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A. Buka[ab]; H. Stegemeyer[a]
[a] Institute of Physical Chemistry, University of Paderborn, Paderborn, F.R.G [b] Central Research Institute for Physics, Budapest, Hungary

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Molecular rotational potentials in the S_C^* phase of binary ferroelectric liquid crystal mixtures

by A. BUKA† and H. STEGEMEYER
Institute of Physical Chemistry, University of Paderborn,
D-4790 Paderborn, F.R.G.

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The spontaneous polarization and tilt angle have been measured as a function of temperature and concentration in the S_C^* phase of four binary ferroelectric liquid crystal mixtures. The substances have been chosen in a way that different situations could be studied, for example mixtures of a chiral substance (P_s non-zero) with a non-chiral one ($P_s = 0$) and mixtures of chiral compounds with the same sign of P_s as well as with opposite signs. The results have been interpreted by means of a molecular rotational model and potentials associated with the tilt as well as with the chirality have been determined as a function of concentration.

1. Introduction

Early theories [1, 2] failed to explain the temperature dependence of the ratio of the spontaneous polarization to the tilt angle (P_s/θ) measured in the S_C^* phase of ferroelectric liquid crystals. However generalized Landau type theories [3] and a thermodynamic model [4] have given a better description. In a previous paper [5] we have adopted the microscopic model [6, 7] and developed it further to describe our experimental data for P_s and θ in a ferroelectric S_C^* liquid crystal system. We obtained good qualitative agreement between theory and experiment and determined reasonable molecular rotational potentials.

In this work we extend the model to binary mixtures. We have chosen our experimental systems so that different situations could be studied; namely binary mixtures of

(*a*) a chiral compound of $P_s > 0$ with a non-chiral substance,
(*b*) two chiral compound both with $P_s > 0$,
(*c*) two chiral compounds one with $P_s > 0$ and the other one with $P_s < 0$.

2. Experimental

The spontaneous polarization and tilt angle have been measured as a function of temperature for five liquid crystal compounds (I–V) and the four binary mixtures I/II; I/III; I/IV and I/V. The chemical formulas and transition temperatures of the

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† On leave from: Central Research Institute for Physics, H-1525 Budapest P.O.B. 49, Hungary.

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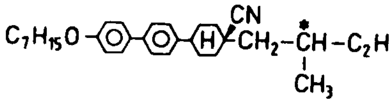
substances are

I. ZLI 4420

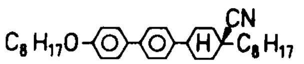


C-66°C-S_C^*-107°C-S_A-112°C-Ch-131°C-I

II. 8008

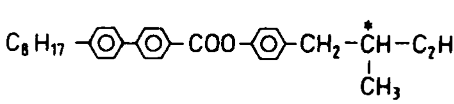
C-62°C-S_C-73°C-N-90°C-I

III. NCB 808



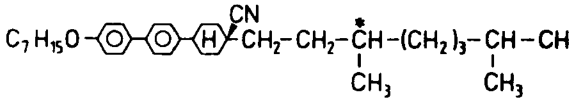
C-81°C-S_C-118°C-S_A-150°C-N-150·3°C-I

IV. CE 8



C-48°C-S_G-63·3°C-S_J^*-64·7°C-S_F^*-66·7°C-S_I^*-69°C-S_C^*-
85°C-S_A-135°C-Ch-141°C-I

V. ZLI 4421



C-89°C-S_C^*-109°C-118°C-I

The substances ZLI 4420; ZLI 4421 and NCB 808 are products of Merck Darmstadt. CE 8 was purchased from BDH. 8008 was prepared and purified as described elsewhere [8]. Compounds I and IV are chiral and both exhibit a positive P_s. Substance V is also chiral but has a negative P_s. II and III are non-chiral and both have S_C phases.

The spontaneous polarization was measured by a Diamant bridge [9] and the tilt angle was derived from the optical switching angle of the sample. Both P_s and θ have been measured on the same sample with 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 temperature of the sample was controlled by an improved version of a Mettler FP5/52 hotstage with a relative accuracy of 1/100 K.

3. Interpretation of the results

In a previous article [5] we have introduced a model in order to describe the temperature dependence of the spontaneous polarization and that of the tilt angle in the S_C^* phase of a chiral liquid crystal. It was assumed that the ordering of the transverse molecular dipoles, μ, was induced by the tilt only and a hindered rotation of the molecules around their long axes was taken into account. The single particle potential describing this rotation was of the form

$$U(\psi) = U_1(0)\cos\psi + U_2(0)\cos 2\psi, \tag{1}$$

where $U_1(0) = -a_1\theta$ is the chiral part of the potential at $\psi = 0°$; $U_2(0) = -a_2\theta^2$ is part of the potential associated with the tilt at $\psi = 0°$; ψ describes the orientation of the transverse dipole moment μ in the plane perpendicular to the long molecular axis; a_1 and a_2 are material constants. In the systems studied here (pure compounds as well as binary mixtures) the temperature dependence of the tilt angle could be described very accurately with a power law

$$\theta = \theta_0 \Delta T^{\alpha}, \tag{2}$$

($\Delta T = T_c - T$, where T_c is either the S_C^*–S_A or S_C^*–Ch phase transition temperature) over the whole range of existance of the S_C^* phase. We used the potential (1) to calculate the temperature dependence of the absolute value of the spontaneous polarization P_s; details of the calculation are given in [5]. The final expression is

$$\begin{aligned} P_s &= \rho\mu\langle\cos\psi\rangle \\ &= C_1(\Delta T)^{\alpha}\frac{(T_c - \Delta T) + C_2(\Delta T)^{2\alpha}}{(T_c - \Delta T)^2 + (C_1/\rho\mu)^2(\Delta T)^{2\alpha} + C_2^2(\Delta T)^{4\alpha}}. \end{aligned} \tag{3}$$

Here C_1 is $\rho\mu\theta_0 a_1/2k$ and C_2 is $a_2\theta_0^2/2k$, where ρ is the particle density.

We now apply this model to chiral binary mixtures composed of liquid-crystalline substances. Taking into account only pair intermolecular interactions, the effective rotational potential of a molecule in a mixture is

$$U_{\text{eff}}(\psi) = \sum_{i,j} x_i x_j U^{ij}(\psi), \tag{4}$$

where x_i and x_j are the mole fractions of components i and j. $U^{ij}(\psi)$ is the rotational potential for a molecule of type i surrounded by molecules j. We deal only with binary mixtures: $i, j = $ A or B and hence $x_A = 1 - x_B \equiv 1 - x$. With $U^A = U^{AA}$ and $U^B = U^{BB}$ we obtain

$$\begin{aligned} U_{\text{eff}}(\psi) &= U^A(\psi) + x[U^{AB}(\psi) + U^{BA}(\psi) - 2U^A(\psi)] \\ &\quad + x^2[U^A(\psi) + U^B(\psi) - U^{AB}(\psi) - U^{BA}(\psi)] \\ &= U_1(0)_{\text{eff}}\cos\psi + U_2(0)_{\text{eff}}\cos 2\psi. \end{aligned} \tag{5}$$

The two parts of the amplitude of the potential $U_{\text{eff}}(\psi)$ can be written in a general form with $n = 1, 2$

$$\begin{aligned} U_n(0)_{\text{eff}} &= U_n^A(0) + x[U_n^{AB}(0) + U_n^{BA}(0) - 2U_n^A(0)] \\ &\quad + x^2[U_n^A(0) + U_n^B(0) - U_n^{AB}(0) - U_n^{BA}(0)]. \end{aligned} \tag{6}$$

We have studied four mixtures with A = II, III, IV, V and B = I and analysed our experimental data using equations (2) and (3). We have fitted equation (2) to our $\theta(T)$ experimental data and obtained θ_0 and α with a good accuracy of 2 per cent. In order to analyse the $P_s(T)$ data with equation (3) we have used the θ_0 and α values obtained before, and performed a two parameter fit, again determining C_1 and C_2 with an accuracy of 5 per cent. Plots representing the accuracy and sensitivity of both fitting procedures are presented in [5].

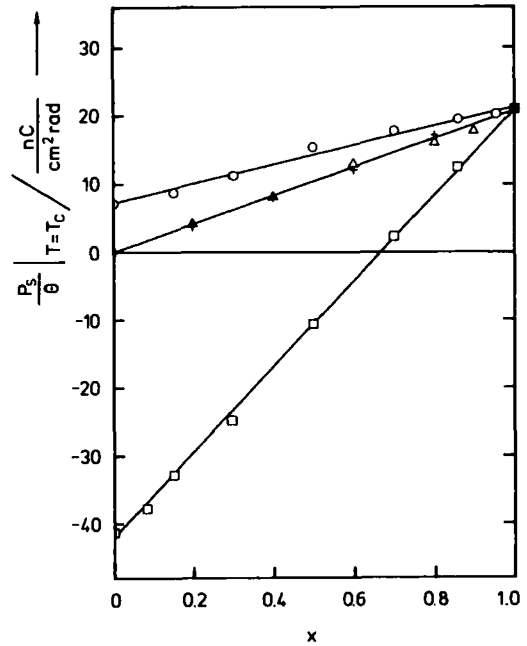


Figure 1. Dependence of P_s/θ at T_c on the mole fraction x for four binary mixtures (△, I/II; +, I/III; ○, I/IV; □, I/V), calculated from the fit parameters C_1, θ_0 and α.

The advantage of the model is that we can determine separately the two parts U_1 and U_2 (for chiral and tilt, respectively) of the rotational potential. First, we deal with the chiral part U_2 of the potential. In figure 1 we show the concentration dependence of $C_1/\theta_0 T_c$ for our systems. This quantity is identical with the value of P_s/θ extrapolated to $T = T_c$ and as such it is a temperature and tilt independent measure of the spontaneous polarization; it shows a linear concentration dependence for each system. The identity of the two curves for systems I/II and I/III shows that P_s/θ at the transition is only determined by the chiral guest molecules and is independent on the nature of the non-chiral host, as has been found for other mixed systems [8].

A linear concentration dependence was also found for the quantities C_1 and $C_1 T_c^{\alpha}$. The last expression is proportional to the temperature independent part of the amplitude of the rotational potential $U_1(0)_{\text{eff}}$

$$C_1 T_c^{\alpha} = (\rho\mu/2k)U_1(0)_{\text{eff}}$$

at $T = 0$. The concentration dependence of ρ is weak within the S_C^* phase and can be neglected; then the straight lines obtained describe the behaviour of $\mu U_1(0)_{\text{eff}}$ as a function of the mole fraction. In order to eliminate the influence of the dipole moment we have to speculate about its effective value in the mixtures. In systems I/II and I/III μ is zero at $x = 0$ (for the two non-chiral substances II and III) and has a value of about 4·2 D at $x = 1$. Assuming a linear concentration dependence between the two limiting values we conclude that $U_1(0)_{\text{eff}}$ does not depend on concentration. In system I/IV the ratio of the $\mu(\text{I})/\mu(\text{IV})$ is approximately 3, and the same value was found for the ratio of $\mu U_1(0)$ in the two pure compounds (see figure 1). Assuming a linear concentration dependence for μ, the potential $U_1(0)_{\text{eff}}$ should also be concentration independent. In system I/V the transverse molecular dipole moment of the

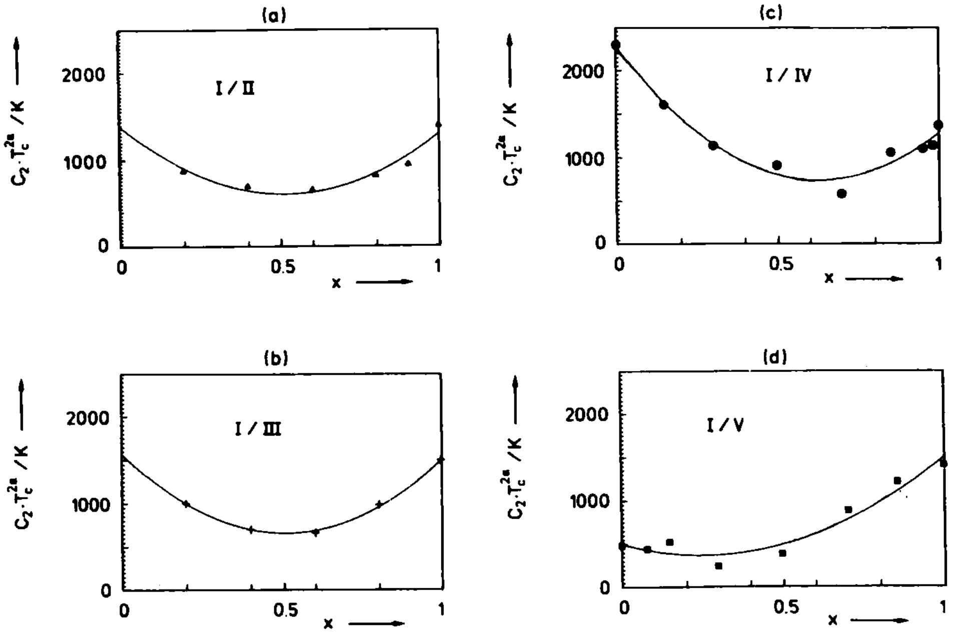


Figure 2. Dependence of the non-chiral part of the molecular rotational potential on the mole fraction x for four binary mixtures. Full lines represent mean square fits to equation (6).

two pure compounds should be the same. $U_1^I(0)/U_1^V(0)$ is negative because of the phase shift of π in cos ψ. It means that the absolute value of the function shown in figure 1 for system I/V demonstrates the concentration dependence of the potential $U_1(0)_{\text{eff}}$.

Summarizing we can say that in all of the cases studied, the rotational potential $U_1(0)_{\text{eff}}$ has a linear concentration dependence. If we compare that with function (6) we can conclude that in our systems

$$U_1^A(0) + U_1^B(0) = U_1^{AB}(0) + U_1^{BA}(0),$$

consequently the amplitude of the chiral part of the potential is independent of the surrounding. This is in agreement with previous results [8] showing $P_s/\sin \theta$ measured at $T_c - T = 5$ K independent of the non-chiral host. The potential barrier for molecule A is equally deep whether it is surrounded by molecules A or B.

The situation is totally different for the other part of the potential U_2 associated with the tilt. The results can be interpreted more easily since we do not have to speculate about the concentration dependence of other physical quantities. The fit parameter C_2 is directly proportional to the amplitude of the potential. In figures 2(*a*)–(*d*) we show the concentration dependence of $C_2 T_c^{2\alpha}$ which is the temperature independent part of the potential $U_2(0)_{\text{eff}}$. We can see that in all four cases the experimental data show a strong negative deviation from linearity. We have fitted a second order polynomial according to equation (6) which is denoted by the full lines in figures 2(*a*)–(*d*). The figure also shows the accuracy of the fitting. Since all of the curves have a minima, $U_2^A(0) + U_2^B(0)$ must be larger than $U_2^{AB}(0) + U_2^{BA}(0)$. In fact (to our surprise) we found values for the sum of the mixed terms as small as our experimental uncertainty. Since, for all four systems, $U_2^{AB}(0) + U_2^{BA}(0)$ lies within the limit of 10 per cent of the sum $U_2^A(0) + U_2^B(0)$ we conclude that the mixed terms can be neglected. The physical consequence of this is that the tilt part of the rotational potential $U_2(0)_{\text{eff}}$, contrary to the chiral part $U_1(0)_{\text{eff}}$, is very sensitive to the surroundings. The potential barrier decreases strongly when the molecule A has neighbours B instead of A, independent of whether B is chiral or non-chiral.

In the table we have collected data obtained from the fitting procedure for the five pure substances I–V investigated. In order to obtain the quantities in the table we have used the fit parameters θ_0, α and C_2 obtained for each system and concentration. Then we used equation (6) to carry out a fit for the concentration dependence (see figure 2). In this way we were able to determine quantities such as the tilt angle, θ, and the rotational potential, U_2, for non-chiral compounds from our polarization and optical tilt measurements (see data with † in the table).

The fitting parameters in the rotational potential

Substance		$U_2(0)(2k)^{-1}$/K at $\Delta T = T_c$	$U_2(0)(2k)^{-1}$/K at $\Delta T = 1$ K	$a_2(2k)^{-1}$/K rad^{-2}	$\theta(0)$/rad at $\Delta T = T_c$
I.	(ZLI 4420)	1500	90	1700	0·9
II.	(8008)	1400†	420†	5600†	0·5†
III.	(NCB 808)	1580†	7†	1750†	0·95†
IV.	(CE 8)	2300	20	1080	1·62
V.	(ZLI 4421)	500	40	600	0·85

† Values extrapolated to $x = 0$ in systems I/II and I/III.

We now make an attempt to discuss the fit parameters of the table in terms of the molecular structure and the phase sequence of the pure compounds. First, the value of $U_2(0)$ at ΔT of 1 K for substance II is obviously large compared with the other compounds. This may be due to the fact that II has a direct phase transition S_C–N without an intervening S_A phase. The large value of U_2 in the vicinity of T_c means that the two equilibrium positions of the molecule during its rotation around the long molecular axis corresponding to positions $\psi = 0$ and π are separated by a large potential barrier, i.e. other rotational positions are less favourable. In an S_A phase, however, all positions around the molecular long axis should be of nearly equal probability. Consequently, in II a nematic phase with no layer structure is preferred over the S_C rather than an S_A phase. In contrast the lower value of $U_2(0)$ in the vicinity of T_c for I, III, IV and V allows an S_A phase which is actually observed in these compounds. Thus the high value of $U_2(0)$ at ΔT of 1 K reflects the vicinity of the nematic phase, whereas this phase does not influence the potentials $U_2(0)$ at $\Delta T = T_c$ (second column in the table), i.e. far below T_c. The same holds for the high value of a_2 for compound II (see the fourth column of the table). The small value of the potential $U_2(0)$ at $\Delta T = T_c$ and that of a_2 for compound V could be connected with the flexibility of the molecule. The alkyl side group is rather long in V and is double branched which may cause an enhanced flexibility, thus the dipole reorientation could be achieved via an intramolecular rearrangement.

In the last column of the table we present the maximum tilt angle $\theta(0)$ to be reached at $\Delta T = T_c$. These values are not real tilt angles in the S_C phase but demonstrate the tendency of the system to form a tilted phase and give a hypothetical tilt which the given system would reach at 0 K. $\theta(0)$ is very large in compound IV which is known to form several highly ordered tilted smectic phases [10]. Obviously $\theta(0)$ is rather similar for I, III and V all of them having a strong transverse dipole moment, a cyano group angularly positioned at a cyclohexane ring. This similar tilt value for molecules exhibiting similar molecular structure independent of the molecular chirality, supports the model of Goosens [11] in which the molecular interaction giving rise to the director tilt is due to the electrostatic quadrupole moments.

From our fit procedure it follows that in compound II the temperature dependence of the tilt in the S_C phase is extremely small. This explains the very small value of $\theta(0)$ at 0 K. From experimental data it is well-known that in $S_C(S_C^*)$ phases with a nematic (cholesteric) phase above, the tilt is nearly temperature independent [12], because the S_C–N phase transition is first order [13]. Consequently our fit parameter $\theta(0)$ reflects the well-known physical behaviour of the S_C phase.

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