An isotopic effect in the dielectric spectra of Ark. 9/water systems

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An isotopic effect in the dielectric spectra of Ark. 9/water systems

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Dielectric spectra of H_2O and D_2O molecules in the L_α liquid crystalline phase of nonylphenoxy-poly(ethylenoxy)ethanol(Ark. 9)/water lyotropic systems have been investigated by dielectric time domain spectroscopy in the frequency range from 10 MHz to 10 GHz. By fitting the Cole–Cole formula to the dielectric spectra, obtained at different temperatures the dielectric increments, the relaxation times and the distribution parameters have been calculated. A strong retardation of water molecules has been found for the lamellar phase with low water content, i.e. 10 water molecules (H_2O or D_2O) per one Ark. 9 molecule. The relaxation times obtained at room temperature for the light and heavy water are 63 and 93 ps, respectively. It means that the retardation factor for D_2O molecules in the L_α phase is close to 1·5 and higher than that found for pure heavy water (1·25). Any decomposition of the dielectric spectra obtained seems to be unsubstantiated. The temperature dependences of the relaxation times acquired for both kinds of water obey the Arrhenius behaviour.

1. Introduction

Dielectric spectra of polar liquid crystals are very important to study as they bear some information about molecular motion. The dielectric spectra are usually measured in frequency domain but recently time domain spectroscopy (TDS) [1] is becoming very useful, particularly in aqueous solutions. In the case of aqueous lyotropic systems the dielectric spectra, observed in GHz frequency range, are dominated by the water molecules which give rise to the Cole–Cole type spectrum [2] showing a distribution of the relaxation times. This distribution comes from the hydrogen bond interaction between the water layers and the aggregates of surfactant molecules.

The reorientation of surfactant molecules around their long axes can also contribute to the low frequency region of the dielectric spectrum. However, one cannot isolate this effect from the complex spectrum since the dielectric increment coming from the Ark. 9 molecules is one order of magnitude lower than the one connected with the water molecules [2].

Another characteristic feature of the dielectric spectra of lyotropic systems is that there is a pronounced retardation of the water relaxation as seen in an increase of the mean relaxation time. In addition, the retardation is concentration dependent and also seems to be structure dependent.

In this study the dielectric spectra of the L_α phase of Ark. 9/water systems will be presented for both normal and heavy water. In the latter case the retardation turns out to be distinctly stronger. The results shed more light upon the interactions between the surfactant and water molecules.

2. Experimental

Nonylphenoxy-poly(ethylenoxy)ethanol is a well known non-ionic soap of the form

$$CH_3(CH_2)_8\text{-}\langle\bigcirc\rangle\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_{n-1}\text{-}CH_2\text{-}CH_2\text{-}OH$$
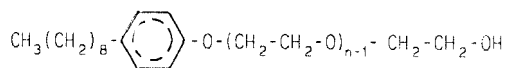
The commercial name of this compound is Arkopal$_n$ or shorter Ark. n. In this study Ark. 9 has been investigated. When dissolved in water it exhibits at room temperature three liquid crystalline phases: (1) the lamallar phase (L_α) for $\gamma < 0.39$ where γ denotes concentration of H_2O molecules in wt %. (2) the cubic phase $(0.39 < \gamma < 0.52)$ and (3) the hexagonal phase $(H_\alpha, 0.52 < \gamma < 0.57)$ [3].

In our previous paper [2] the results of dielectric studies of all three phases have been reported. It was shown that the dielectric relaxation process originating from the motion of water molecules is retarded for all liquid crystalline phases by a factor between 1·35 and 1·65 as compared with pure water. However, it was impossible to resolve separate relaxation regions coming from different kinds of water, for instance, from the free and bound water and from Ark. 9 molecules as well. So, in this study the low water content systems have been investigated for both normal and heavy water as to find better resolution circumstances. The composition studied were the following: (1) $\gamma_1 = 22.64$ wt % which corresponds to $c.$ 10 H_2O molecules per one Ark. 9 molecule and (2) $\gamma_2 = 25.02$ wt %, i.e. $c.$ 10 D_2O molecules per one Ark. 9 molecule.

The Ark. 9 substance was bought from the GAF corporation and used without further purification. The normal water used was triple distilled and deionized. The purity of heavy water was of 99·84 percent. The samples were prepared in glass tubes properly sealed. In order to obtain good homogeneity they were centrifuged and heated up to $c.$ 40°C. However, one needs more time to get completely homogeneous sample for the D_2O/Ark . 9 system. In both cases the L_α phase was obtained with characteristic texture of oily streaks.

3. Results and discussion

3.1. *Experimental results*

Measurements of the complex electric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, have been done in the frequency range between 10 MHz and 10 GHz. Figures 1 and 2 present the dielectric spectra of the H_2O/Ark. 9 and D_2O/Ark. 9 systems, respectively. The experimental points are evenly spaced on the logarithmic scale. For both systems the dielectric spectrum is dominated by the water molecules relaxation and shifted towards lower frequencies as compared with a spectrum of pure water with the dispersion centred around 15 GHz.

The high values of the static electric permittivity suggest that the main contribution to the dielectric increment is due to the water molecules which preserve the hydrogen bonded quasi-structure inside the water layers. This leads to an enhanced value of the Fröhlich–Kirkwood g-factor characteristic for parallel correlations of dipole moments of the water molecules. This effect is well known for pure water [4].
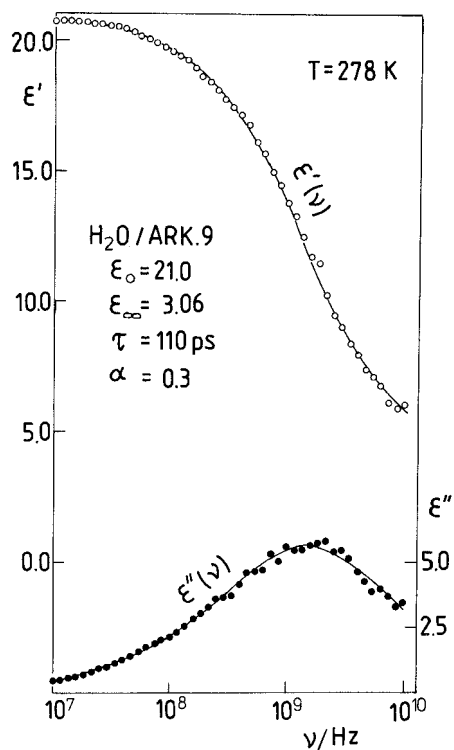
Figure 1. Dielectric spectrum of the H_2O/Ark. 9 system in the L_α phase.
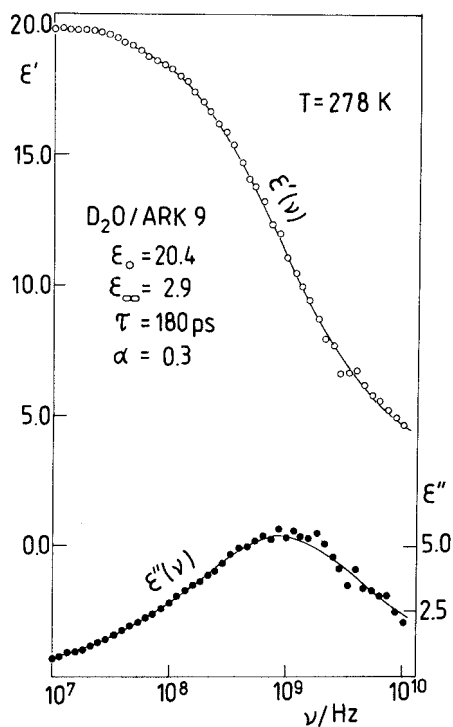
Figure 2. Dielectric spectrum of the D_2O/Ark. 9 system in the L_α phase.

One should notice that in the case of H$_2$O/Ark. 9 system (figure 1) the static electric permittivity is higher than for D$_2$O/Ark. 9 (figure 2) which is due to the greater density of water molecues in the former case.

3.2. *Dielectric spectra of water/Ark. 9 systems*

The high frequency dielectric spectrum of water/Ark. 9 systems is dominated by the water molecules and can be described by the Cole–Cole formula

$$\varepsilon^* = \varepsilon_{\infty k} + \frac{\varepsilon_{0k} - \varepsilon_{\infty k}}{1 + (i\omega\tau_k)^{1-\alpha_k}} \tag{1}$$

where ε_{ok} is the static electric permittivity ($k = $ H for H$_2$O and $k = $ D for D$_2$O/Ark. 9 system). $\varepsilon_{\theta k}$ is the high frequency limit of the electric permittivity, and τ_k is the mean relaxation time.

The solid lines in figures 1 and 2 are the theoretical fits of equation (1) to the experimental data. The data do not warrant an analysis in the form of two or three separated dispersion regions instead of fitting one Cole–Cole function. This may mean that in the system studied one has to do only with bound water exhibiting a distribution of the dielectric relaxation times.

Table 1 contains all dielectric parameters computed for both water system studied. From the data presented in table 1 and in figures 1 and 2 the following conclusions may be drawn:

(1) The static electric permittivity (ε_{0k}) is high and increasing with decreasing temperature for both normal and heavy water system. It means that in the L_α phase the structure of water layers is a water like hydrogen bonded structure with some interface defects. This is consistent with the results obtained previously for the liquid crystalline structures containing only normal water [2].

(2) These defects seem to be the main reason for the pronounced distribution of the dielectric relaxation times ($\alpha_H \approx \alpha_D \approx 0\cdot3$, see table 1).

(3) Both relaxation times (τ_H and τ_D) are distinctly longer than the corresponding values for both kinds of pure water [5]. In addition, there is a pronounced retardation of heavy water molecules in comparison with normal water in the L_α phase (table 1). The effect can be expressed by means of the retardation factor defined in the following way:

$$g_{L_\alpha} = \frac{\tau_D}{\tau_H}. \tag{2}$$

This factor is a good measure of the isotopic effect influencing the dielectric spectra of the water/Ark. 9 systems.

(4) Temperature dependences of the dielectric relaxation times follow the Arrhenius behaviour (figure 3) with energy barriers of about 25 and 27 kJ/mole, respectively. In the case of deuterium isotope the interactions are somewhat stronger than found for pure water [5]. However, for the D$_2$O/Ark. 9 system three experimental points were taken into account only because the last one, taken at $\pm5°$C, seems to belong to a gel phase (figure 3).

In the end it would be worth noting that for rotational phases of the solid hydrogen halides (HBr and HJ) the dielectric relaxation times are longer for the

Table 1. Dielectric parameters versus temperature obtained for the L_α phase of H_2O and D_2O/Ark. 9 system.

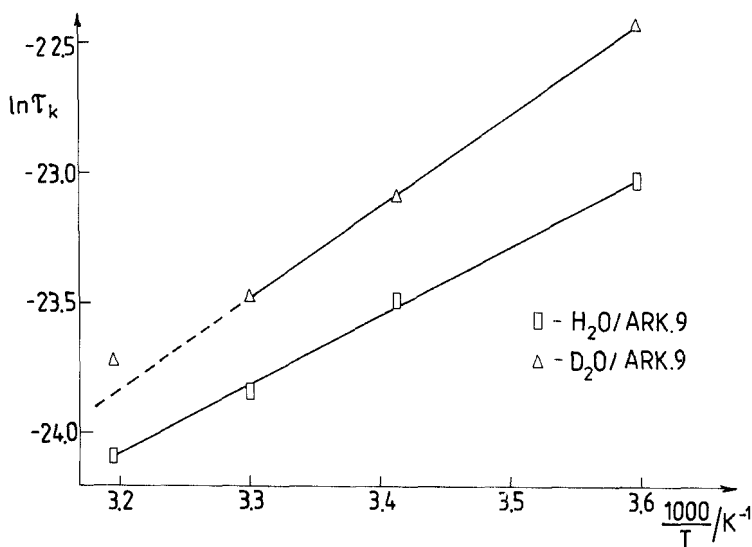| $t/^\circ C$	Normal water (H_2O)				Heavy water (D_2O)				
	ε_{0H}	$\varepsilon_{\infty H}$	τ_H/ps	α_H	ε_{0D}	$\varepsilon_{\infty D}$	τ_D/ps	α_D	g_{L_α}
5	21·0	3·1	110	0·29	20·1	2·91	180	0·28	1·64
20	19·1	2·9	62	0·33	20·0	2·87	93	0·28	1·49
30	18·72	3·1	44	0·32	19·5	2·93	64	0·27	1·45
40	19·6	3·4	34	0·29	19·4	3·36	50	0·24	1·45
	$\Delta E_H = 25\,kJ/mole$				$\Delta E_D = 27\,kJ/mole$				

Figure 3.   Arrhenius plots for the H_2O and D_2O/Ark. 9 water systems.

deuterium isotope by factors 1·3 to 4·0 [6]. As was mentioned for pure heavy water the retardation factor varies from 1·2 to 1·3 [5]. In the case of the L_α phase of Ark. 9 the value is around 1·5 (table 1). This supports the idea that the relaxation times as well as the retardation factors are also structure dependent. Table 2 contains the retardation factors for deuterated pure heavy water [5] and for deuterated water bound in the L_α phase obtained in this study.

Table 2.   Retardation factors for deuterated pure water [5] and deuterated water bound in the L_α phase of Ark. 9.

$t/°C$	5	10	20	30	40
g_0	–	1·30	1·27	1·24	1·21
g_{L_α}	1·64	–	1·49	1·45	1·45

4.   Conclusions

(1) The dielectric spectra obtained indicate the existence of bound water in the H_2O and D_2O/Ark. 9 systems resulting in slowing down of the dielectric relaxation process. Additionally, the relaxation of D_2O molecules is distinctly slower.

(2) The isotopic effect found in this study is, on one hand, stronger than for pure water and, on the other, weaker than for some amorphous solids which is consistent with the idea of structure dependence of the retardation factors.

(3) Further experimental and theoretical studies should be undertaken to find retardation factors for other lyotropic liquid crystalline structures and for surfactant molecules as well.

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