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Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article Chao, Jessie Lorenzo , Vakhovskaya, Zinaida , Grebenchikov, Ilja , Tschierske, Carsten and Kresse, H.(2005) 'Dielectric investigation of a binary system of self-organized diols', Liquid Crystals, 32: 10, 1295 — 1300

To link to this Article: DOI: 10.1080/02678290500361914

URL: http://dx.doi.org/10.1080/02678290500361914

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Liquid Crystals, Vol. 32, No. 10, October 2005, 1295–1300

Dielectric investigation of a binary system of self-organized diols

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(*Received 13 May 2005; accepted 10 August 2005*)

Dielectric measurements on a binary system of two liquid crystalline diols were carried out. These show a SmA and a cubic phase. In the middle concentration range of the system, a columnar phase is induced. The self assembly of the molecules giving different liquid crystalline phases is clearly seen in the dielectric spectrum, and therefore details of this process may be discussed. All the samples show a high frequency dielectric absorption which is related to the dynamics of the network of hydrogen bonds. In the columnar phase an additional low frequency mechanism is seen which may be caused by the internal dynamics in the columns.

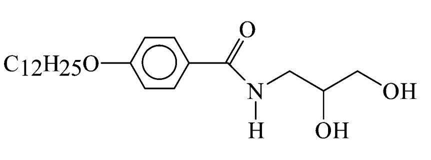
1. Introduction

The molecules of the amphiphilic diols investigated consist of hydrophobic alkyl chains and two hydroxyl groups as the hydrophilic unit. Both, the hydrophobic interaction and the tendency to build a hydrogen-bonded network, are responsible for the self-assembly of these compounds. Thus, thermotropic and lyotropic polymorphism can be observed in such amphotropic samples [1–4]. As is known from water, a network of hydrogen bonds can produce a high dielectric permittivity. This effect has also been observed in simple alkyldiols forming a smectic L_β phase with a two-dimensional network of hydrogen bonds [5]. Depending on the number of aliphatic chains in the hydrophobic part of the molecules, the lamellar (SmA) phase as well as columnar and cubic superstructures can appear. In the latter case, the hydrogen bonds are ordered like a wire in the central part of the columns which are arranged in a hexagonal packing ($\mathrm{Col}_{\mathrm{H2}}$). Cubic phases are formed by inverse spherical micells ($\mathrm{Cub}_{\mathrm{I2}}$) with even more localized hydrogen bonds. In samples showing the polymorphism $\mathrm{Cub}_{\mathrm{I2}}/\mathrm{Col}_{\mathrm{H2}}$ a strong increase of the dielectric absorption intensity has been observed at this phase transition [6]. There was also some indication of low frequency dynamics in the columnar phase. Clear evidence of this process was difficult to obtain because all diols exhibit a high conductivity.

A binary system consisting of components with the same hydrophilic part has now been investigated. The components differ only in the number of alkyl chains. The advantage of a binary system is that the phase behaviour can be systematically changed by a variation in the concentration of the components. This now gives the possibility of relating changes in the dielectric behaviour more clearly to differences in the superstructure. This possibility is interesting particularly in our case because a $\mathrm{Col}_{\mathrm{H2}}$ phase is induced in the middle concentration range of the binary mixture.

2. Substances and binary system

The substances were synthesized as described elsewhere [7] and characterized by DSC and polarizing microscopy. Substance **1**, *p*-*n*-dodecyloxy-*N*-(2,3-dihydroxypropyl)benzamide, shows the polymorphism Cr 358 SmA 403 I (phase transition temperatures in K from the first heating run). For the second compound, 3,4,5-tridodecyloxy-*N*-(2,3-dihydroxypropyl)benzamide, **2**, the polymorphism Cr 344 $\mathrm{Cub}_{\mathrm{I2}}$ 399 I was confirmed [7].



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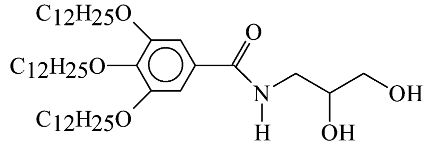

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis
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DOI: 10.1080/02678290500361914

The phase diagram shown in figure 1 was first published by Borisch *et al.* [7] and extended by our measurements. The molar fractions of compound **2** (x_2) investigated are indicated by arrows.

3. Dielectric investigations

The components and mixtures were heated to about 410 K in order to evaporate additional water and filled, after a waiting time of about 20 min, into the calibrated measuring capacitor (brass cell coated with gold, d=0.05 mm). The samples could not be oriented, resulting in problems which will be discussed later. Dielectric measurements were made during slow cooling using the Solartron–Schlumberger Impedance Analyzer Si 1260 and a Chelsea Interface. Experimental details are given elsewhere [8]. The complex dielectric function $\varepsilon^*=\varepsilon'-\mathrm{j}\varepsilon''$ ($\mathrm{j}^2=-1$) of both substances at low temperatures and the fits to equation (1) are presented in figures 2 and 3. In particular at low frequencies and high temperatures, the contribution of the conductivity to ε'' and that of the electrical double layer to ε' dominate the spectrum. As seen in figure 2, the real part of the measured dielectric function ε' approaches the 'static' dielectric permittivity ε_0 at frequencies of about 10 kHz. At frequencies of about 1 MHz an absorption range is seen which is much more pronounced in substance **2** because this sample could be cooled to lower temperatures without crystallization.

The experimental data could be well fitted to two Cole–Cole mechanisms,

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1+(\mathrm{j}\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1+(\mathrm{j}\omega\tau_2)^{1-\alpha_2}} - \frac{\mathrm{j}A}{f^M} + \frac{B}{f^N} \quad (1)$$

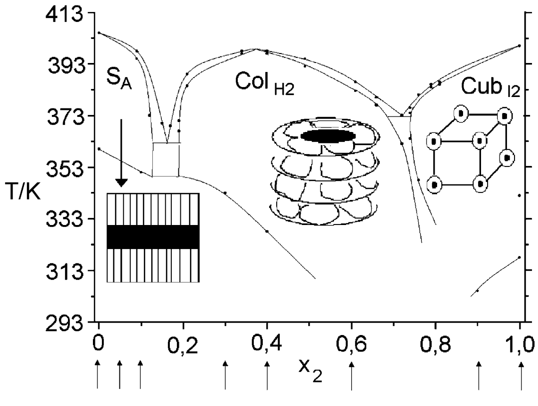

Figure 1. Phase diagram of the binary system as a function of the concentration of compound **2** with inserted structure models in which the black part indicates the network of hydrogen bonds. The arrows give the molar fractions of compound **2** investigated.

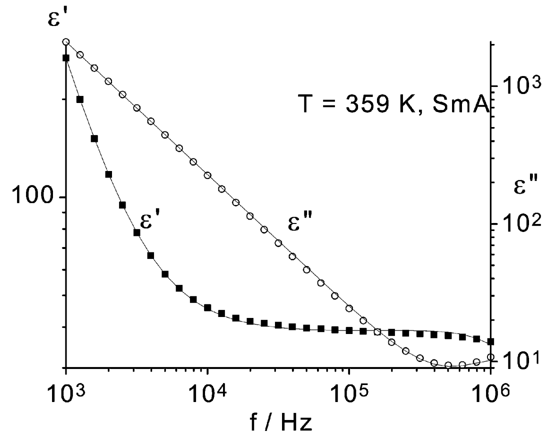

Figure 2. Complex dielectric function of sample **1** and the fitted curve.

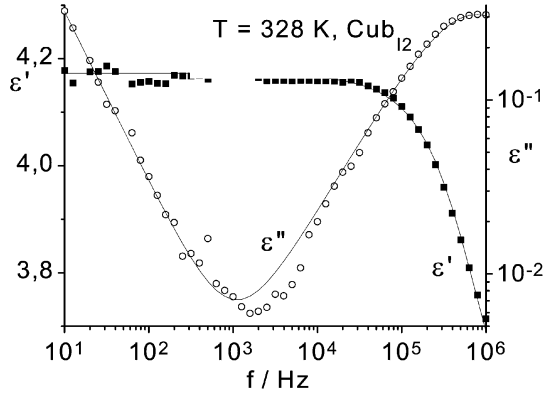

Figure 3. Complex dielectric function of sample **2** in the $\mathrm{Cub}_{\mathrm{I2}}$ phase.

and the limiting values ε_i of the dielectric permittivity and the corresponding relaxation times τ_i with $\omega=2\pi f$ (f=frequency), α_i-Cole–Cole distribution parameters, the conductivity term A as well as M, B and N as further fit parameters responsible for the slope of conductivity and capacity of the double layer were calculated. These last terms become important for our samples and mixtures because of the high conductivity. In most cases only one relaxation process or even only the static dielectric permittivity ε_0 was necessary for the description of the data as demonstrated in figures 2 and 3. For calculation of the specific conductivity, data of the dielectric loss ε'' between 100 and 1000 were fitted to the fourth term in equation (1) under the condition M=1. This limitation was necessary in order to exclude saturation effects seen at very high dielectric losses, and on the other side the influence of dielectric relaxation. The condition M=1 was practically also fulfilled with M as an open parameter, because the data for M obtained in this way are in the range $0.985<M<1.000$.

From the fitted A-parameter the specific conductivity κ was calculated according to

$$\kappa = A\,2\,\pi\,8.85\times10^{-12}\,\mathrm{S\,m^{-1}}[9]. \tag{2}$$

The errors in the static dielectric permittivity ε_0 fitted in the SmA and $\mathrm{Cub_{I2}}$ phases are about 1% at low and 2% at high temperature. The fitted ε_1 and τ_1 parameters show an uncertainty of about 2% and 20%, respectively, and a specific conductivity of 1%. All data measured in anisotropic phases additionally contain a much higher error of the permittivities, which arises from the unknown orientation of the samples.

Experimental results for both components are presented in figures 4–7. The static dielectric permittivity of compound **1** increases with a step at the phase transition and then increases continuously with decreasing temperature to a value of about 40. This indicates that 2D networks of hydrogen bonds dominate the dielectric behaviour in the SmA phase. In the isotropic state the dielectric permittivity increases linearly with falling temperature. This should result from the dielectric response of the isotropic distribution of single molecules. Both the aggregation of molecules to the SmA phase, and the resulting formation of the 2D network of the hydrogen bonds, take place at the phase transition. The increase in conductivity at the I/SmA transition demonstrated in figure 5 may indicate that smectic A layers are oriented preferentially parallel to the measuring electric field (see also [9]). In this configuration also, the contribution of the hydrogen bonds to ε_0 is higher.

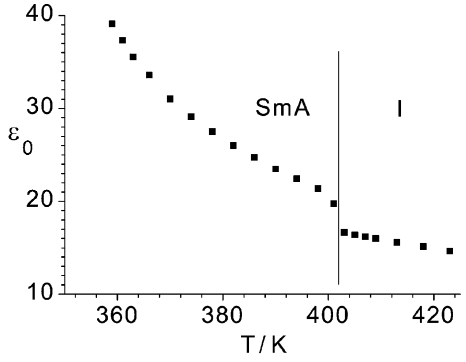

Figure 4. Static dielectric permittivities of sample **1**.

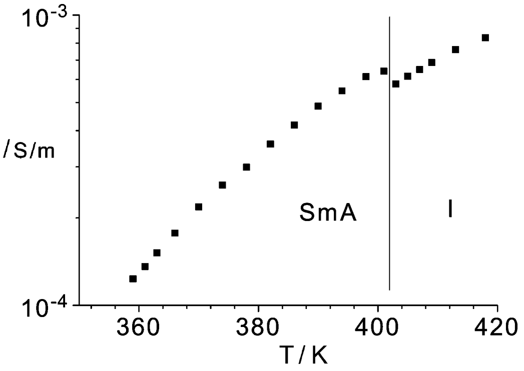

Figure 5. Specific conductivity of sample **1**.

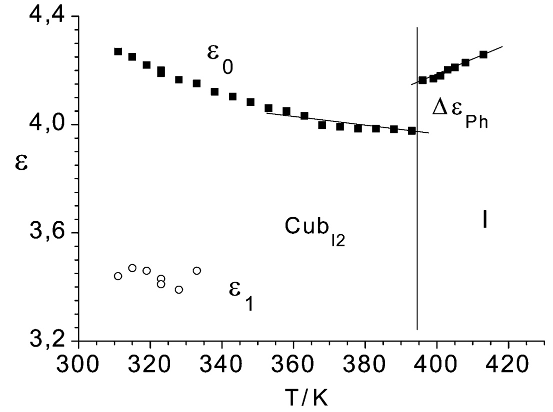

Figure 6. Dielectric permittivities of sample **2**.

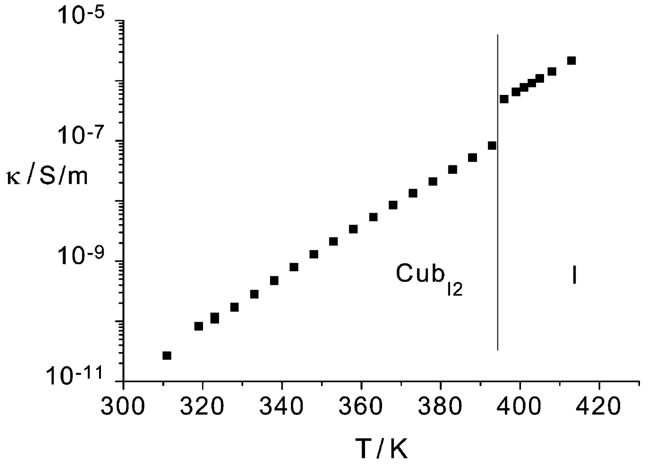

Figure 7. Specific conductivity of sample **2**.

The dielectric data for substance **2** are presented in figures 6 and 7. Due to the appearance of the cubic phase no orientation effects need be discussed here. In contrast to the results for compound **1**, the static dielectric permittivity ε_0 decreases in this case at the I/$\mathrm{Cub_{I2}}$ transition and increases in the isotropic phase with increasing temperature (figure 6). The unusual last effect can only be explained by an equilibrium between spherical micells with a compensation of the longitudinal dipole moments of the molecules and single molecules. This equilibrium is shifted at higher temperatures in the direction of single molecules. This means that at the clearing temperature only the cubic lattice, but not the micelles, are completely destroyed. The negative step of the static dielectric permittivity at the I/Cub$_{I2}$ transition $\Delta\varepsilon_{Ph}$ is caused by the formation of the cubic lattice. This may indicate that this process also influences the equilibrium between micelles and single molecules. The change in the order is also seen in the decrease in the specific conductivity at the I/Cub$_{I2}$ phase transition, which reflects a stepwise formation of the isolated system of hydrogen bonds. Similar results were obtained for the mixture with x_2=0.9 which also forms the Cub$_{I2}$ phase.

In order to demonstrate the influence of the orientation on ε_0, two measurements of the same sample with x_2=0.05 are shown in figures 8 and 9. For the first measurement, the layers of the SmA phase are preferentially oriented perpendicular to the measuring field, therefore both the static dielectric permittivity and the conductivity increase at the transition into the isotropic phase. For the second run, which was performed two days later, essentially no step in these quantities is seen, which indicates a more statistical orientation of the layers to the measuring electrical field. The difference in conductivity for both measurements in the isotropic phase may be due to different water contents of the samples. Such extreme behaviour was only found for this concentration.

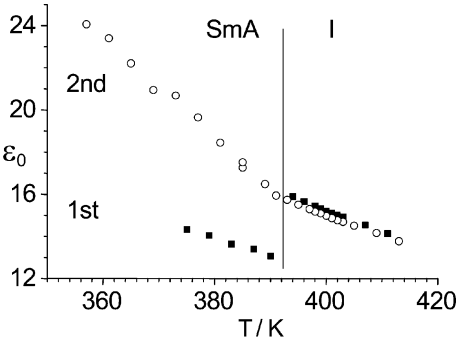

Figure 8. Static dielectric permittivities of the sample with x_2=0.05, for two runs.

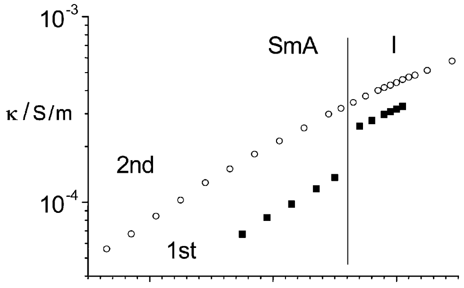

Figure 9. Specific conductivity of the sample investigated in figure 8.

As mentioned earlier, in the middle concentration range of the binary system the Col$_{H2}$ phase appears. The Col$_{H2}$ phase shows an additional dielectric absorption at low frequencies. This process is difficult to detect and is only seen in the real part of the dielectric function. For example, the experimental data for the isotropic and Col$_{H2}$ phases of the same sample are compared with each other in figure 10. The real part of the dielectric function in the isotropic phase can well be fitted by the last term of equation (1) and the static dielectric permittivity ε_0. To demonstrate this, the two limiting lines for ε_0 and the influence of the double layer are given in figure 10. This simple fit fails for the raw data of the Col$_{H2}$ phase, particularly in the range of 10 kHz. In this case the two limiting lines for ε_1 and the double layer show a much larger difference from the raw data in the range between 1 and 10 kHz. Therefore an additional absorption range has to be introduced, and the fit gives a relaxation frequency of 23 kHz (ε_0=19.0, ε_1=14.3, α=0.26). Thus, the data in the columnar phase may be well described. Due to the dominating term of the double layer the error in ε_0 and in the related relaxation time is large. At lower temperatures a pronounced second relaxation range appears. The raw data of this absorption shown in figure 11 could only be well fitted under the assumption of the two processes. A fit using only one Havriliak–Negami process [9] is also possible. Therefore we do not try to assign the high frequency process of this relaxation range as a separate mechanism.

Equation (1) contains only two relaxation ranges instead of the required three. Therefore the high

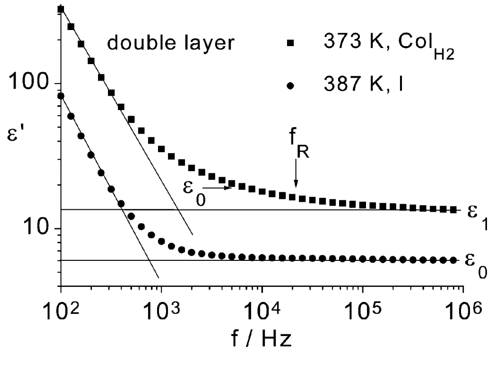

Figure 10. Raw data of the real part of the dielectric function in the I and Col$_{H2}$ (upper curve) phases for x_2=0.6. The static dielectric permittivity and the relaxation frequency are indicated by arrows.

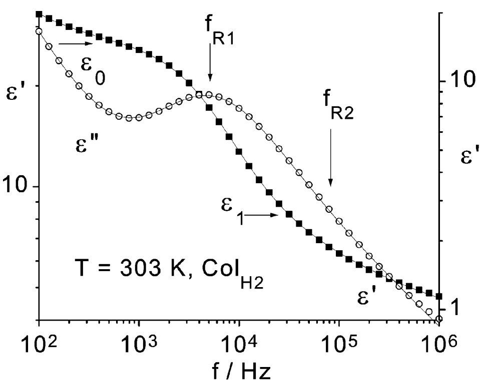

Figure 11. Dielectric function and fitted curves for the mixture with x_2=0.6; ε_3 was fitted to 3.71.

frequency part was fitted separately and the beginning of the low frequency mechanism described formally as a double layer of ions at the interface and the appearance of a d.c. conductivity. The exponent M in the last term of equation (1) responsible for the 'conductivity' in this case is 0.73 and not between 0.98 and 1.00 as is usually the case. This also proves the existence of the low frequency relaxation discussed earlier. The results of the fit for the mixture x_2=0.6 are presented in figures 12 and 13. The specific conductivity is shown in figure 14.

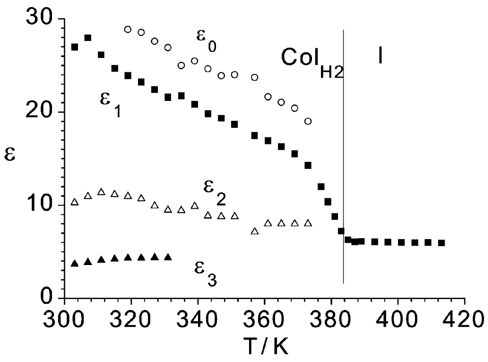

Figure 12. Limits ε_i for the molar fraction x_2=0.6.

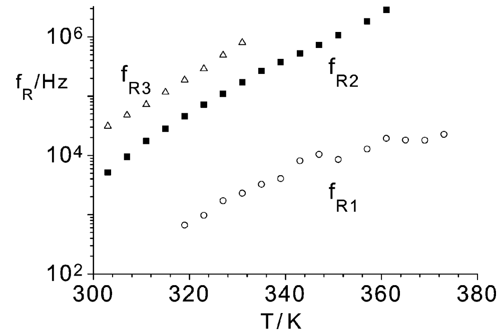

Figure 13. Relaxation frequencies for the mixture with x_2=0.6.

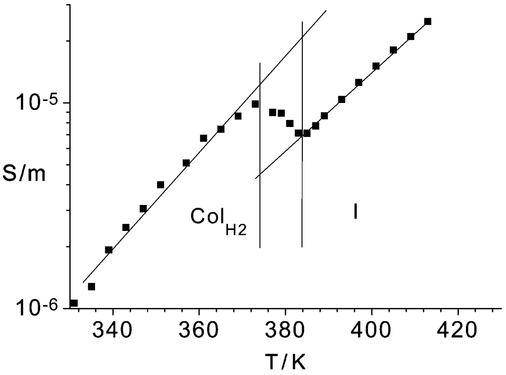

Figure 14. Specific conductivity for the mixture x_2=0.6.

The dielectric permittivity in the isotropic phase decreases only very slightly with increasing temperature. The strong increase of ε_1 and the appearance of an additional low frequency absorption range with the limit ε_0 in the Col_{H2} phase demonstrate the formation of the columns and the organization to a hexagonal lattice. Similar behaviour was found for the other two mixtures showing the Col_{H2} phase.

The conductivity shown in figure 14 increases at the transition into the Col_{H2} phase. This means that the columns are ordered preferentially in the direction of the measuring field. Thus, the current can pass through the network of the hydrogen bonds in the centre of the columns as in a 'wire'. The irregular behaviour of the specific conductivity at about 380 K arises from the two phase range of the binary system. The lines in figure 14 are only guides for the eye.

4. Summary

The dielectric results provide insight into the process of the self-assembly of both components. This was discussed before in detail. In order to see special effects in the middle concentration range the data have to be summarized. Figures 15 and 16 show the absolute values of the dielectric permittivities of the different mesophases at 363 K and the steps in the dielectric permittivities ε_0 and ε_1 at the phase transition from the liquid crystalline phase into the isotropic state; $\Delta\varepsilon_{Ph}=\varepsilon_{LC}-\varepsilon_I$ estimated from linear extrapolation of the data (see figure 6). The data near to the phase transition were excluded in order to avoid the influence of the two-phase range. Open symbols denote date taken from a second run at the same concentration. Particularly in the SmA phase, large differences between the two experimental runs (closed and open symbols) of the ε data, but not in the relaxation frequencies, are seen. This points to orientation effects. Generally the dielectric permittivity increases with the formation of

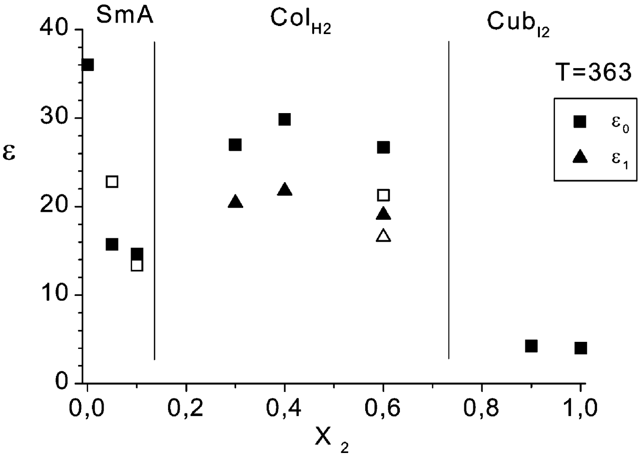

Figure 15. Fitted dielectric permittivities at 363 K for different molar fractions.

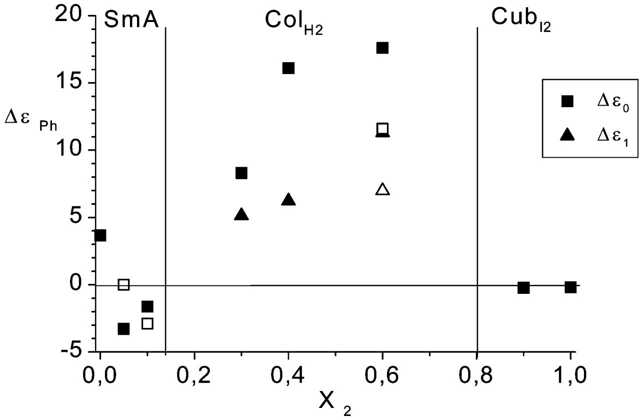

Figure 16. Dielectric permittivity steps $\Delta\varepsilon_{Ph}$ at the clearing temperature for different molar fractions of compound **2**. For the estimation of the data see figure 6.

the Col_{H2} phase from the Cub_{I2} state at about $x_2=0.7$ as seen in figure 15. This indicates the much higher dipole moment due to the 2D network of hydrogen bonds and a columnar structure.

In the SmA and Cub_{I2} phases only one relaxation process with a relaxation frequency of about 1 MHz at 343 K was detected, which is also seen in the Col_{H2} state. We have related this process to the dynamics of the hydrogen-bonded system but it may also be due to the reorientation of the carboxylic groups. The additional low frequency process seen only in the Col_{H2} phase must be attributed to the appearance of the columns. The simple explanation is a rise in the collective process within the columns, for example an elastic deformation of the columns. Possible processes are a bend of the whole column or, more probably in our case, a change of the symmetric distribution of the molecules in the plane perpendicular to the column axes (see figure 1, inserted structure model). Whether the NH...OC hydrogen bond between different molecules in the plane orthogonal to the column axes produces a 'rotating' dipole moment [6], which reacts to the external electrical field, is not clear at this time.

The steps $\Delta\varepsilon_{Ph}$ in the dielectric permittivities at the clearing temperature reflect the changes in the dipolar arrangement at this phase transition. Large steps are only detected at the Col_{H2}/I transition as shown in figure 16. For the interpretation of these steps we have additionally to consider the very weak linear decrease of the dielectric permittivity in the isotropic phase seen in figure 12. This slope may consist of two parts, the normal decrease of the static dielectric permittivity with increasing temperature, as seen in compound **1** (figure 4), and an increase due to the destruction of a part of the columns. Consequently, the step $\Delta\varepsilon_{Ph}$ at the Col_{H2}/I transition must contain contributions, from (a) the organization of the molecules to columns and (b) that of columns to the hexagonal phase.

Acknowledgements

The authors are indebted for financial support to the 'Graduiertenkolleg 894'.

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