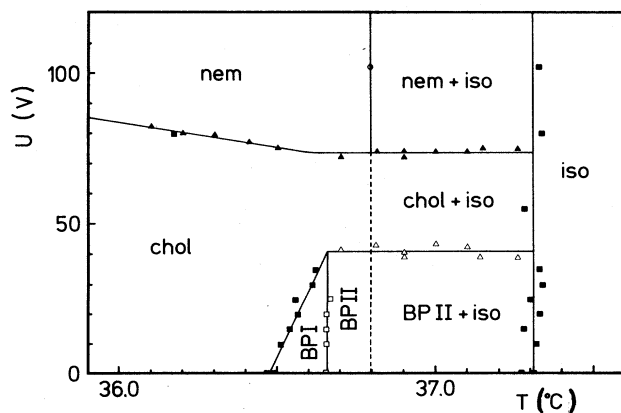

FIG. 1. Electric field–temperature phase diagram of a mixture CB 15/M 18 (with 47 mol% CB 15); sample thickness 12 μm.

mentioned that the smaller ΔH value compared with Helfrich's system[8] enabled us to apply smaller field strengths than in his experiments. Thus we avoided electrohydrodynamical effects and obtained the phase transition temperatures by observation of *static* textures in the polarizing microscope.

From Eq. (1) one can understand why the transition temperatures for BP I/BP II and BP II/isotropic have not been found to be field dependent. The phase transition enthalpy ΔH for BP I/BP II actually has been found to be similar to that of cholesteric/BP I.[1,10] As both BP's show a cubic structure[2] their permittivities, however, are expected to be quite similar resulting in a value of $\Delta\epsilon \approx 0$. ΔH for the BP II/isotropic transition is much larger than for BP I/BP II and cholesteric/BP I. Additionally, the difference of the permittivities should be rather small. Consequently, the ΔT values resulting from Eq. (1) for both transitions are expected to be so small that they cannot be detected by our experimental method. According to Eq. (1) the temperature shift ΔT is quadratically dependent on the field strength E. In Fig. 2 we present a log-log plot of ΔT versus the ac voltage U for three different CB 15/M 18 mixtures. Contrary to Helfrich's result[8] we found slopes of the curves smaller than 2 ($m < 2$). That means that the quadratic field dependence of Eq. (1) does not hold for the cholesteric/BP I transition. This result can be understood if we assume that $\Delta\epsilon = \epsilon_{ch,\perp} - \epsilon_{BP}$ decreases on increasing field strength. First, we wish to demonstrate that $\epsilon_{ch,\perp}$ is field independent under our experimental conditions: The field strengths at the BP I/cholesteric transition $E_{BP/ch}$ are always much smaller than the threshold field E_c for the cholesteric/nematic transition (cf. Fig. 1). The maximum value we found is $E_{BP/ch}/E_c = 0.56$. From the results of Kahn[13] giving the cholesteric pitch p as a function of E/E_c we derive that p in our cases is only 2% larger than p_0 at zero field. Consequently, $\epsilon_{ch,\perp}$ can be taken as field independent. ϵ_{BP}, however, seems to depend on E: Recently, we reported that the cubic structure of the BP I can be distorted by an external electric field inducing an optical biaxiality.[14] This field-induced anisotropy of BP I has been explained in terms of a nonlinear electro-optic effect. We expand the BP I permittivity ϵ_{BP} in powers of E:[15]

$$\epsilon_{BP} = \epsilon_{BP}^0 + \xi_1 E + \xi_2 E^2 + \cdots \ . \tag{2}$$

ϵ_{BP}^0 is the second-rank permittivity tensor at zero field; ξ_1 and ξ_2 are tensors of third and fourth rank, respectively. ξ_1 in Eq. (2) exhibits the symmetry of the piezoelectric tensor which vanishes in all centrosymmetric crystal classes and in the class 432.[16] There are strong experimental evidences obtained from morphological studies of BP I liquid single crystals that the BP I belongs to the space group $I4_132$.[17] Thus, all terms with odd powers of E must be canceled in Eq. (2). Inserting Eq. (2) after this correction into Eq. (1), we obtain

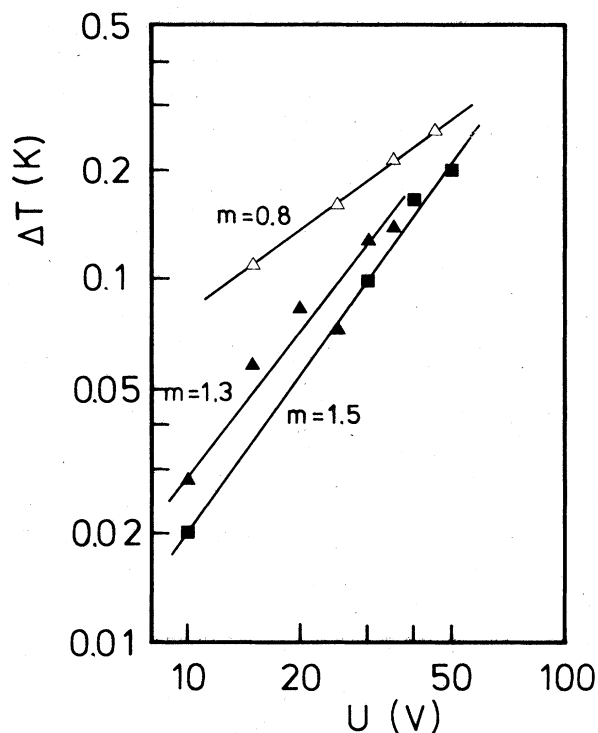$$\Delta T = C[(\epsilon_{ch,\perp} - \epsilon_{BP}^0)E^2 - \xi_2 E^4 - \cdots] \ , \tag{3}$$

FIG. 2. Shift of the cholesteric/BP I transition temperature vs ac voltage $\Delta T = \text{const} \times U^m$ (log-log plot) of CB 15/M 18 mixtures (▲ 47, ■ 52, △ 57 mol% CB 15); sample thickness 12 μm.

with $C = T_0 M\epsilon_0/2\rho\Delta H$. It follows straightforward from Eq. (3) that the field dependence of ΔT is not quadratic as in Helfrich's system (where the permittivities of the nematic and the isotropic state can be taken as field independent) but can be described formally by an exponent $m < 2$ as shown in Fig. 2.

Recently, Motoc and Honciuc[18] investigated electric field effects on phase transitions in cholesteric systems. They observed a strong *decrease* of the cholesteric nucleation temperature in a supercooled blue phase. These results cannot be discussed in terms of Eq. (1) because they are not obtained in an equilibrium state which immediately can be seen from the wrong sign of ΔT and the value of ΔT which is about two orders of magnitude larger than expected from Eq. (1). It should be emphasized in this connection that our phase transition data have been obtained on increasing temperatures to avoid the well-known supercooling of the BP I.[1]

[1]H. Stegemeyer and K. Bergmann, in *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke, Springer Series in Chemical Physics, Vol. 11 (Springer, Berlin, 1980), p. 161.
[2]P. P. Crooker, Mol. Cryst. Liq. Cryst. **98**, 31 (1983).
[3]H. Onusseit and H. Stegemeyer, Chem. Phys. Lett. **89**, 95 (1982); **94**, 417 (1983).
[4]H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983).
[5]H. Kelker and R. Hatz, *Handbook of Liquid Crystals* (Verlag Chem-

ie, Weinheim, 1980), p. 207.

[6]P. L. Finn and P. E. Cladis, Mol. Cryst. Liq. Cryst. **84**, 159 (1982).

[7]G. Heppke, M. Krumrey, and F. Oestreicher, Mol. Cryst. Liq. Cryst. **99**, 99 (1983).

[8]W. Helfrich, Phys. Rev. Lett. **24**, 201 (1970).

[9]J. G. Kirkwood, 1950, cf. Ref. 3 in Ref. 8.

[10]H. Onusseit, thesis, University of Paderborn, 1983 (unpublished).

[11]*Liquid Crystal Information* (British Drug House).

[12]M. F. Vuks, Opt. Spectrosc. **20**, 361 (1966).

[13]F. J. Kahn, Phys. Rev. Lett. **24**, 209 (1970).

[14]F. Porsch, H. Stegemeyer, and K. Hiltrop, Z. Naturforsch. Teil A **39**, 475 (1984).

[15]J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1972), p. 241.

[16]W. Kleber, *Einführung in die Kristallographie, 15. Auflage* (VEB Verlag Technik, Berlin, 1983), p. 278.

[17]Th. Blümel and H. Stegemeyer, J. Cryst. Growth **66**, 163 (1984).

[18]C. Motoc and M. Honciuc, Rev. Roum. Phys. **28**, 541 (1983).