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Dielectric relaxation of water molecules in different lyotropic structures of nonylphenoxypoly(ethylenoxy)ethanol (Ark. 9)

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Dielectric relaxation of water molecules in the lamellar, L_α, cubic and hexagonal, H_α, lyotropic structures of nonylphenoxy-poly(ethylenoxy)ethanol (Ark. 9) has been studied by dielectric time domain spectroscopy in the frequency range between 10 MHz and 10 GHz. The values of the relaxation times, obtained at room temperature, are the following: 41 ps for the L_α phase, 29 ps for the cubic phase and 22 ps for the H_α phase. As is seen, the relaxation time of bound water is distinctly higher than that of pure water, and it depends strongly on the phase structure. The relaxation times measured for the liquid-crystalline phases as well as for pure Ark. 9 obey the Arrhenius law, and the energy barriers obtained have the following values: (20 ± 2) kJ/mol for all the liquid-crystalline phases, and (30 ± 3) kJ/mol for pure Ark. 9. The former is in good agreement with the value found for bound water in lipid systems whereas the latter is characteristic of the isotropic phase of thermotropic liquid crystals.

1. Introduction

Thermotropic polar liquid crystals composed of rod-like molecules differ from normal liquids in the fact that they exhibit a very remarkable dielectric spectrum coming from highly anisotropic molecular motions. Usually, the reorientation around the short molecular axis gives a low frequency Debye-type absorption falling within the megahertz (or even kilohertz) range depending upon the molecular as well as the phase structure. On the other hand the reorientation around the long molecular axis is the origin of the dielectric dispersion showing up in the microwave frequency range [1, 2]. In addition the high frequency dispersion is of a Cole–Cole type, i.e. there is a distribution of the relaxation times, especially for molecules with long side chains, caused by some intramolecular motions. In some cases two pure Debye-type dielectric dispersions are observed, and they are connected with reorientations around the principal axes of the molecules. From the molecular dynamics standpoint the dielectric spectra in many cases give practically microscopic relaxation times.

For lyotropic liquid crystals the molecular dynamics become much more complex because usually they are at least two component systems. So, their dielectric spectra are influenced by many molecular and collective processes, for example,

1. (1) the reorientation of bound water molecules which gives a large contribution to the dielectric increment;
2. (2) the reorientation of surfactant molecules around their long and short axes as well as some intramolecular motions;

(3) the Maxwell–Wagner relaxation which is due to the anisotropy of the electric permittivity and conductivity; and
(4) the conductivity effect which smears out the last process and also disturbs the low frequency part of the spectrum.

In consequence it is difficult to study dielectric spectra especially for ionic lyotropic systems. That is why there are so few papers [3–5, 14] devoted to dielectric properties of lyotropic liquid crystals. Recently non-ionic surfactants have become of great interest. In this paper the dielectric spectra obtained for Ark. 9 by time domain spectroscopy (T.D.S.) will be discussed in terms of molecular motions.

2. Experimental

The sample of nonylphenoxypoly(ethylenoxy)ethanol (in short: Ark. 9) was supplied by the GAF Corporation. Dielectric measurements were performed on pure Ark. 9 and its aqueous mixtures without further purification of the surfactant. Ark. 9 is a non-ionic soap of the form

$$CH_3(CH_2)_8\text{-}C_6H_4\text{-}(OCH_2CH_2)_n\text{-}OH$$

with $n = 9$. Depending upon the water concentration, at room temperature Ark. 9 exhibits the following liquid-crystalline phases: (1) the lamellar phase (L_α, for wt % of water less than 39), (2) the cubic phase (for water concentrations between 39 and 52), and (3) the hexagonal phase (H_α, for water concentrations higher than 52 [5].

The aim of this study was to investigate the dielectric relaxation spectra for the lyotropic structures and also for pure Ark. 9. To this end the following samples were prepared:

(1) 35 wt % of water in Ark. 9, which corresponds to the lamellar phase. D.S.C. and polarizing microscope investigations [7] revealed that the L_α phase transforms into an isotropic solution at about 322 K. The transition enthalpy was found to be 9·13 kJ/mol for the surfactant itself. The lamellar phase exhibits a texture of oily streaks [12];
(2) 46 wt % of water in Ark. 9, which possesses a highly viscous cubic phase, stable until 359 K;
(3) 55 wt % of water in Ark. 9, which corresponds to the H_α phase showing up between 300 and 370 K. Below 300 K there is a transparent solid phase with a non-geometric texture [12]. As we shall show later, the transition taking place at 300 K does not affect the dielectric relaxation of the water molecules.

In addition the measurements were performed for an isotropic solution and for pure Ark. 9.

Dielectric measurements were made using the T.D.S. method, which consists of the study of the dielectric response of the material to a fast rising step voltage [8–11]. The pulse passing through a sample, as well as the reference pulse, are monitored by the sampling oscilloscope, controlled by a minicomputer which is also used for data processing. Generally the total complex dielectric permittivity is calculated,

$$\begin{aligned}\varepsilon_t^* &= \varepsilon^* - i\sigma/\omega\varepsilon_0 \\ &= \varepsilon' - i\varepsilon'' - i\sigma/\omega\varepsilon_0, \qquad (1)\end{aligned}$$

where ε' is the dielectric permittivity, ε'' is the dielectric loss, σ is the ionic conductivity and ε_0 is the dielectric permittivity of free space.

The design of the measurement cell allows cleaning and replacement of the sample without dismantling the coaxial line. In such a way very small changes in the dielectric parameters with temperature as well as with the sample composition could be detected. In all measurements a time window of 20 ns was used. The complex dielectric permittivity was calculated at 40 frequencies between 10 MHz and 10 GHz, evenly spaced on the logarithmic scale. The temperature was stabilized by a temperature controller with an accuracy of about 0·2 K.

3. Results and discussion

3.1. *Dielectric spectra of pure Ark. 9*

The complex dielectric permittivity versus frequency has been calculated for pure Ark. 9 at 293, 308 and 323 K. The dielectric relaxation spectra obtained are presented in figure 1. By fitting the Cole–Cole formula

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}}, \tag{2}$$

to the dielectric spectra the following parameters have been obtained: ε_0, the static dielectric permittivity; ε_∞, the high frequency limit of the dielectric permittivity; τ_0, the average dielectric relaxation time; and α, the parameter describing the distribution of the relaxation times. The values of these parameters are listed in the table. As we can

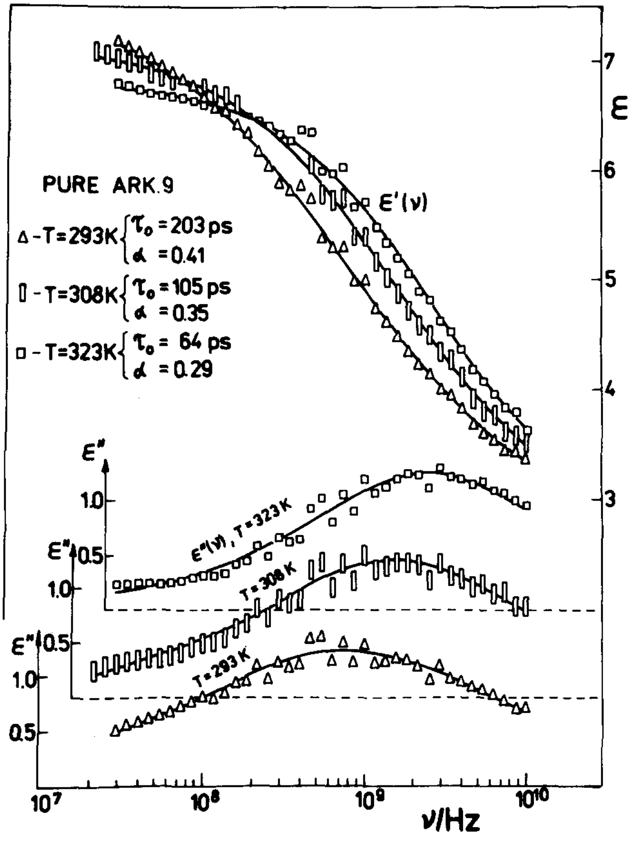

Figure 1. Dielectric spectra of Ark. 9 obtained at different temperatures.

Dielectric parameters obtained for pure Ark. 9 and its different lyotropic phases as well as for pure water [11, 13].

Xwt %	T/K	τ_0/ps	α	ε_0	ε_∞	$10^2 \cdot \sigma$/S m^{-1}	ΔE/kJ mol^{-1}
100 per cent Ark. 9	293	203 ± 20	0·42	7·61	2·66	-	30 ± 4
	308	105	0·35	7·19	2·74	-	
	323	64	0·29	6·85	2·81	-	
35 per cent L_α	278	68	0·30	31·0	3·7	21·7	20 ± 2
	293	41	0·25	27·2	3·7	28·1	
	318	22	0·26	24·8	3·7	48·3	
46 per cent Cubic	278	47	0·24	37·6	4·1	29·2	20 ± 2
	293	29	0·23	35·9	4·1	42·0	
	318	15	0·25	33·3	4·1	83·2	
55 per cent H_α	278	33	0·19	43·1	4·4	39·9	20 ± 2
	293	22	0·20	40·0	4·4	55·1	
	318	10·9	0·23	38·3	4·4	114·3	
65 per cent	293	11·9	0·0	67·6	5·6	99·6	
100 per cent H_2O	296	8·8 [11]	0·0	78·2 [13]	5·5 [13]	-	
	303	7·22 [13]					19 [13]

see, pure Ark. 9 exhibits a non-Debye-type relaxation with a pronounced distribution of relaxation times ($\alpha = 0{\cdot}3$–$0{\cdot}4$) and with an average value of the dielectric increment ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty = 4$–$5$). The energy barrier, calculated on the basis of the Arrhenius equation, is about 30 kJ/mol. All these values are characteristic of isotropic phases of polar thermotropic liquid crystals [1, 2]. The pronounced distribution of the relaxation times results from the superposition of the two principal intermolecular motions and also from some intramolecular processes inside the ethylenoxy chain. According to the Budo theory [13] the dielectric spectrum of the isotropic phase of Ark. 9 could be represented by

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_a}{1 + i\omega\tau_a} + \frac{\Delta\varepsilon_b}{1 + i\omega\tau_b} + \frac{\Delta\varepsilon_{\mathrm{intra}}}{1 + i\omega\tau_{\mathrm{intra}}}, \tag{3}$$

where subscripts a and b refer to the principal molecular reorientations around its short and long axes, respectively.

On the other hand the dielectric spectrum of pure water is of a Debye-type [11, 13] with the relaxation time more than one order of magnitude shorter than that of pure Ark. 9. It is worth noting that the dielectric increment of pure water is of about 73 at room temperature [13], which is more than one order of magnitude larger than for pure Ark. 9. This will have a considerable impact on the dielectric spectra of the lyotropic structures discussed in the following sub-sections.

3.2. *Dielectric spectra of the lyotropic phases*

Dispersion and absorption curves obtained at different temperatures for the L_α and cubic phases are shown in figures 2 and 3, respectively. The dielectric spectra of the H_α phase look very similar except that they are shifted towards the higher frequency range. In all the lyotropic phases the Cole–Cole formula (see equation (2)) describes the dielectric spectra very well; the dielectric parameters obtained are given

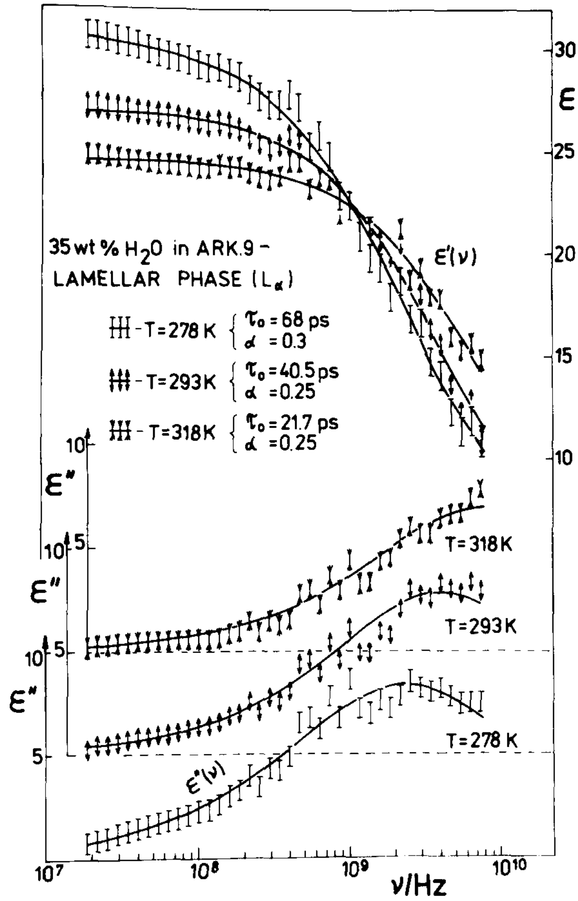

Figure 2. Temperature dependence of the dielectric spectrum measured for the lamellar phase.

in the table. As we can see, the dielectric increments of the lyotropic phases are high and increase with the water content; this dependence is almost linear for the compositions studied. It was found that the dielectric increment extrapolated to 100 per cent water concentration is approximately 10 per cent smaller than the value found for pure water [13]. It might mean that the hydration process which takes place causes partial reduction of dipolar polarization. This may be due to the interaction between the bound water and the micelles. On the other hand ε_∞ is additive for all concentrations.

As we can see (figures 1, 2 and 3 and also the table) the α parameter decreases with the water content at a given temperature. This may mean that for higher water concentrations the influence of free water is of greater importance. However, the experimental data cannot be fitted to two separate relaxation functions, one coming from the bound water and the other from the free water. This is quite unexpected in view of the results for the lysozyme–water systems [14] where two separate absorption regions were found for the two kinds of water. For the Ark. 9/ water systems only a distribution of the relaxation times originating from the interaction between the polar ethylenoxy chain and the bound water is obtained. In addition there may be an exchange between the bound and free water. Yet

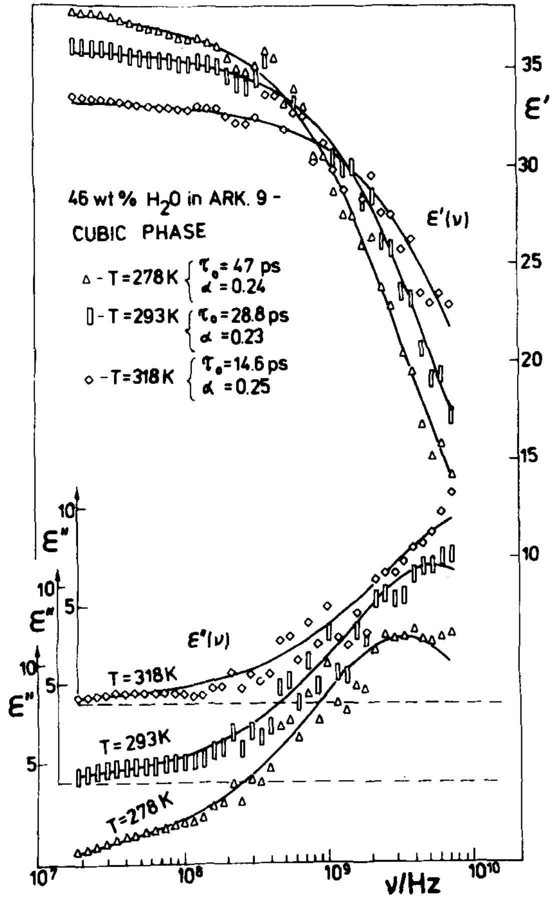

Figure 3. Dielectric spectra measured at different temperatures for the cubic phase.

we cannot exclude two dispersion regions at a lower water content in the L_α phase region.

It is interesting that the activation energy obtained from the Arrhenius plot (see figure 4) is, for all lyotropic structures, slightly higher than the value found for pure water [13] at high temperatures. This may mean that dielectric relaxation in the Ark. 9/water systems consists mainly in the rupture of one hydrogen bond. This also corroborates the idea that the free water dominates over-whelmingly the dielectric spectra of the lyotropic system studied. It is worth noting that the point obtained for the third composition at 278 K does not deviate from the Arrhenius plot for the H_α phase. It means that the dynamics of water molecules in the solid phase (below the transition at 300 K), which is most probably a gel phase, must be similar to that of the H_α phase above the transition.

We should add that Ark. 9 was a very pure substance from the dielectric measurements standpoint. Its conductivity was less than 10^{-2} S/m which seems to be unique for non-ionic materials. On the other hand the lyotropic systems exhibit rather high conductivities (see the table) most probably connected with the H^+ (or OH^-) ions which are formed by a hydrolysis process. Activation energies obtained from the temperature dependence of the conductivity, σ, are 14·8, 19·4 and 19·6 kJ/mol for the L_α, cubic and H_α phases, respectively.

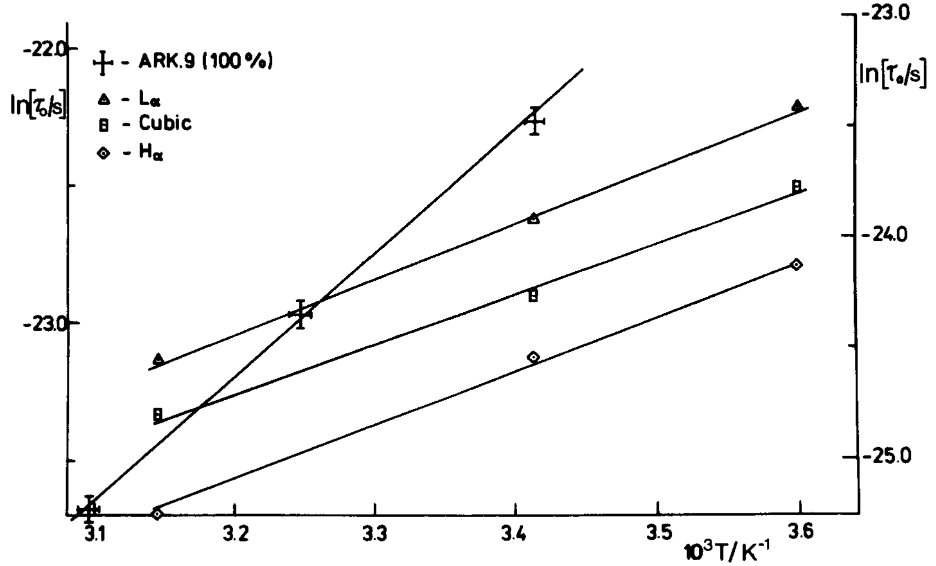

Figure 4. Arrhenius plots for the L_α, cubic and H_α phases (the right-hand side scale) as well as for pure Ark. 9 (the left-hand side scale).

As is known, there are some other dielectrically active low frequency relaxation processes observed in lyotropic systems [3–5, 14]. For instance, reorientation of surfactant molecules about the short axes should give a dispersion region in the megahertz range for all liquid-crystalline phases, but for the systems studied it is smeared out by the conductivity effect.

4. Conclusions

(A) The dielectric relaxation spectrum of pure Ark. 9 is of a Cole–Cole type with a pronounced distribution of the relaxation times and a dielectric increment of about 5. The most probable relaxation time is connected with reorientation of the Ark. 9 molecule around its long axis.

(B) Dielectric relaxation in the L_α, cubic and H_α phases as well as in the isotropic solution is dominated by the water molecules.

(C) Retardation of the molecular motion of bound water in all lyotropic structures is caused by a strong interaction (hydrogen bonds) between the water molecules and the polar tail of the Ark. 9 molecule.

(D) The energy barriers obtained for each lyotropic structure are about the same and almost equal to that of pure water.

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