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Effect of molecular rotational hindrance on the spontaneous polarization in the S_C^* phase of a ferroelectric liquid crystal

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The spontaneous polarization, P_s, and the tilt angle, θ, have been measured simultaneously in the S_C^* phase of binary mixtures of two ferroelectric liquid crystals as a function of temperature and concentration. A molecular rotational model was used in order to calculate the temperature dependence of the P_s/θ ratio. A two parameter fit of the experimental data was carried out which showed good agreement. The molecular rotational potentials have been determined from the fit parameters and are presented as a function of concentration. It is shown that the chiral part of the potential depends very weakly on the composition in contrast to the non-chiral part which shows a strong negative non-linear deviation with a minimum corresponding to the concentration at which the smectic C^* phase width is maximal.

1. Introduction

There are only few experimental results in the literature [1–3] reporting the temperature dependence of the spontaneous polarization (P_s) and the tilt angle (θ) determined simultaneously in a ferroelectric liquid crystal. All of the experimental results have a common feature showing a temperature dependent P_s/θ ratio in contradiction to the early theories [4–5] based on the Landau expansion of the free energy of the system. This predicts the spontaneous polarization to be proportional to the tilt in the whole temperature region. Generalized Landau theories [6] and a thermodynamic model [7] have given a better description of the temperature dependence of the ratio P_s/θ.

The investigation of the properties of two or more component ferroelectric liquid crystal systems, apart from their basic interest, is important from the point of view of applications. Systems composed of an achiral S_C host with a chiral dopant (induced chirality) [14] are often used. There are only a few studies of both the temperature and concentration dependence of P_s and θ in mixtures [8, 9, 13]. In the present work we have investigated the concentration and temperature dependence of the spontaneous polarization and that of the tilt angle in the S_C^* phase of binary mixtures of two chiral liquid-crystalline compounds.

2. Theory

We adopt the microscopic model of Zeks *et al.* [10, 11] to describe the temperature dependence of the spontaneous polarization. In this model it is assumed that the

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ordering of the transverse electric dipoles (μ) is induced by the tilt only. Hindered rotation of the molecules around their long axes is taken into account. The angle ψ describes the orientation of μ in the plane perpendicular to the long molecular axis. Let $\psi = 0$ when μ is perpendicular to the plane of the tilt and parallel to the direction of P_s. A single particle potential $U(\psi)$ can be given for the rotation of the molecule around its long axis:

$$U(\psi) = U_1 + U_2 = -a_1\theta\cos\psi - a_2\theta^2\cos 2\psi. \tag{1}$$

The first term U_1 is of chiral character and is analogous to the piezoelectric coupling in the Landau expansion [4]. The tilt tends to align the transverse dipoles in the direction where $\psi = 0$. The second term U_2 is of non-chiral character and exists in tilted systems. There are two preferred directions of the transverse dipole during the rotation when $\psi = 0$ and π, but the minimum of the potential U at $\psi = 0$ is deeper than that at $\psi = \pi$. The expected relation between the magnitudes of the two parts of the potential is: $a_1\theta \ll a_2\theta^2$ because the chiral interactions are supposed to be weak with the exception of very small θ ($< 10^{-2}$), i.e. in the vicinity of $T_{S_C^*S_A}$.

We use the potential $U(\psi)$ to calculate the temperature dependence of the absolute value of the spontaneous polarization P_s

$$P_s = \varrho\mu\langle\cos\psi\rangle \tag{2}$$

where ϱ is the particle density and

$$\langle\cos\psi\rangle = \frac{\int_0^{2\pi}\cos\psi\exp(-U/kT)\,d\psi}{\int_0^{2\pi}\exp(-U/kT)\,d\psi}. \tag{3}$$

We expand $\exp(-U/kT)$ in a series, keep terms up to second order and carry out the integration. After some algebra we find

$$P_s = \varrho\mu\theta a_1\frac{2kT + a_2\theta^2}{4(kT)^2 + (a_1\theta)^2 + (a_2\theta^2)^2}. \tag{4}$$

In order to obtain the complete temperature dependence of the spontaneous polarization we substitute for

$$\theta = \theta_0(T_{S_C^*S_A} - T)^\alpha, \tag{5}$$

where $T_{S_C^*S_A}$ is the temperature of the S_A–S_C^* phase transition. We use equation (5) to describe the temperature dependence of the tilt angle in the whole temperature interval over which the S_C^* phase exists. Finally we have

$$P_s = A(\Delta T)^\alpha\frac{B(T_{S_C^*S_A} - \Delta T) + BC(\Delta T)^{2\alpha}}{(T_{S_C^*S_A} - \Delta T)^2 + B^2\theta_0^2(\Delta T)^{2\alpha} + C^2(\Delta T)^{4\alpha}}, \tag{6}$$

where $A = \varrho\mu\theta_0$; $B = a_1/2k$; $C = a_2\theta_0^2/2k$ and $\Delta T = T_{S_C^*S_A} - T$.

In order to demonstrate the qualitative temperature dependence of the function (6) we have evaluated it for arbitrary parameters as follows: $a_2/2k = 1000\,\mathrm{rad}^{-2}\,\mathrm{K}$; $a_1/2k = 3\,\mathrm{rad}^{-1}\,\mathrm{K}$; $T_{S_C^*S_A} = 380\,\mathrm{K}$; $\alpha = 0{\cdot}2$ and $\theta_0 = 0{\cdot}2\,\mathrm{rad}\,\mathrm{K}^{-0{\cdot}2}$. The plot of $P_s/\varrho\mu\theta$ as a function of ΔT is shown in figure 1, which describes a similar temperature dependence to that given by Urbanc and Zeks [11]. The function $P_s/\varrho\mu\theta$ has a value of $a_1/2kT_{S_C^*S_A}$ at $\Delta T = 0$ and grows with a positive slope and curvature up to its maximum.

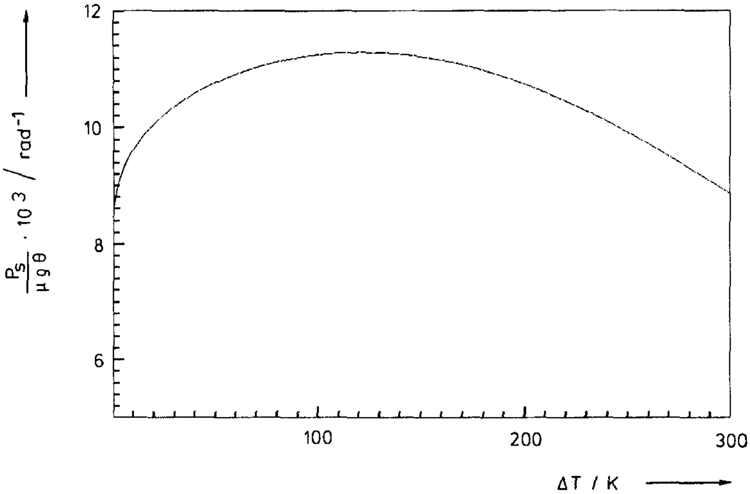
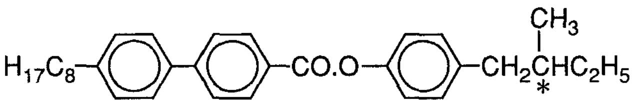


Figure 1. Calculated $P_s/\theta\mu\varrho$ versus ΔT for arbitrary parameters (see the text).

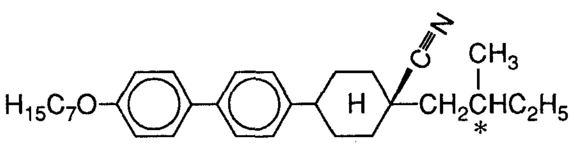
3. Experimental

We have used mixtures of two chiral liquid-crystalline compounds CE8 and ZLI 4420 purchased from Merck with the molecular structures

CE8



ZLI 4420



The phase diagram of the two chiral substances given in figure 2 has been determined by polarizing microscopy and DSC. The temperature of the sample was controlled by an improved version of a Mettler FP5/52 hot stage with a relative accuracy of 1/100 K. Both the spontaneous polarization and the tilt angle have been measured on the same sample of dimensions 0·7 cm × 0·7 cm × 18 μm. Planar alignment of the S_C^* phase was achieved by slow cooling from the isotropic phase in the presence of an applied electric voltage of 100 V. The spontaneous polarization was measured by a Diamant bridge [12], and the tilt angle was derived from the optical switching angle of the sample.

4. Comparison of theory and experiment

We have measured the tilt angle and the spontaneous polarization in our binary mixture as a function of temperature and concentration. We show the temperature behaviour of both quantities in figures 3 (*a*) and (*b*) for the composition with 0·85 mole fraction of ZLI 4420. The points are the experimental data and the lines demonstrate a fit of $\theta = \theta_0(T_{S_C^*S_A} - T)^\alpha$ and $P_s = P_0(T_{S_C^*S_A} - T)^\beta$. It is convincing that the power law fit works very well for $\theta(T)$ but describes $P_s(T)$ poorly. This statement,

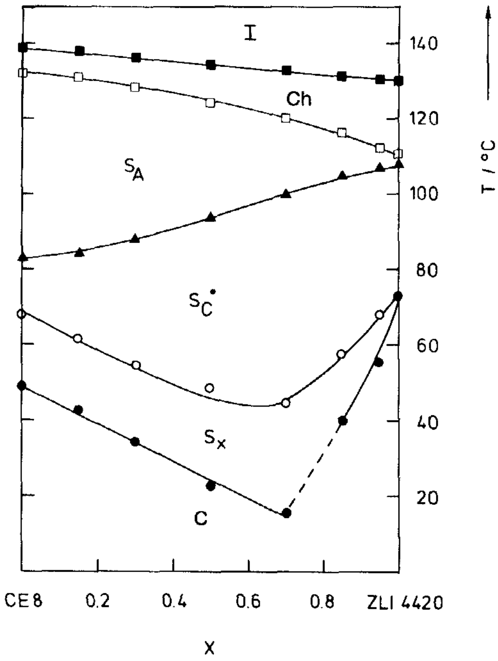


Figure 2. Phase diagram for the CE 8/ZLI 4420 system; x is the mole fraction of ZLI 4420. The S_X area denotes the existence range of higher ordered smectic phases [15] which are not shown separately.

as well as the fact that $\beta > \alpha$ holds for our system over the whole concentration region. For this reason we use the power law fit for θ to describe its temperature dependence in the whole S_C^* range. In this case the value of α is not necessarily the critical exponent at the S_C^*–S_A phase transition. The fit parameters θ_0 and α are given in the table. The value of α changes with the concentration between 0.23 and 0.43, therefore we do not use the approximation $\theta^2 = \theta_0^2(T_{S_C^*S_A} - T)$. The temperature dependence of the spontaneous polarization we describe by equation (6).

In figure 4 we show the experimental results, i.e. measured data for $P_s/(\Delta T)^\alpha$ versus ΔT. A qualitative analysis of the experimental data shows that:

(1) The temperature dependence of $P_s/\Delta T^\alpha$ is practically linear with a positive slope in the concentration region up to $x = 0{\cdot}85$. For higher concentrations a positive curvature appears with a decreasing radius towards $x = 1{\cdot}0$.

(2) The value of the function $P_s/\Delta T^\alpha$ at $\Delta T = 0$ increases gradually with increasing mole fraction of ZLI 4420.

(3) A strongly non-linear change of parameters can be expected in the concentration region $x = 0{\cdot}85$–$1{\cdot}0$.

(4) The temperature range ΔT of our binary mixtures is too short to decide whether the experimental curves are going to have a maximum as predicted in the microscopic theory [10] (cf. figure 1) or saturate at low temperatures according to the thermodynamic model [7].

We carry out the quantitative analysis of the data with a fit procedure. As a starting formula we use equation (6) which contains three parameters: A, B and C. Because the range ΔT of the S_C^* phase (cf. figure 2) varies between 15 and 60 K for our

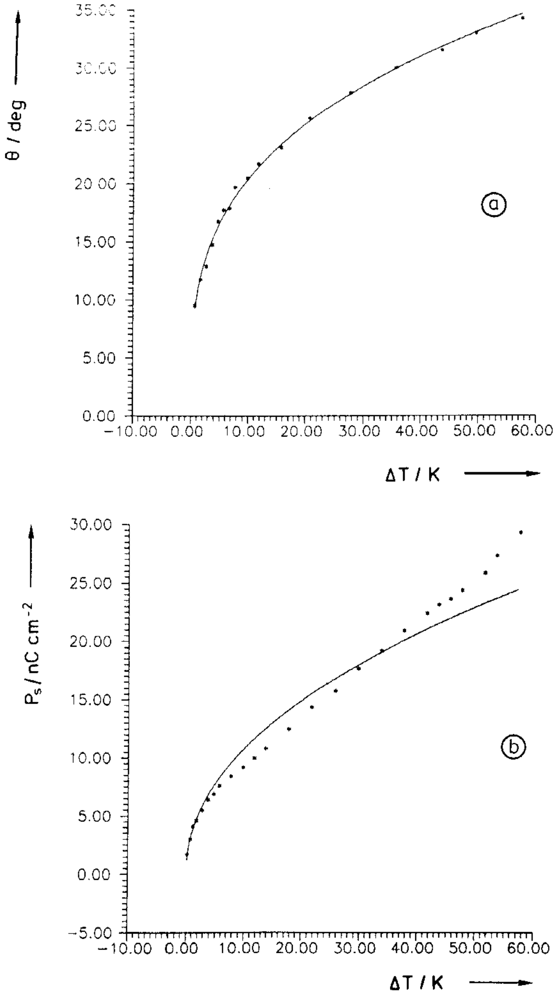


Figure 3. The temperature dependence of the measured tilt angle (*a*) and spontaneous polarisation (*b*) for $x = 0{\cdot}85$ mole fraction. The continuous lines show a power law fit.

system (cf. figure 1), the parameters A and B cannot be determined separately. In order to facilitate the fit procedure we neglect the term with $\Delta T^{4\alpha}$ in equation (6). The continuous lines in figure 4 correspond to this simplified version of equation (6) and demonstrate the fit for mole fractions: 0·0; 0·5; 0·95 and 1·0 of ZLI 4420. Fit parameters ($A \times B$) and C are given in the table. In figure 5 we present the concentration dependence of a quantity $(A \times B)/(T_{S_C^*S_A} \times \theta_0)$ which is the value of P_s/θ at $T = T_{S_C^*S_A}$. We suggest the use this extrapolated, temperature and tilt independent quantity as a measure of the polarization for different substances. Figure 5 shows a linear concentration dependence of P_s/θ at $T = T_{S_C^*S_A}$ for the mixture of two chiral compounds. A similar quantity $P_s/\sin\theta$ at $T_{S_C^*S_A} - T = 5\,\mathrm{K}$ has been measured in chiral-nonchiral binary mixtures and an analogous linear concentration dependence was found [9, 13]. By multiplying this quantity with $T_{S_C^*S_A}$ we can easily calculate $(\varrho \times \mu \times a_1)$ for each concentration. Unfortunately, we cannot determine the quantity a_1 explicitly, because the effective molecular dipole moment is unknown.

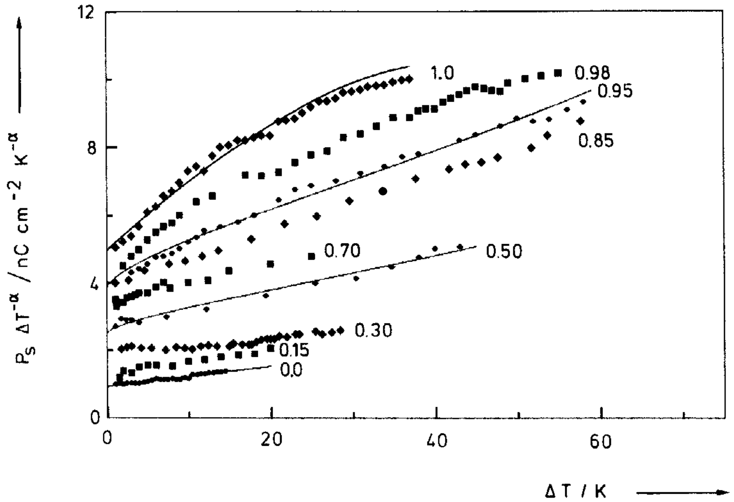


Figure 4. Temperature dependence of the experimental values of $P_s/\Delta T^{\alpha}$ for different mole fractions, x. The continuous lines show the fitted curves for x = 0·0; 0·5; 0·95 and 1·0.

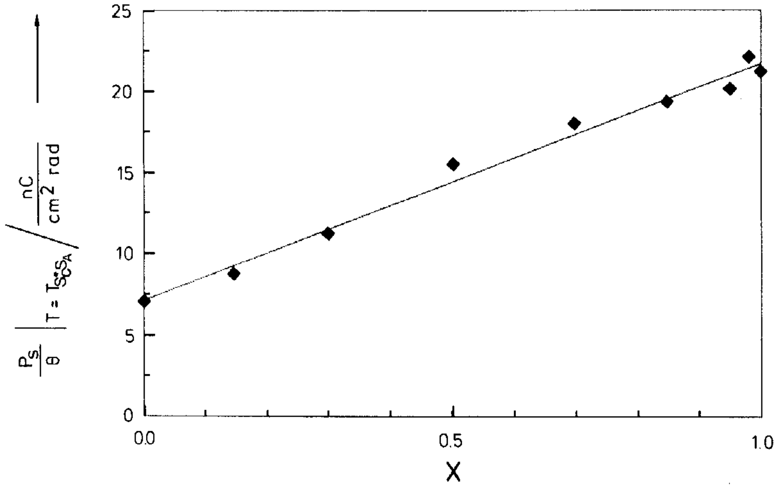


Figure 5. The concentration dependence of P_s/θ at $T = T_{S_C^*S_A}$ calculated from the fit parameters ($A \times B$) and θ_0.

The S_C^*–S_A transition temperatures and the fit parameters in the system ZLI 4420/CE8 for different mole fractions x of ZLI 4420.

x	$T_{S_C^*S_A}$/K	α	θ_0/rad K$^{-\alpha}$	AB/nC cm^{-2} K$^{-(1+\alpha)}$	C/K$^{1-2\alpha}$
1·00	381	0·23	0·23	1810	90·7
0·98	380·5	0·28	0·19	1610	39·8
0·95	380·5	0·30	0·19	1444	31·8
0·85	379	0·30	0·18	1315	31·0
0·70	373	0·29	0·18	1221	17·9
0·50	366	0·32	0·16	921	21·4
0·30	358·5	0·40	0·12	498	10·4
0·15	357	0·37	0·14	432	20·8
0·00	357	0·43	0·13	326	14·7

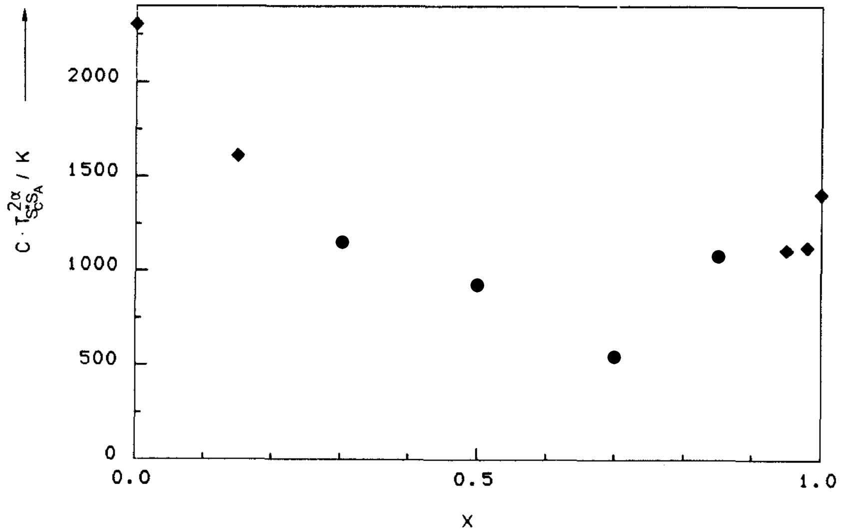


Figure 6. The concentration dependence of the non-chiral part of the molecular rotational potential calculated from the fit parameter C.

However we can speculate about its concentration dependence. We assume that the particle density ϱ is concentration independent and the ratio of μ for the two pure substances is approximately 1 : 3. The only polar group in CE8 is the carboxyl group with a transverse dipole moment of about 1·4 D and the nitrile group in ZLI 4420 with μ of 4·2 D. In this case the concentration dependence of $\varrho \times \mu \times a_1$ corresponds to that of the effective dipole moment and consequently a_1 depends very weakly on concentration if at all. For a quantitative estimation of the chiral part of the potential we assume $\varrho = 1{\cdot}5 \times 10^{27}\,\mathrm{m}^{-3}$ and $\theta = 0{\cdot}5$ rad and we obtain $a_1\theta = 7 \times 10^{-23}$ J which is two orders of magnitude lower than kT in the temperature range of the S_C^* phase.

From the other fit parameter C we can determine directly the non-chiral part U_2 of the molecular rotational potential (the second term in equation (1)). In figure 6 we show the concentration dependence of the quantity $C \times T_{S_C^*S_A}^{2\alpha}$. From equations (1), (5) and (6) it follows that the temperature independent part of the potential U_2 is $C \times T_{S_C^*S_A}^{2\alpha} \times 2k$. It shows a strong negative deviation from linearity with a minimum around $x = 0{\cdot}7$. At this concentration the width of the S_C^* phase is maximal and the system exhibits a eutectic point (compare figures 2 and 6), indicating that the lower the molecular rotational potential the more stable the S_C^* phase is. The width of the S_C^* phase temperature region correlates with the reciprocal value of the potential.

We calculate the non-chiral part U_2 of the potential in equation (1) for the two pure substances and we find for $a_2\theta^2$ a value of $1{\cdot}2 \times 10^{-20}$ J and 6×10^{-21} J for ZLI 4420 and CE8, respectively. These values are roughly two orders of magnitude higher than the chiral potential ($a_1\theta$) and of the order of kT as expected.

5. Summary

A molecular rotational model was used to interpret the temperature dependence of the experimental P_s/θ values. A two parameter fit was carried out which showed good agreement between theory and experiment. From the fit parameters we have calculated a temperature and tilt independent quantity: P_s/θ at $T = T_{S_C^*S_A}$ which is a normalized measure of the spontaneous polarization and we suggest its use for comparison of different ferroelectric liquid crystals. It is shown that P_s/θ at $T = T_{S_C^*S_A}$ is a linear function of concentration in the binary mixtures of two chiral compounds CE8 and ZLI 4420. We have determined from the fit parameters both the chiral and non-chiral parts of the molecular rotational potential U and presented them as a function of concentration. It is shown that the chiral part of the potential depends very weakly on the composition in contrast to the non-chiral part which shows a strong negative non-linear deviation with a minimum corresponding to the concentration at which the smectic C^* phase width is maximal. The quantitative analysis of the data shows that the chiral part of the potential is two orders of magnitude smaller than the non-chiral potential, as expected.

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