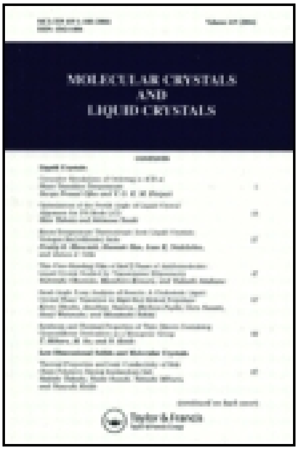

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Dielectric Investigations of Diols Showing Columnar Hexagonal Phases

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Dielectric Investigations of Diols Showing Columnar Hexagonal Phases

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Dielectric investigations of two diols with different molecular shape are carried out in the MHz-range and discussed.

Keywords: diols; micellar hexagonal units; dielectric measurements

INTRODUCTION

Recently dielectric investigations of different diols in GHz-range were published in which the dynamics of the OH-dipoles in different mesophases were studied [1-2]. There have been detected only small changes in the relaxation times at the phase transitions [1]. Insertion of a third dipole unit into the molecule results in the appearance of a second relaxation range at nearly the same frequency [2]. In contradiction to this, wedge-shaped diols forming columnar hexagonal and inverse micellar cubic phases show a dielectric absorption at 10 kHz [3]. The relaxation times follow the Arrhenius-equation with an activation energy of about 120 kJmol^{-1} (data given in [3] have to be multiplied by 2.3). Therefore, this process was regarded as a collective motion related to the structure of the phase. In order to obtain more information about the nature of this additional relaxation two samples with different molecule structure were synthesized and characterized by the dielectric method.

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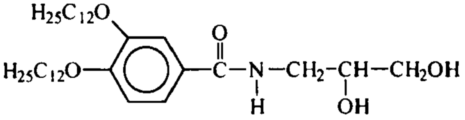
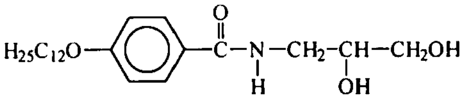
* author for correspondence

SAMPLES

Samples and phase transition temperatures in °C are given below.



Cr 98 Col$_{H2}$ 148 I **(A)**



Cr$_1$ 80 Cr$_2$ 89 S$_A$ 132 I **(B)**

For comparison we have used the sample with three symmetrical dodecyloxy-groups published before [3] which shows different transition temperatures at heating and cooling:

Cr 61 Col$_{H2}$ 72 Cub$_{I2}$ 82 I (I 80 Cub$_{I2}$ 65 Col$_{H2}$) **(C)**

The number of dodecyloxy-groups attached at the phenyl system is responsible for the molecular shape and the formation of different phases. The stronger the wedge-like shape of the molecule the stronger the tendency to form spherical or columnar micells which in its turn are building units of the respective mesophases.

DIELECTRIC INVESTIGATIONS

Dielectric investigations have been carried out in a glass cell coated with gold electrodes ($A = 1$ cm^2, $d = 0{,}1$ mm). Measurements were done with a Solartron Schlumberger Impedance Analyzer in combination with a Chelsea Interface. Experimental data of the dielectric loss ε'' of sample A are presented the 3D-plot in Figure 1. The dielectric loss was fitted together with the dispersion data to two COLE-COLE mechanisms and the conductivity term A/f (f-frequency):

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{\left(1 + j\omega\tau_1\right)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{\left(1 + j\omega\tau_2\right)^{1-\alpha_2}} + \frac{A}{f} \qquad (1)$$

ε^*-complex dielectric constant, ε_2, ε_1-high and low frequency limit of the dielectric constant, ε_0-used for formal description of double layer, τ_2-relaxation time, α_2-distribution parameter, $\Delta=\varepsilon_1-\varepsilon_2$ (dielectric increment)

The low-frequency part of Equation (1) was used as formal description of the electrical double layer which results from the relatively high conductivity. The interesting dielectric part at higher frequencies could be separated in this way from the low-frequency contribution as demonstrated in Figure 2.

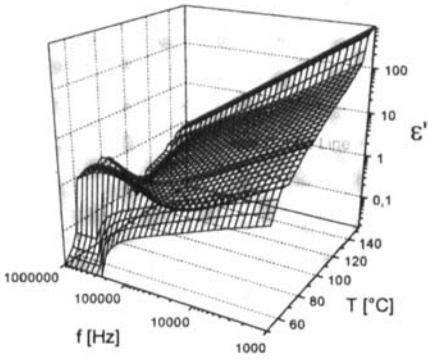


FIGURE 1: ε'' of sample A as function of frequency and temperature.

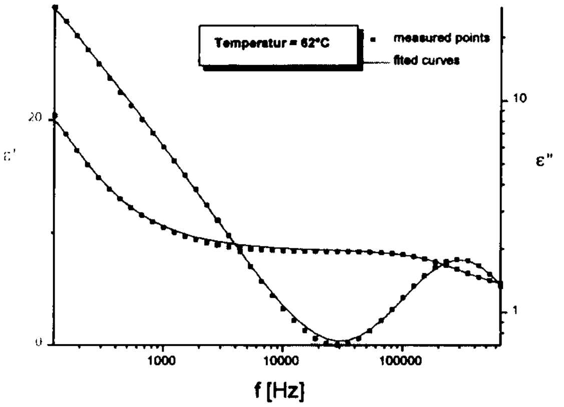
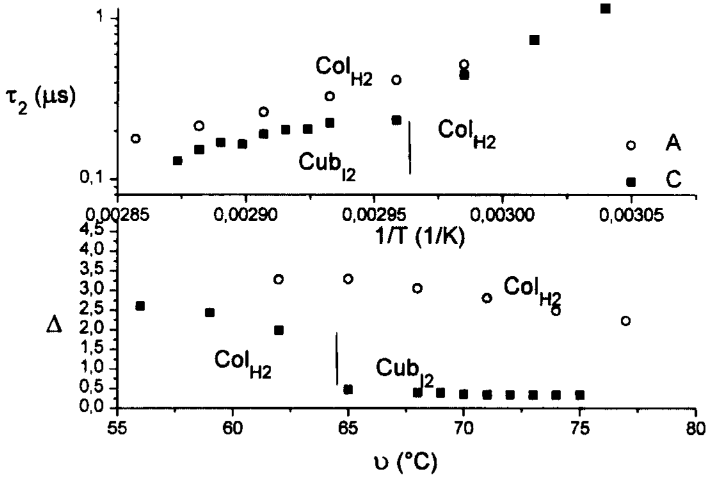


FIGURE 2: Measured and fitted absorption and dispersion curves of sample A. The parameters are: $\varepsilon_0=31.7$; $\varepsilon_1=8.30$; $\varepsilon_2=4.87$; $f_{R1}=1.24E2$; $f_{R2}=3.10E5$; $\alpha_1=0.24$; $\alpha_2=0$, $A=2.36E3$.

The obtained distribution parameter $\alpha_2 = 0$ indicates a Debye mechanism. Dielectric increments and relaxation times are shown in Figures 3 and 4. They are compared with the respective data of sample C which was investigated before. Both measurements were carried out during cooling.



FIGURES 3 and 4: Relaxation times and increments of A(○)and C(■).

The 3-D plot of sample **B** in Figure 5 shows no dielectric absorption in the measured frequency range. The high frequency limits of the dielectric

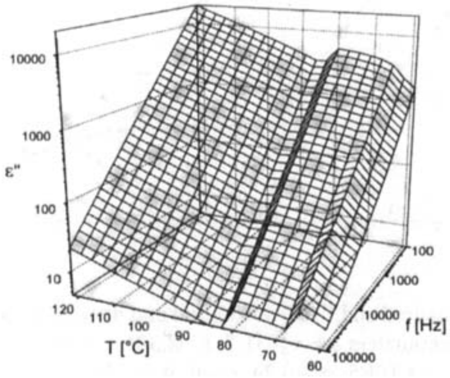


FIGURE 5: ε'' of sample **B** as function of frequency and temperature.

constants ε_2 of **A** and **C** according to Equation (1) or the dielectric constant of **B** are higher than 3.7 indicating an additional dielectric absorption in the GHz-range (fast dynamics of OH-groups) which has been already found in **C** [3].

DISCUSSION

The described dielectric absorption could be detected only in samples showing phases which are build up from inverse micelles. Therefore, one can assume that the nature of this relaxation phenomenon is based on these aggregates. Furthermore, the intensity (increment) of the absorption is higher for the columnar then for the cubic phase (see Figure 4). Using the model that the length of cylinders in the cubic phase (nearly spherical aggregates [4]) is much smaller than that of the hexagonal one can understand the stronger response of the columnar aggregates. Another question is related to the dipole moments responsible for this effect. Due to the action of the hydrogen bonds between the CO- and the NH-groups in the middle part of the molecule the motion of the dipoles is restricted. Consequently, the dipoles are partially circular ordered. The measured response is in this model related to a deformation of the columns. Further investigations are necessary to become a better understanding of this effect.

Acknowledgments

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