Dielectric characterization of substituted diols

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Dielectric properties of four diols having different chemical structures of the hydrophobic part were determined by the time domain spectroscopy method in the frequency range from *c*. 15 MHz to *c*. 7 GHz. The static permittivity clearly reflects the changes in the position of the dipole moments in the molecules. The dielectric relaxation times characterizing the diol part of the molecules are similar for all the substances studied. In the case where the phenylthiadiazole unit is built into the alkyl chain, two well separated processes were observed: one connected with the 'hydrophobic' and the second with the 'hydrophilic' part of the molecule. This emphasizes the amphotropic character of such molecules.

1. Introduction

Alkandiols form intra- and inter-molecular hydrogen bonds [1–3] which try to be separated from the hydrophobic aliphatic chain. Therefore, such amphiphilic molecules are preferably packed in bilayers in which the molecules are oppositely arranged [4]. Thereby, the aliphatic chains are packed with or without order within the layers. In the second case, smectic A (L_α-like) and in the first case smectic B (L_β-like) structures are formed. X-ray studies [4] show a pronounced double layer structure with higher order reflections. Observations under the polarizing microscope [5] reveal textures like those of normal smectics. At the clearing temperature, these phases transform into the isotropic state. Besides the thermotropic phases, lyotropic behaviour on addition of water is detected [5]. In these cases, the molecules of the solvent are arranged up to a certain content between the diol groups. This is the reason why these samples are characterized as amphotropic liquid crystals.

Previous dielectric measurements in the GHz frequency range on *n*-alkan-1,2-diols at different temperatures have shown [6] that: (a) the relaxation process observed in both the isotropic and smectic phases is complex, characterized by the Cole–Cole distribution parameter $\alpha \sim 0.20$; (b) the transition from the isotropic to the smectic phase is accompanied by an increase in the activation barrier hindering dipolar reorientations; (c) in the isotropic phase, the activation barrier linearly increases with the length of the *n*-alkyl chain; (d) static permittivity ε_s monotonically decreases with

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increasing length of the alkyl chain. This indicates the influence of the hydrophobic part on the dynamics of the hydrophilic OH groups which provide the only permanent dipoles in these samples. In the present study, the dielectric properties of diols having different chemical structures of the hydrophobic part are analysed.
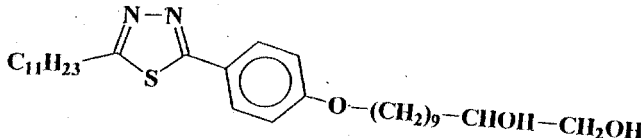
2. Experimental

All substances were synthesized in Halle. The chemical formulae, the transition temperatures (in K) and the abbreviations used are shown in table 1.

n-Pentadecan-1,2-diol (DA) was used to provide a comparison with previous dielectric studies [6]. In order to increase the flexibility of the alkyl chain, diols with an ether group in different positions in the same length of chain were synthesized [7]—DO3 and DO8. In all these cases, the LC phases are metastable and can be observed by cooling (however, the S_B phase of DA can be maintained, with luck, to enable experimental studies). On building in a phenylthiadiazole unit and elongation of the flexible part of the molecule, no thermotropic LC phase was observed (DT). However, DT can be regarded as an intermediate state between amphotropic and thermotropic liquid crystals.

The dielectric properties of the diols could not be investigated at frequencies below 1 MHz due to the high conductivity of the samples. Therefore, the time domain spectroscopy (TDS) method was applied for the frequency range from *c*. 10 MHz to *c*. 3 GHz. Experimental details can be found elsewhere [6, 8, 9]. In the case of the DA, DO3 and DO8 samples, the measurements were made with one time window of 10 ns which allowed

Table 1. Characterization of the substances studied.

Chemical structure	Phase situation	Abbrev.
$C_{13}H_{27}$–CHOH–CH_2OH	Cr 341 (S_B 338) I	DA
$C_3H_7O(CH_2)_9$–CHOH–CH_2OH	Cr 313 S_B 299) I	DO3
$C_8H_{17}O(CH_2)_4$–CHOH–CH_2OH	Cr 309 (S_B 285) I	DO8
	Cr 384 I	DT

analysis of the dielectric spectra in the frequency range *c.* 100 MHz to 3 GHz. For DT two time windows were used (10 and 100 ns) and the spectra were spliced as described in [9], thus giving good quality of the spectra in the range *c.* 15 MHz to 7 GHz.

3. Results and discussion

The spectra for DA were analysed in the same way as in [6], i.e. by using the Cole–Cole equation

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}, \qquad (1)$$

where τ is the relaxation time and α characterizes the distribution of the relaxation times. ε_s and ε_∞ are the static and high frequency permittivities, respectively. Figures 1(*a*) and 1(*b*) show examples of the spectra for the isotropic and S_B phases presented in the form of Cole–Cole plots. The fitting parameters were ε_s, ε_∞, τ and α.

The static permittivities obtained and distribution parameters are presented in Figure 2, while the relaxation times are shown in Figure 3 in the form of Arrhenius plots. It is characteristic that the α parameter is independent of temperature in the S_B phase, whereas it diminishes with rising temperature in the isotropic phase. Good consistency of the activation barrier (42 kJ mol^{-1}) and the static permittivity (4·7) values obtained for this *n*-alkyldiol (DA, *n* = 15) in the isotropic phase with the respective values obtained for materials with shorter molecules ($n \leqslant 11$) [6] should be noted. A marked increase of the static permittivity at the transition to the S_B phase indicates that the layer structure facilitates a parallel ordering of the OH groups see Figure 2(*a*).

The dielectric properties of diols DO3 and DO8 are rather similar. The static permittivities are close together (see figure 2(*a*)), although the slightly higher values of ε_s for DO3 with respect to DO8 seem to indicate that the shorter separation of the R–O–R dipole from the OH dipoles in DO8 reduces the net dipole moment of the molecule. On the other hand, the addition of the O
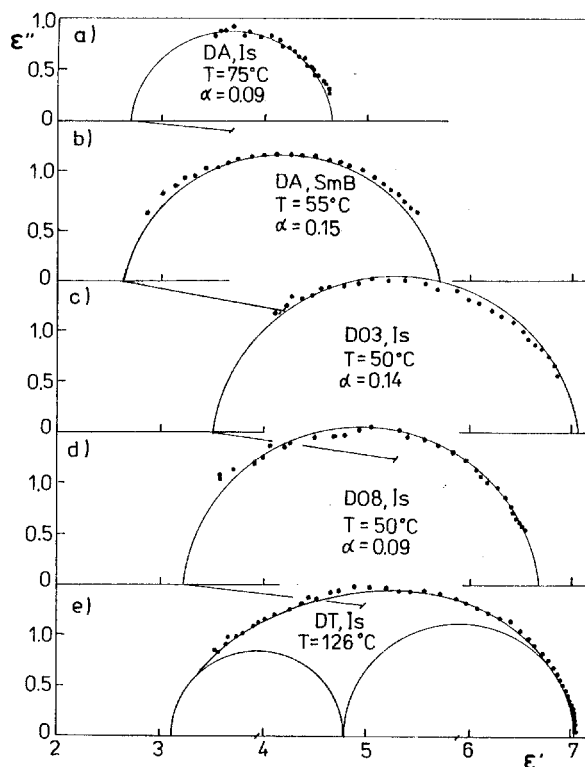

Figure 1. Examples of the TDS spectra for particular diols in the isotropic (DA, DO3, DO8 and DT) and S_B(DA) phases.

atom to the aliphatic chains results in an increase of the dipole moment which is manifested in the increase of the static permittivity in the isotropic phase of these diols in comparison with DA (see figure 2(*a*)). Under the present experimental conditions, the S_B phases could not be obtained for diols DO3 and DO8.

The relaxation spectra of DO3 and DO8 could be described by equation (1) (compare figure 1(*c*) and 1(*d*)) with a considerably increased α parameter if the temperature were decreased (see figure 2(*b*)). The spectra at low temperatures can then also be described by two
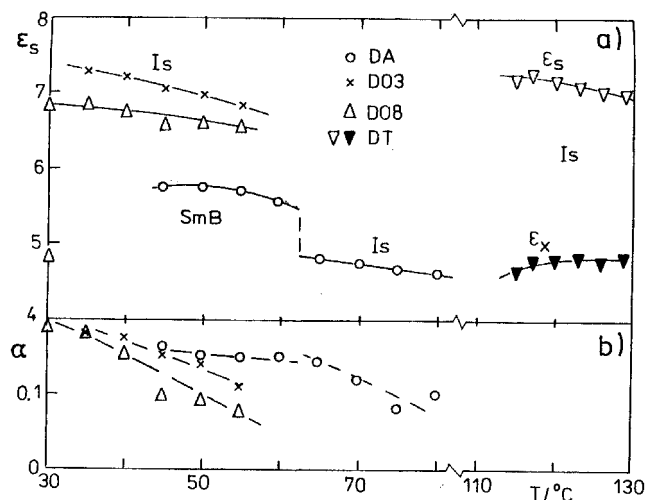
Figure 2. Static permittivity ε_s and the distribution parameter α versus temperature for particular diols. In the case of diol DT, ε_x corresponds to the low frequency permittivity limit of the high frequency relaxation process.

Table 2. Activation enthalpies, for the relaxation processes observed in particular diols.

Substance	Phase	Activation enthalpy /kJ mol^{-1}
DA	Isotropic	42 ± 3
	Smectic B	54 ± 4
DO3	Isotropic	39 ± 3
DO8	Isotropic	35 ± 3
DT	Isotropic I	35 ± 3
	Isotropic II	28 ± 4

relaxation equations dominated by that at lower frequency. This means that the overall molecular reorientations around the main molecular axis (longer times) and the internal rotations of the –OH dipoles (shorter times) become better separated at low temperatures in the isotropic phase of the diols. However, the limited range of frequencies (100 MHz to 3 GHz) does not allow an adequate separation to be given. Therefore we present

in figure 3 the average relaxation times which characterize the overall molecular reorientations around the molecular long axis. From figure 3 one can conclude that in the isotropic phase this motion is dominant in all three diols.

In the case of the diol DT the spectra show stronger deviations from the Debye-type shape than is the case for the other materials (figure 1). The good quality of the spectra enabled us to separate the two main contributions with relaxation times differing by a factor of *c.* 6 (see figures 1 (e) and 3). We tried to fit different combinations of the model functions (Cole–Cole, Debye–Cole, Cole–Debye and Debye–Debye), but consistency in the fitting parameters obtained for all temperatures was achieved only when two Debye processes were assumed. In the case of diol DT, a dipole moment is strongly connected with the five membered ring and therefore one can expect a larger increment for this part than for the other dipole moments. Thus, we attribute the lower frequency relaxation process to the rotation of the stiff (thiadiazole) moiety, and the high frequency process to the diol part of the molecule. This conclusion is supported by the values of the dielectric increments calculated for both processes (compare table 3): $\varepsilon_s - \varepsilon_x \approx 2.4$, whereas $\varepsilon_x - \varepsilon_\infty \approx 1.7$. Additionally, ε_x and τ_2 are very close to the respective values obtained for diol DA in the isotropic phase (see figures 2 (a) and 3). This separation can also be interpreted as separation of the

Table 3. The parameters characterizing the dielectric relaxation spectra of diol DT; two Debye-type processes were assumed.

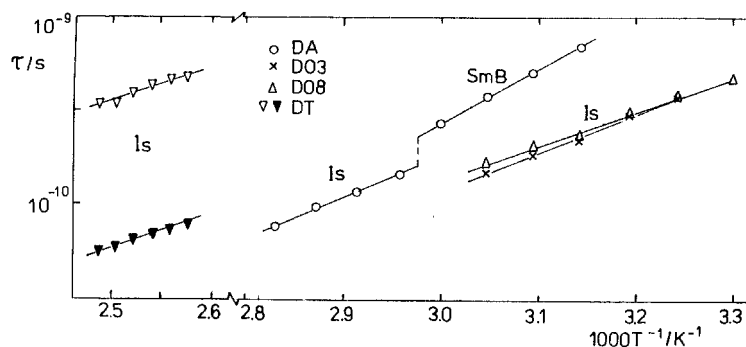| T/K	Permittivities			Relaxation times/ns	
	ε_s	ε_x	ε_∞	τ_1	τ_2
402.2	7.02	4.74	3.07	0.338	0.057
399.6	7.04	4.69	3.08	0.345	0.058
396.8	7.10	4.75	3.09	0.392	0.066
393.9	7.19	4.83	3.16	0.429	0.072
391.0	7.29	4.78	3.14	0.457	0.074
388.3	7.21	4.68	3.13	0.478	0.076

Figure 3. Arrhenius plots for all relaxation processes observed in the diols studied.

'hydrophobic' and 'hydrophilic' units of DA from each other and emphasizes the amphotropic character of such molecules.

4.   Conclusions

In conclusion, one should note the following dynamical properties of the substances under study. In the case of *n*-alkyl diols the overall molecular rotations around the preferred long axis determine the dielectric relaxation processes in both the isotropic and the LC phase. This results from the fact that the activation barrier linearly increases with the length of the molecules. Also the increase of the barrier on approaching the I–S$_B$ transition (from 42 to 54 kJ mol^{-1}, see table 2) seems to support this conclusion. If the oxygen atom is incorporated in the alkyl chain in different positions (diols DO3 and DO8), the molecular dynamics are not changed markedly. The relaxation times and activation barriers in the isotropic phases of these diols and of diol DA are similar (table 2, figure 3). However, the increase in the static permittivity ε_s in relation to diol DA reflects the changes in the dipole moment values (figure 2(*a*)). All these substances can form both thermotropic (but metastable)

and lyotropic LC phases. The addition of a structural element known from thermotropic LCs (the phenylthiadiazole unit) results in no thermotropic LC phase and causes the reorientation of 'hydrophobic' and 'hydrophilic' moieties to become decoupled. This emphasizes the amphotropic character of such molecules.

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