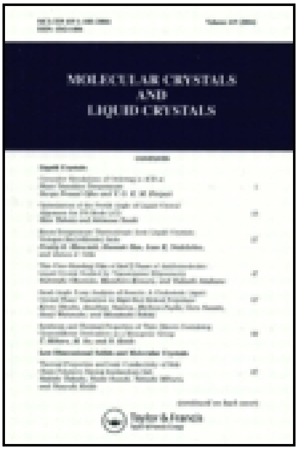

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Proton Spin-Lattice Relaxation in Lyotropic System Nonylphenoxypoly (Ethylenoxy) Ethanol (Arkopal 9) - D_2O

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PROTON SPIN-LATTICE RELAXATION IN LYOTROPIC SYSTEM NONYLPHENOXYPOLY(ETHYLENOXY)ETHANOL (ARKOPAL 9) – D_2O

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Abstract Results of the measurements of proton spin-lattice relaxation time T_1 are presented for lyotropic liquid-crystalline system Arkopal 9/D_2O, as a function of temperature, at resonant frequency 26.5 MHz. Two-exponential relaxation function was found and activation energies for molecular motion were calculated.

MATERIALS AND METHODS

The aim of this paper are investigations of the proton spin-lattice relaxation time T_1 in a system of nonylphenoxypoly(ethylenoxy)ethanol (Arkopal 9)/ D_2O. Measurements were performed in temperatures ranging from 0°– 70°C, for Arkopal 9 concentrations: 100%, 79%, 55%, 49%, 47%, 42%. In this system we expect the presence of different lyotropic liquid crystalline phases (i.e. lamellar, cubic, hexagonal, micellar).[1,2]

Measurements of the magnetization recovery were performed on a home-made spin echo spectrometer SES-26, at the NMR frequency $\omega_0/2\pi$ = 26.5 MHz, using the Carr-Purcell sequence of pulses (π – $\pi/2$ – π). Theoretical relaxation curves were fitted on an IBM PC-compatybile, using Marquardt's minimization method of χ^2.

REZULTS AND DISCUSSION

It was found for all samples that the relaxation function $F(t)$ has a two-exponential form at high temperatures:

$$F(t) = \frac{M_z(t) - M_\infty}{M_z(0) - M_\infty} = A_1 \exp\left(-\frac{t}{T_{1a}}\right) + A_2 \exp\left(-\frac{t}{T_{1b}}\right) \quad (1)$$

where : $M_z(t)$, M_∞, $M_z(0)$ - longitudinal magnetization at time t, $t = \infty$ and $t = 0$ respectively,

T_{1a}, T_{1b} - different relaxation times,

A_1, A_2 - relative contributions ($A_1 + A_2 = 1$).

In this case we fitted a 5-parameters function to experimental data.

At lower temperatures the relaxation function has a one-exponential form ($T_{1a} = T_{1b}$ or $A_2 = 0$) within the limits of estimated errors.

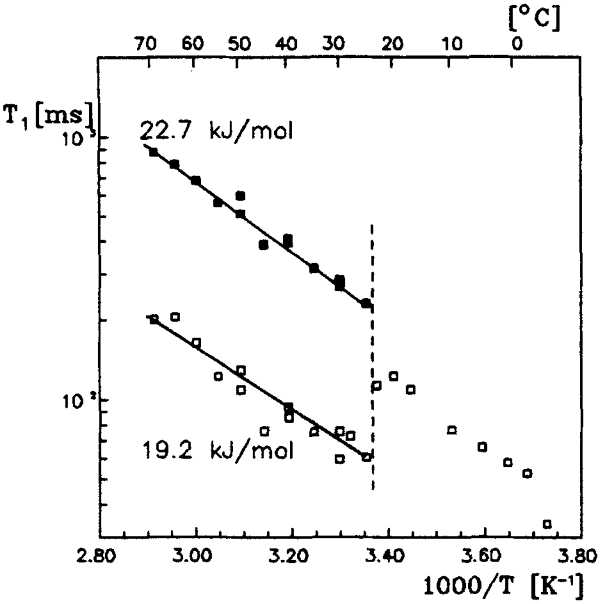

FIGURE 1 The temperature dependence of the spin-lattice relaxation time T_1 for sample 42 % Arkopal 9 in D_2O.

The presented experimental results can be interpreted on the basis of the relaxation theory [4] assuming extreme narrowing case ($\omega_0^2\tau_c^2 \ll 1$), where τ_c is correlation time for molecular motions, which obeys Arrhenius equation. In such a

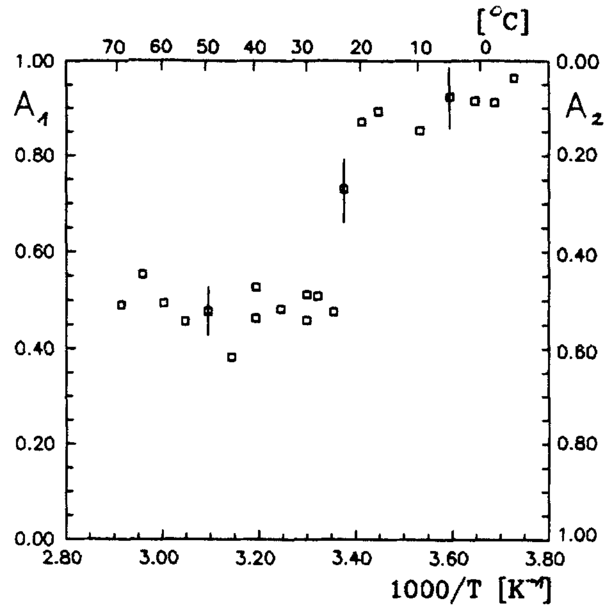

FIGURE 2 The temperature dependence of the relative weights of the component of relaxation function for sample 42 % Arkopal 9 in D_2O.

case one gets $1/T_1 \sim \tau_c$ and then

$$\ln T_1 = - \frac{E_A}{RT} + \text{const} \qquad (2)$$

where E_A is the activation energy for molecular motions. The linear dependence of $\ln T_1$ vs $1/T$ is observed on the Fig 1. From the fitting of Eq (2) to the experimental results one can get the activation energies, noted on Fig 1.

With lowering of a sample's temperature, a stepwise decrease in measured amplitude of the spin echo signal was observed, at temperature in which the relaxation function change its form from two- to one-exponentional.

Connecting obtained results with polarizing microscope observations, we conclude that two-exponentional relaxation is present in liquid and liquid-crystalline phases, while one-exponential one appears in the gel phase. We explain the absence of the strong phase dependence of the high temperature data due to fact that we do not observe relaxation connected with the long-distance, liquid-crystalline order fluctuations.[3] We assume that different relaxation times (T_{1a}, T_{1b}) describe behaviour of hydrophilic and hydrophobic parts of the Arkopal 9 molecule. Transition to the gel phase causes stiffness of the hydrocarbon chains. In these conditions spin-echo signal from hydrophobic part of molecules vanished and we observed contribution from the hydrophilic part only.

Detailed results of the spin-lattice relaxation studies in system Arkopal 9 / D_2O will be published in the next paper.

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