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Liquid Crystals

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To cite this Article Gestblom, B. , Kresse, H. , Tschierske, C. , Urban, S. and Wróbel, S.(1993) 'Dielectric investigations of two liquid crystalline diols', *Liquid Crystals*, 15: 3, 409 – 415

To link to this Article: DOI: 10.1080/02678299308029141

URL: <http://dx.doi.org/10.1080/02678299308029141>

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Dielectric investigations of two liquid crystalline diols

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(Received 3 March 1993; accepted 26 March 1993)

The dielectric spectra of *n*-decane-1,2-diol and *n*-undecane-1,2-diol have been measured with the use of time domain spectroscopy, in the temperature range covering the isotropic and liquid crystalline phases. In the isotropic and smectic phases a relaxation process was observed which could be described by the Cole–Cole equation with the distribution parameter $\alpha \approx 0.20$. It was established that the transitions from the isotropic to smectic phases were not accompanied by a step-wise change of the relaxation times. However, the activation energy increases markedly at the transition to the S_B^* phase, whereas it does not change at the isotropic– S_A^* transition. A discussion of the dielectric parameters obtained for these and other low molar mass diols is presented. It was found that the static dielectric permittivity and the activation barrier change systematically with the increase of the molecular length of *n*-alkyl-1,2-diols.

1. Introduction

The self-association of diols can be observed on the level of intra and intermolecular hydrogen bondings [1–4] as well as by the formation of mesomorphic phases. In the last case, liquid crystalline phases are formed by the interaction of the lyophilic hydrocarbon chains [5–7]. It could be shown by X-ray measurements that the molecules are ordered in layers in which alternating hydrophilic and lyophilic parts exist [5, 6]. Therefore, both thermotropic and lyotropic liquid crystalline behaviour was detected [7]. A complete miscibility between the liquid crystalline phases of diols with that of conventional liquid crystals has not been found up till now.

The aim of these investigations is to study the dynamics of the HO-dipoles by dielectric methods and to relate the results to the mesomorphic behaviour. Preliminary measurements were performed on *n*-decan-1,2-diol [8] where no step of the dielectric relaxation time at the phase transition from the isotropic to the lamellar S_A^* phase was detected. However, the GHz frequencies used in this experiment correspond to the condition $\omega\tau \gg 1$ and thus it could not give accurate values of the relaxation times τ . Additionally, the sample exhibited a strong tendency to align at a surface and the measurements of the dielectric relaxation spectra in the same measuring cell were preferred. For these reasons the experiment was repeated using the time domain spectroscopy technique which can cover a large frequency range in a single measurement.

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2. Measurements

The following samples were studied:

<i>n</i> -decan-1,2-diol, C ₁₀ H ₂₂ O ₂ ,	C 319 K (S _B * 304 K S _A * 308 K) I	1
<i>n</i> -undecan-1,2-diol, C ₁₁ H ₂₄ O ₂ ,	C 322 K (S _B * 315 K) I	2

The samples were synthesized according to van Rheenen *et al.* [9]. The phase transitions were detected by differential scanning calorimetry. The molecules of these compounds are ordered in the layers like in S_A or S_B phases.

The dielectric spectra were obtained by the total reflection time domain spectroscopy technique [10–12]. This method is based on the monitoring of the shape of a step pulse, which is reflected from the dielectric sample terminating a coaxial line. From the Fourier transform of reflected pulse shapes a reflection coefficient can be calculated at chosen frequencies. Transmission line theory gives for the ratio of reflected signal to incoming signal

$$S(\omega) = \frac{\rho + \exp(-i2\omega\ell\sqrt{\epsilon^*/c})}{1 + \rho \exp(-i2\omega\ell\sqrt{\epsilon^*/c})} \quad (1)$$

Here c is the speed of light in a vacuum and $\rho = (1 - \gamma\sqrt{\epsilon^*}) / (1 + \gamma\sqrt{\epsilon^*})$, where γ is determined by the diameter of the centre pin of effective length ℓ . In the measurement cell used $\gamma = 1.12$ and the effective pin length $\ell = 3.9$ mm.

In the present measurements chloroform was used as a reference liquid. The reflected pulse shapes from the diols and chloroform were observed within the time window of 10 ns. The step pulse was obtained from an HP 1106B pulse generator, the pulse shape being monitored by an Iwatsu SAS 8130 Wave Form Analyser. From the known dielectric spectrum of chloroform and the application of equation (1), the dielectric spectra were then evaluated at 45 frequencies between 35 MHz and 6 GHz.

The temperature of the measurement cell was controlled by a water jacket and a thermostat. The sample was melted into the cell at 60°C, the temperature then being lowered in steps of 5°C or less. Additionally, sample 2 was measured at 5.65 and 9.40 GHz in the wave guides with rectangular geometry [13].

3. Results

The results of dielectric studies of *n*-undecan-1,2-diol are presented in the form of dispersion, $\epsilon'(\nu)$, and absorption, $\epsilon''(\nu)$, spectra in figure 1 and in the form of Cole–Cole diagrams in figure 2. The points obtained by the standing wave method coincide very well with the spectra measured by the TDS technique. The spectra obtained for *n*-decane-1,2-diol show the same features and therefore we omitted them in this presentation.

In the Cole–Cole representation the spectra appear as depressed arcs in both the isotropic and liquid crystalline phases. This indicates that the appropriate model function for describing the permittivity spectrum within the studied frequency range is given by the Cole–Cole function

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (2)$$

Here ϵ_s is the static permittivity, ϵ_∞ the high frequency permittivity, τ the mean relaxation time, $\omega = 2\pi\nu$, and α a distribution parameter. The resulting parameters, from a least squares fit of equation (2) to the experimental spectra, are given in table 1

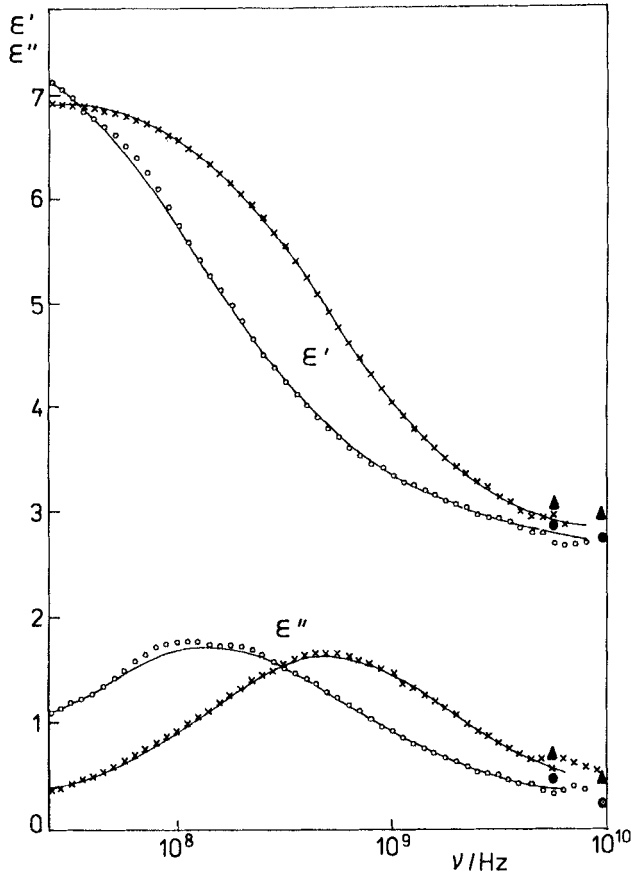


Figure 1. The dielectric dispersion, ϵ' , and absorption, ϵ'' , spectra of *n*-undecane-1,2-diol measured for the isotropic (323 K) (\times) and S_B^* (304 K) (\circ) phases. The black points were obtained by the standing-wave method. The lines show the theoretical spectra calculated from equation (2) and fitted to the experimental ones with the parameters quoted in table 2.

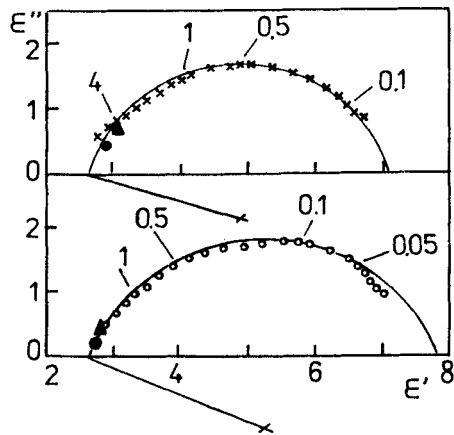


Figure 2. Cole-Cole plots of the spectra presented in figure 1. (\times) 323 K; (\circ) 304 K.

Table 1. The dielectric parameters for *n*-decan-1,2-diol, C₁₀H₂₂O₂.

<i>T</i> /K	ϵ_s	ϵ_∞	τ /ns	α	Phase
333	7.4	2.8	0.17	0.15	
328	7.6	2.7	0.22	0.16	
323	7.8	2.7	0.27	0.17	
318	7.9	2.7	0.34	0.17	I
313	8.1	2.7	0.43	0.18	
311	8.2	2.7	0.48	0.18	
309	8.3	2.7	0.53	0.18	
307	8.6	2.7	0.62	0.20	S _A *
305	8.6	2.7	0.68	0.19	

Table 2. The dielectric parameters for *n*-undecan-1,2-diol, C₁₁H₂₄O₂.

<i>T</i> /K	ϵ_s	ϵ_∞	τ /ns	α	Phase
333	6.8	2.6	0.20	0.18	
328	6.9	2.6	0.24	0.20	
323	7.1	2.6	0.31	0.20	I
318	7.2	2.7	0.39	0.21	
313	7.4	2.7	0.55	0.24	
310	7.5	2.7	0.67	0.24	
307	7.6	2.7	0.83	0.25	S _B *
304	7.9	2.6	1.10	0.26	
299	7.7	2.7	1.50	0.25	

for *n*-decan-1,2-diol. For the *n*-undecan-1,2-diol sample a small contribution to the dielectric loss at the lower frequencies could be observed due to a slight conductivity $< 10^{-3}$ S/m. The resulting parameters, after correction for this conductivity contribution, are given in table 2. The root mean square deviation between the Cole–Cole model function (2) and the experimental permittivities is of the order of 0.05.

4. Discussion

Dielectric relaxation studies of conventional thermotropic liquid crystals exhibit two main relaxation processes, even in the highly ordered smectic phases, for example, S_B [14]. One such process falls within the MHz range of frequency and is connected with the molecular reorientations around the short axes. This motion exhibits jump-wise changes of the relaxation times and activation barrier in the phase transitions between liquid-like phases (I, S_A and S_C) and highly ordered phases (S_B, S_E, ...) [14, 15]. The second motion is connected with the rotations of molecules around the long axes and is observed in GHz frequencies. The phase transitions between different LC phases do not influence this motion [14, 15]. In the case of the substances under study an additional motion must be taken into consideration: the rotation of the HO-dipoles around C–O bonds. This motion is connected with the breaking of the hydrogen bonds between the molecules. A large conductivity at low frequencies did not allow us to carry out the dielectric measurements below to 10 MHz. Nevertheless, symmetrical shapes of

the spectra of dielectric losses, $\epsilon''(\omega)$, obtained for both the isotropic and smectic phases (see figure 1), and very good agreement between the measured spectra and the model function (2) (see figures 1 and 2) suggests that there is one dominating relaxation mechanism with a distribution of τ . Additionally, the Arrhenius plots presented in figure 3 show that the transitions from the isotropic to smectic phases are not accompanied by a step-wise change of the relaxation times. These features indicate that in both the isotropic and smectic phases we are dealing with the same motion—the intramolecular rotations of the HO-groups accompanied by the breaking of hydrogen bonds. However, large values of the α parameter (see tables) seem to indicate that the HO-groups are in different energetic positions due to different associates formed by inter and intramolecular hydrogen bonds. Also other dipolar rotations, like whole molecule reorientations around the long axes, may influence the relaxation spectra.

As one can see in figure 3 the activation energy does not practically change at the transition from the isotropic to the S_A^* phase (substance 1, $E_A^{S_A^*} \approx E_A^I = 41$ kJ/mol), whereas the transition to the S_B^* phase results in marked increase of the activation energy (substance 2, $E_A^I = 40$ kJ/mol; $E_A^{S_B^*} = 55$ kJ/mol). One can conclude from these data that the reorientation process of the HO-dipoles is influenced by the structure of the phase. Probably the hexagonal order of the alkyl chains in the layers of the S_B^* phase [5, 6] results in a stabilization of the hydrogen bridges and therefore the mobility of the HO-groups increases with temperature in comparison with the S_A^* and isotropic phases.

Some additional conclusions concerning molecular associations in the isotropic phase of n -alkyl-1,2-diols ($C_nH_{2n+2}O_2$) can be deduced from the comparison of the dielectric properties of the series of compounds. Gestblom *et al.* [4, 16], have studied the dielectric behaviour of four short chain diols: ethane, propane and butane ($n=2, 3$ and 4) [4] and hexane ($n=6$) [18]. The spectra obtained could be described with the

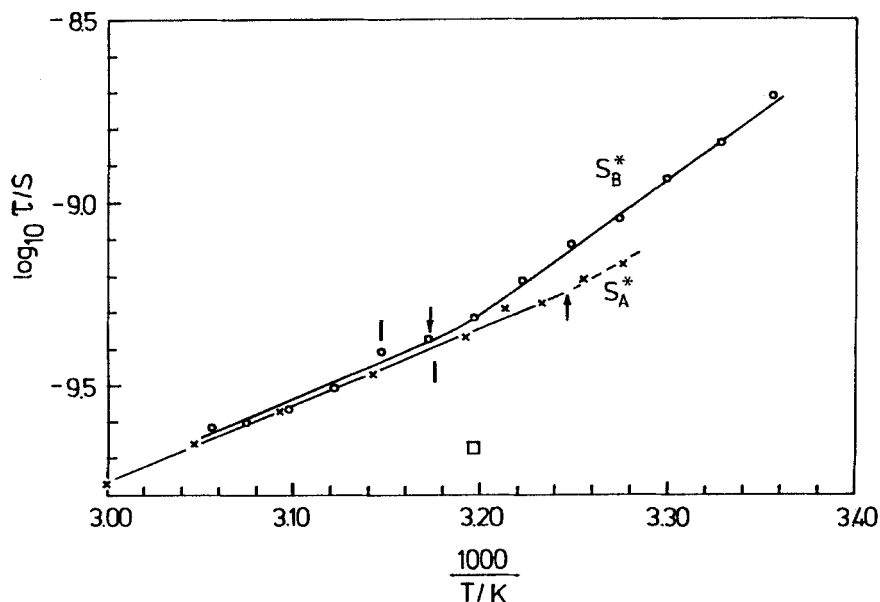


Figure 3. Activation plots for the isotropic and smectic phases of n -decane (\times) and n -undecane (\circ) 1,2-diols. \square denotes the τ value obtained for n -decane from microwave measurements [8]. The arrows show the transition points detected by DSC.

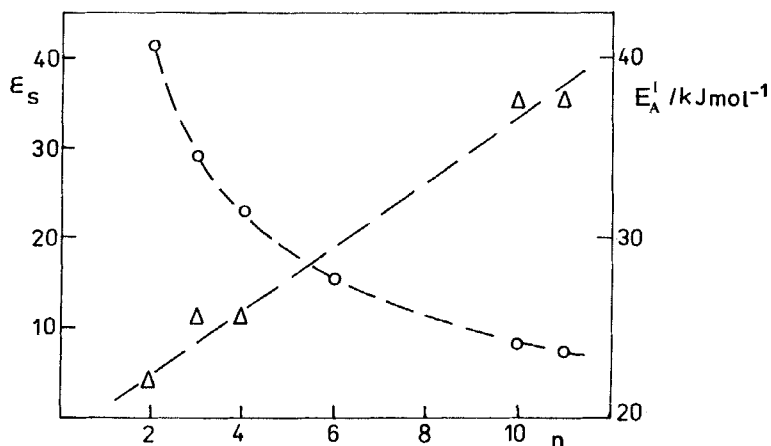


Figure 4. Dependence of the static permittivity, ϵ_s (○), and activation energy, E_A^\ddagger (Δ), on the length of alkyl chain, n , in the n -alkyl-1,2-diols. The value of ϵ_s for $n=6$ was taken from [16].

assumption of two Debye-type relaxation processes characterized by the relaxation times τ_1 and τ_2 , with $\tau_1 \approx 10\tau_2 \approx 0.4$ ns. By analogy to monoalcohols, τ_2 was attributed to the monomer dipolar reorientation, whereas the main relaxation time τ_1 represents a cooperative motion connected with a breaking up of hydrogen bonded complexes. The dielectric increment, $\delta\epsilon(2) = \epsilon_{s2} - \epsilon_{\infty 2}$, of the second relaxation process diminishes with the increase of n . However, in the case of the substances under study ($n=10$ and 11) we observe a marked difference between ϵ_{∞} and the square of the refractive index (≈ 0.6) which suggests that this process could be detected at frequencies above 10 GHz.

The importance of the hydrogen bonding with the increase in molecular length may be seen if the static permittivity, ϵ_s , and the activation energies, E_A^\ddagger , are compared (see figure 4). According to Fröhlich-Kirkwood theory [17] the static permittivity $\epsilon_s \sim N\mu^2 g_K / T$, where N is the number of molecules in the unit volume, μ is the dipole moment of free molecule, and T is the temperature. The correlation factor g_K describes the dipole-dipole interactions. Its deviation from unity is a measure of hindered molecular rotation due to short range intermolecular forces. For alcohols, it is an increasing function of molar mass being greater than unity [18] corresponding to a parallel alignment. Figure 4 shows that ϵ_s , for n -alkyl-1,2-diols, exhibits the same tendency. Simultaneously, a distinct increase of the activation energy is observed (see figure 4). This effect can be attributed to two factors: the increase in the strength of the hydrogen bonds and the increase of the interaction of the hydrocarbon chains [5-7]. In consequence, this leads to the appearance of the liquid crystalline phases for sufficiently long molecules of n -alkyl-1,2-diols.

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