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Molecular mobility and N.M.R. relaxation in the binary system Triton X 114–water

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The proton spin lattice relaxation time T_1 has been measured for several samples of the binary system Triton X 114–water in the concentration range 20–90 per cent by weight. The correlation time, the activation energy and the constant of the dipole–dipole interaction C were calculated for all samples. The results show the existence of two relaxation mechanisms connected with the mobility of the alkyl chains and the oxyethylene chains.

1. Introduction

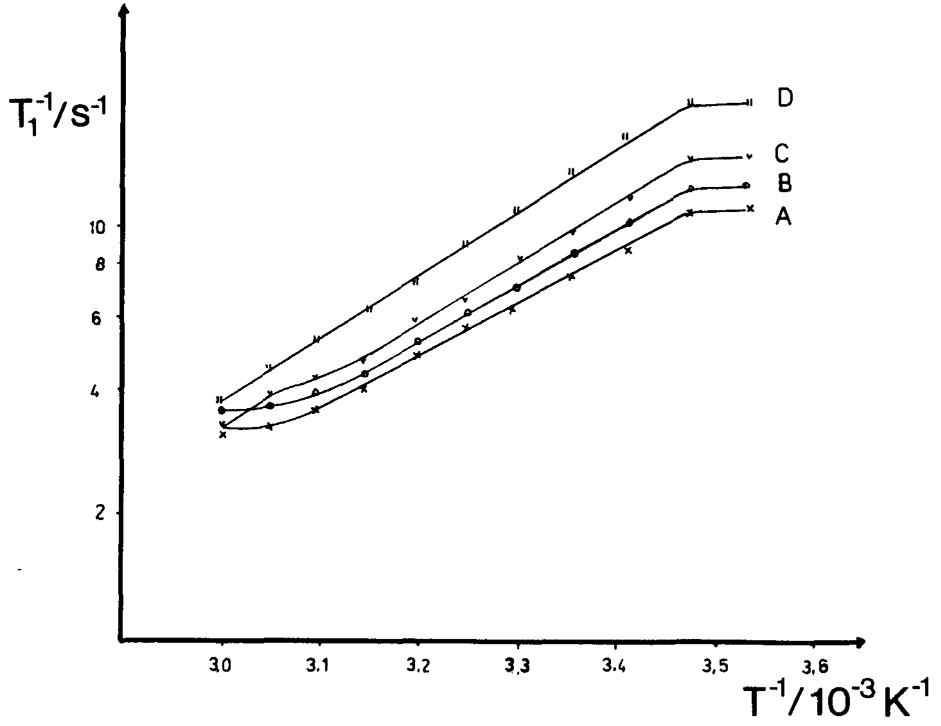
N.M.R. spectroscopy is one of the most flexible experimental techniques for investigating the properties of lyotropic liquid crystals at the molecular level. The chemical shift and the relaxation parameters of different magnetic nuclei in the lyotropic system depend on the individual molecular properties. A careful choice of the method allows a more exact study of the type of the supramolecular organization. The spin lattice relaxation time T_1 is determined by motions with correlation time $\tau_c = 1/\omega_0$. It is connected with changes in the structure or in the movement of the aggregates, or with phase transitions in the system. A characteristic property of amphiphilic molecules is the formation of aggregates of various types when they are dissolved in water or in organic solvents.

2. Materials and methods

The subject of our investigations was the binary system alkylphenylpolyethylene glycol (Triton X 114)–heavy water (D_2O) studied every 5 per cent in a concentration interval from 20 per cent to 90 per cent detergent by weight. We used Triton X 114 which was a FLUKA product, and deuteriated water with a purity of 99·98 per cent. The samples were prepared in glass tubes with a diameter $d = 7$ mm and the tubes were sealed. In order to obtain good homogeneity the samples were centrifuged many times. The spin lattice relaxation time T_1 of the protons of Triton X 114 was measured for all samples in the temperature interval from 283 K to 333 K at every 5 K. The measurements were performed on a Brucker B-KR 322s N.M.R. pulse spectrometer at a frequency $\nu_0 = 32$ MHz using the conventional $\pi/2$–τ–$\pi/2$ pulse sequence. The dependence of the free induction signal after the second $\pi/2$ pulse on τ was determined. Our results show that the logarithm of the amplitude of this signal depends linearly on τ. Consequently because of strong spin–spin diffusion all the protons in our samples relax according to an exponential law. The ^{2}H absorption spectra (of the heavy water) of all samples were recorded by means of a Brucker spectrometer HFX 90 at room temperature ($T = 298$ K). From their shape the phase of the binary system of each sample was determined. Thus the investigated samples were divided into three groups: (1) at concentrations lower than 50 per cent, isotropic micellar phase; (2) at concentrations between 50 and 80 per cent, liquid crystal phase (it was identified by us as lamellar through microscopic observations, that is in agreement with Walsh [1]); and (3) at concentrations above 80 per cent, isotropic phase.

3. Results and discussions

The relaxation rate of the proton N.M.R. of Triton X 114 is shown on the figure as a function of the reciprocal of the absolute temperature for four typical weight concentrations of the detergent: A, 30 per cent; B, 45 per cent; C, 60 per cent; and D, 90 per cent. The curves for all samples of the first concentration interval exhibit two plateau *X* and *Y*, which are shown in figures (*a*) and (*b*). The second plateau moved to the left with the increase in the concentration. The curves from the second and third concentration intervals have simpler forms. They have only one plateau each (see figures (*c*) and (*d*)).



Relaxation rate of the proton N.M.R. of the binary system Triton X 114–heavy water as a function of the inverse of the absolute temperature for different weight concentrations of the detergent. A, 30 per cent; B, 45 per cent; C, 60 per cent; D, 90 per cent.

We now consider the relaxation processes from the first concentration interval. The form of those curves, which include two plateau *X* and *Y*, shows the combined influence of two relaxation mechanisms, a low-temperature relaxation mechanism and a high-temperature mechanism denoted by *X* and *Y*, respectively. With the aid of an iterative program the relaxation rate was expanded in this case as a sum of two components (i.e. the two relaxation processes),

$$\left(\frac{1}{T_1}\right) = \left(\frac{1}{T_1}\right)_X + \left(\frac{1}{T_1}\right)_Y. \qquad (1)$$

According to Jeffrey *et al.* [2] and after the accepted theory [3], for these processes the equation

$$\left(\frac{1}{T_1}\right)_i = C_i\left(\frac{\tau_{ci}}{1+\omega_0^2\tau_{ci}^2}+\frac{4\tau_{ci}}{1+4\omega_0^2\tau_{ci}^2}\right) \tag{2}$$

is valid. In our case

$$\left(\frac{1}{T_1}\right)_X = C_X\left(\frac{\tau_{cX}}{1+\omega_0^2\tau_{cX}^2}+\frac{4\tau_{cX}}{1+4\omega_0^2\tau_{cX}^2}\right), \tag{3}$$

$$\left(\frac{1}{T_1}\right)_Y = C_Y\left(\frac{\tau_{cY}}{1+\omega_0^2\tau_{cY}^2}+\frac{4\tau_{cY}}{1+4\omega_0^2\tau_{cY}^2}\right), \tag{4}$$

where

$$\tau_{ci} = \tau_{0i}\exp(E_i/kT);$$

here E is the activation energy for the process, C is a coupling constant for the interaction between the magnetic dipoles which depends on the distance between these dipoles and on their magnitude, and ω_0 is the N.M.R. resonance frequency being $\omega_0 = 2\pi\nu_0 = 2\pi \times 32 \times 10^6\,\mathrm{s}^{-1}$ in our experiments. From equations (1), (3) and (4) we obtain the total relaxation rate as

$$\left(\frac{1}{T_1}\right) = C_X\left(\frac{\tau_{cX}}{1+\omega_0^2\tau_{cX}^2}+\frac{4\tau_{cX}}{1+4\omega_0^2\tau_{cX}^2}\right)+C_Y\left(\frac{\tau_{cY}}{1+\omega_0^2\tau_{cY}^2}+\frac{4\tau_{cY}}{1+4\omega_0^2\tau_{cY}^2}\right).$$

The values of C_X and C_Y, τ_{0X} and τ_{0Y} and E_X and E_Y were determined. The magnitudes of τ_{cX} and τ_{cY} at room temperature ($T = 298\,\mathrm{K}$) were calculated. The values of all these parameters are given in the table. For process X the correlation time τ_{cX} was found to have similar values (about $1 \times 10^{-9}\,\mathrm{s}$) for all concentrations showing a weak tendency to increase with the concentration. Process Y revealed a stronger dependence of τ_{cY} on concentration; τ_{cY} changed its value by a factor of six within the concentration interval of the measurements (from $6 \times 10^{-9}\,\mathrm{s}$ to $34 \times 10^{-9}\,\mathrm{s}$).

To explain the origin of the relaxation process we have calculated the rotational diffusion rate of the micellar aggregates in the first concentration interval. We used the Debye formula

$$\tau_r = 4\pi\eta R^3/3kT$$

where η is the viscosity of the medium and R is the radius of the micelle. We assume a spherical aggregate radius R of 40 Å [4–6], then we obtain the correlation time of the rotational diffusion τ_r of $6 \times 10^{-8}\,\mathrm{s}$. So the value of the micellar rotational correlation time τ_r obtained in this way is higher than τ_{ci} calculated on the basis of our experimental data (cf. the table).

The lateral molecular diffusion in the aggregate is another possible mechanism of reorientation for the amphiphilic molecules. According to Wennerstrom *et al.* [7] the correlation time of this motion is $\tau_D = R^2/6D$, where D is the diffusion coefficient of the lateral motion. Accepting the radius for the spherical aggregates of 40 Å, and D equal to $2 \times 10^{-8}\,\mathrm{cm}^2/\mathrm{s}$ (preliminary data obtained by us by means of gradient N.M.R.), we calculated $\tau_D = 1{\cdot}3 \times 10^{-6}\,\mathrm{s}$. This value is much higher than the value τ_{ci} calculated from our experimental data. In consequence it is reasonable to accept that lateral diffusion makes no contribution to our experimental data.

Table 1. The relaxation parameters determined by fitting the results to theory.

Per cent	$C_X\,\mathrm{s}^{-2}$	$C_Y\,\mathrm{s}^{-2}$	$E_X/\mathrm{J\,mol}^{-1}$	$E_Y/\mathrm{J\,mol}^{-1}$	$\tau_{0X}\,\mathrm{s}$	$\tau_{0Y}\,\mathrm{s}$	$\tau_{cX}\,\mathrm{s}$	$\tau_{cY}\,\mathrm{s}$
30	$1{\cdot}9 \times 10^{9}$	$0{\cdot}6 \times 10^{8}$	31·0	49·0	$3{\cdot}4 \times 10^{-15}$	$0{\cdot}2 \times 10^{-16}$	$0{\cdot}9 \times 10^{-9}$	6×10^{-9}
45	$2{\cdot}1 \times 10^{9}$	$0{\cdot}9 \times 10^{8}$	31·0	44·8	$3{\cdot}6 \times 10^{-15}$	$5{\cdot}2 \times 10^{-16}$	$0{\cdot}92 \times 10^{-9}$	34×10^{-9}
60	$2{\cdot}2 \times 10^{9}$	—	36·4	—	$0{\cdot}5 \times 10^{-15}$	—	$1{\cdot}03 \times 10^{-9}$	—
90	$3{\cdot}3 \times 10^{9}$	—	35·6	—	$0{\cdot}6 \times 10^{-15}$	—	$0{\cdot}95 \times 10^{-9}$	—

The conclusion of these speculations is that neither the first, X, nor the second, Y, relaxation mechanism could be explained by rotational diffusion of the spherical micelle as a whole or by the lateral diffusion of the surfactant molecules. This gives us reason to relate both relaxation processes to intramolecular motions, one of them to the protons of the hydrophobic alkyl chains and the other to the protons of the hydrophilic oxyethylene chains.

In the concentration interval 20–50 per cent detergent by weight a phase change takes place from spherical micelles at 20 per cent to lamellar phase at 50 per cent, passing probably through a region of cylindrical or disk-like micelles. The spherical micelles possess a large value of curvature of their surface. Because of this the oxyethylene chains are not so densely packed. They have a larger freedom for intramolecular motion and so a comparatively short correlation time. The cylindrical micelles, as well as the flat aggregates (disk-like micelles and lamellar layers) lead to a more dense packing of the oxyethylene groups. This results in a more hindered movement and greater value of the correlation time.

In contrast to the hydrophilic region, the hydrophobic one is densely packed for all kinds of aggregates of detergent molecules. Consequently the phase changes will influence the intramolecular motions of the hydrophobic alkyl chains in a less pronounced way. This allows us to assume that the first process, X, having an almost constant value of the correlation time τ_{cX} (about 1×10^{-9} s) refers to the protons of the hydrophobic chains and the second process, Y, with the stronger dependence of its correlation time τ_{cY} on the detergent concentration (changing from 6×10^{-9} s to 34×10^{-9} s), to the protons of the hydrophilic oxyethylene chains.

Our treatment of the processes, X and Y, is justified by the behaviour of the values of the constants C_X and C_Y. C_X expresses the interaction of the densely packed protons with equal spins; consequently C_X has a relatively high value of $2 \times 10^9\,\mathrm{s}^{-2}$. C_Y reflects the behaviour of the protons of the oxyethylene chain which are located at a larger distance from each other in an environment of ^{2}H nuclei of the structured water. That is why C_Y has a comparatively low value. In the concentration interval 20–50 per cent, C_Y changes from $6 \times 10^7\,\mathrm{s}^{-2}$ to $9 \times 10^7\,\mathrm{s}^{-2}$. This increase can be explained by the decrease of the screening influence of the D_2O molecules over the intermolecular proton spin–spin interaction, which is caused by the decrease of the quantity of water in the samples.

The similar values of the activation energy for both processes, E_X and E_Y, show a strong correlation between the intramolecular motion in the hydrophobic and hydrophilic parts of the amphiphilic molecules (see the table).

As we have already mentioned, the curves of the second and third concentration interval have only one plateau. This indicates that there is only one relaxation process, which was determined by equation (2). The calculated values of the magnitudes C and τ_c are very close to C and τ_c obtained for the process X in the samples of the first concentration interval. In agreement with our assumption the spin lattice relaxation time for the second and third concentration intervals was determined mainly by the spin–spin interaction of the protons of the densely packed alkyl chains. τ_{cY} in the first concentration interval shows a strong tendency to increase with increasing concentration. Thus it can be asserted that the τ_{cY} value in the concentration intervals (2) and (3) is too high to be measured in the temperature region studied by us.

The C value increased in all concentration intervals from $1{\cdot}9 \times 10^9\,\mathrm{s}^{-2}$ to $3{\cdot}3 \times 10^9\,\mathrm{s}^{-2}$ (see the table). This can be explained in the following manner; the decrease of the quality of water in the sample leads to both a closer packing of the alkyl chain, and to a decrease in the number of the water molecules penetrated between them.

The results obtained confirm the dependence of N.M.R. relaxation processes on the characteristics of the lyotropic liquid crystal systems.

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