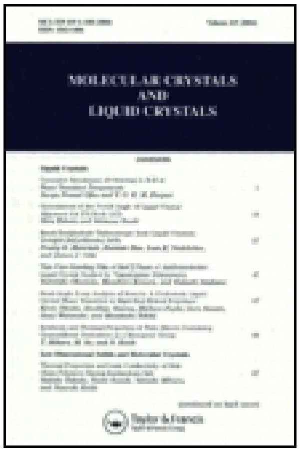

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Dynamics of Molecules in Two Highly Ordered Smectic Phases of Didodecyldimethylammonium Bromide Studied by Dielectric Spectroscopy

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In this work the dielectric results obtained by time domain spectroscopy for two highly ordered smectic phases of didodecyldimethyl-ammonium bromide are presented. High temperature SmB phase exhibits freedom of molecular reorientation around the long molecular axis with the relaxation time of the order of 100 ps. Upon the transition to the lower temperature biaxial smectic phase the reorientation around the long axis becomes restricted. Dielectric spectra of the system studied are complex with the Cole–Cole distribution parameter of 0.4, which indicates merging of a few molecular processes originating from intra- and intermolecular stochastic motions.

Keywords: Didodecyldimethylammonium bromide; time domain dielectric spectroscopy; ionic liquid crystals; highly ordered smectic phases

INTRODUCTION

In recent years considerable attention is devoted to the studies of the properties of quaternary ammonium salts containing two long alkyl chains, in particular dialkyldimethylammonium bromides [1–6]. These compounds are synthetic amphiphiles which serve as model systems for biomembranes and which are also known for their applications as commercial detergents.

Dialkyldimethylammonium bromides are very interesting from the point of view of their liquid crystalline behavior because they exhibit smectic-like character in the melt in addition to their well-known lyotropic properties. Phase situation of didodecyldimethylammonium bromide (DDAB) was studied in details in [7] by means of differential scanning calorimetry, X-ray diffraction and optical microscopy methods. A complex and interesting polymorphism was detected. Apart from the crystalline phase, on heating there are two phases below the isotropic liquid and on a cooling a third phase appears. The study showed that DDAB exhibited highly ordered liquid crystalline structures. The aim of the present work was to study the dynamics of molecules of DDAB using dielectric relaxation method.

EXPERIMENTAL

Time domain spectroscopy (TDS) allows one to study dielectric spectra in time domain. A Fourier transformation of the time domain spectrum leads to frequency domain dispersion and absorption curves. The dielectric spectra of DDAB have been measured on cooling in the frequency range from 10^7 to 10^{10} Hz at the Physics Department of Uppsala University by using a TDS reflectometer with Iwatsu digital scope. Time domain spectra have been measured using two time windows: 10 ns and 50 ns. Finally the spectra were spliced to obtain a better evidence of the dielectric spectrum in the low frequency range. Before taking the dielectric spectra the cell was calibrated using *n*-hexane and chloroform as standard liquids. The sample was put into a coaxial cell at the temperature of about 100°C. At this temperature the sample was in the high-temperature smectic phase which was soft and due to this property good packing of the cell was possible.

The sample was purchased from Aldrich (purity 98%) and purified by recrystalization from ethyl acetate/heptane mixtures.

RESULTS AND DISCUSSION

Polymorphism of DDAB was studied in detail in [7]. Apart from the crystalline phase, on heating there are two liquid crystalline phases and on cooling an additional phase appears between about 70°C and 60°C. The high-temperature phase appearing below the isotropic phase can be identified as SmB phase. At about 60° the texture changes from a mono-colored lancet-like one into another texture with color spots indicating that the new phase is a biaxial highly ordered phase.

DDAB is an ionic material which shows high electrical conductivity at radio frequencies. So it was not possible to measure its static dielectric permittivity (ε_0) using classical methods such as bridges and impedance analyzers. The conductivity measured for DDAB at 54°C is equal to $3.51 \cdot 10^{-1}$ S which gives a large contribution to dielectric loss at low frequenices. TDS spectroscopy is the only method which allows to measure temperature dependence of ε_0 for such materials.

Figure 1 presents the ε_0 static dielectric permittivity acquired on cooling for DDAB. As one can see there is a transition starting at about 70°C below which the static dielectric permittivity strongly decreases with temperature. It reaches a value of 2.547 at 25°C which is a typical value for solid dielectrics with frozen out reorientational movements. The values of ε_0 have been obtained from fitting the Cole–Cole equation [8] to the experimental dielectric spectra:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \tag{1}$$

where $\varepsilon^* = \varepsilon' - i\varepsilon''$ is the complex dielectric permittivity where in turn ε' is the dielectric permittivity (dispersion) and ε'' is the dielectric absorption (or dielectric loss), ε_0 is the static dielectric permittivity, ε_∞ is the high frequency limit of dielectric permittivity connected with the atomic and electronic polarization, τ is the dielectric relaxation time, α denotes the relaxation times distribution parameter and ω stands for circular frequency. The difference

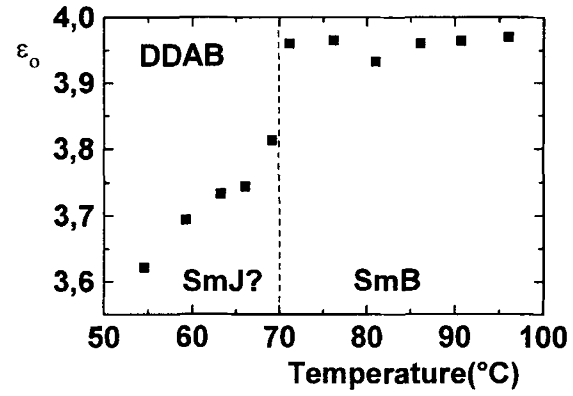

FIGURE 1 Static dielectric permittivity of DDAB vs. temperature obtained by fitting eq. (1) to the experimental points (cf. Fig. 2).

$(\varepsilon_0 - \varepsilon_\infty)$ is the dielectric increment originating from dipolar reorientation due to stochastic motiòn of molecules. Figure 2 shows an exemplary dielectric spectrum fitted to the experimental points obtained by TDS method.

The data presented in Figure 1 show evidently that there is a restriction of molecular reorientation around the long axis in the highly ordered smectic phase below about 70°C. The distribution parameter is about 0.4 for all temperatures which seems to be connected with contributions to the dielectric increment resulting from different inter- and intramolecular reorientations. Figure 3 shows that the average dielectric relaxation time changes only slightly at the transition. The activation energy computed for the high temperature phase is equal to 41.2 kJ/mol and upon the transition to the low temperature phase it increases only to 43.3 kJ/mol. It means that the reorientation around the long axis is not frozen out at the transition. On the other hand the dielectric increment is strongly reduced below the

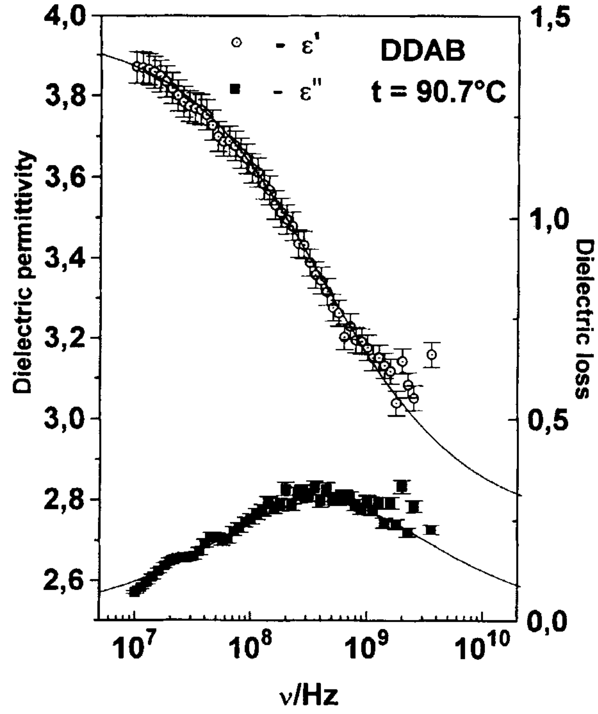

FIGURE 2 Dielectric spectrum obtained for the SmB phase of DDAB by TDS method. Solid lines are the least-square fits of eq. (1) to the experimental points.

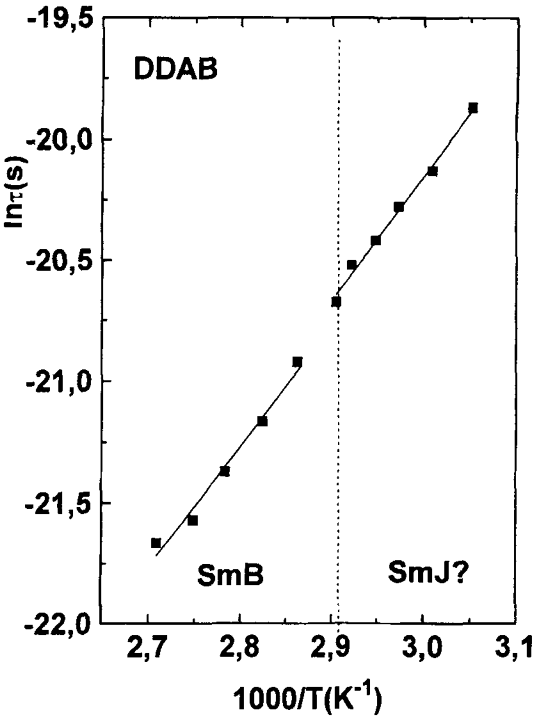

FIGURE 3 Arrhenius plots obtained for both liquid crystalline phases of DDAB.

transition (Fig. 1) which indicates that the reorientation around the long axis is limited.

Table I gives all the dielectric parameters obtained at different temperatures. As it is seen in Figure 1 and from Table I the static dielectric permittivity decreases with decreasing temperature which means that there is some negative dipole–dipole correlation leading to antiparallel ordering of dipole moments. This effect is clearly seen in the low temperature biaxial phase. To describe this effect qualitatively one can use a modified Kirkwood-Froelich model [8, 9]:

$$\varepsilon_0 - \varepsilon_\infty \sim \frac{g(T)\cdot\mu^2}{k_B T}(1 - \Gamma(T)^2) \tag{2}$$

where μ is permanent molecular dipole moment,
k_B is Boltzmann's constant,

TABLE I Dielectric parameters obtained for liquid crystalline phases of DDAB by fitting eq. (1) to the dielectric spectra

$T/^{\circ}C$	ε_0	ε_∞	$\tau \cdot 10^{10}$ s	α
96.0	3.9807	2.7923	3.8638	0.42
90.7	3.9468	2.8060	4.5687	0.39
86.1	3.9963	2.7246	5.0565	0.45
81.0	4.0030	2.6986	5.9484	0.48
76.2	3.9788	2.8288	9.4387	0.37
71.1	3.9614	2.7189	10.1030	0.41
69.1	3.8286	2.7013	11.8560	0.41
66.0	3.7342	2.7386	14.7551	0.39
63.2	3.7847	2.6609	17.8494	0.48
59.2	3.7023	2.6849	19.3878	0.42
54.5	3.5659	2.7273	23.0080	0.36

$g(T)$ is temperature dependent Kirkwood factor,
$\Gamma(T)$ is the Froelich order parameter

$$\Gamma = 1 - 2\frac{\exp(-V(T)/k_B T)}{1 + \exp\,(-V(T)/k_B T)}$$

where $V(T)$ is a potential barrier hindering reorientational motion of molecules. $\Gamma = 1$ corresponds to a very high energy barrier [10] and at such circumstances $\varepsilon_0 = \varepsilon_\infty$ which means that the dielectric increment is zero. It means that the reorientational motions of molecules are frozen out.

CONCLUSIONS

Time domain dielectric spectroscopy was used to study highly ordered smectic phases of DDAB. Complex dielectric spectra were obtained with the distribution parameter equal to about 0.4. The smectic B phase exhibits fast reorientational motions around the long axis with the average relaxation time of the order of 10^{-10} s. This reorientation becomes distinctly restricted in the low temperature biaxial phase. At room temperature it is frozen out.

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