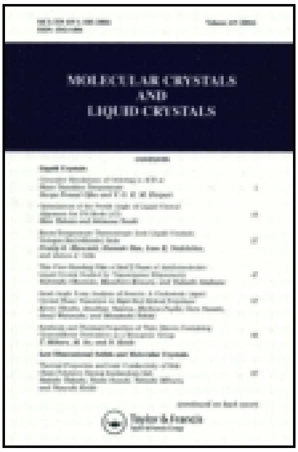

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Lyomesophase-Liquid Phase Transitions in Decyldimethylphosphine Oxide-Water System: Spin Probe Method

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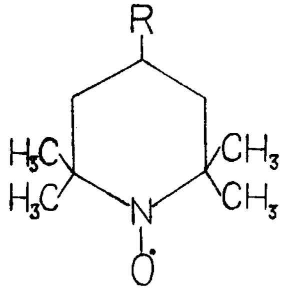
Rotational and translational diffusion of a hydrophilic spin probe tanol have been studied for the hexagonal, lamellar and isotropic phases of a lyotropic system containing water and a nonionic surfactant decyldimethylphosphine-oxide. Rotation of the probe in the aqueous region of the lyomesophases and of the micellar solutions is only to a small extent hindered in comparison with rotation of tanol in pure water. The observed high values of translational diffusion coefficient of tanol provide complementary evidence of the high mobility of water molecules in lyomesophases. The hexagonal/liquid phase transition causes only subtle changes in the ESR spectra parameters whereas changes at the lamellar/liquid phase transition are more pronounced. Transition enthalpies and changes in diffusion parameters have been compared for the phase transitions in the system studied and in phospholipid-water systems. Existence of direct specific interaction of tanol molecules with the polar head groups on the surface of micelles is suggested in order to explain the obtained values of hyperfine splitting constant and of translational diffusion coefficients.

Keywords: Spin probe method, lyomesophase, decyldimethylphosphine oxide-water

INTRODUCTION

Structure and molecular motions in lyotropic liquid crystals formed by surfactants and phospholipids have been studied by various magnetic resonance techniques.[1-5] In a spin probe technique stable nitroxyl radicals are applied, whose molecules contain a nitroxyl fragment NO and a hydrophobic or hydrophilic substitute R:



The electron spin resonance (ESR) spectra obtained at low spin probe concentrations characterize the process of the spin probe rotational diffusion and allow to determine the local viscosity of the environment of the probe molecule. When high spin probe concentrations are applied translational diffusion of the probe can be investigated. So far spin probes containing a hydrophobic substitute (R is a long-chain fatty acid or steroid residue) have been used most frequently. Due to the amphiphilic character of these probe molecules they are readily incorporated into micelles and lipid bilayers and are oriented by mesophase, which allows to measure the local viscosity of the hydrophobic region and the mesophase order parameter.[1-3] Rotation of the oriented probe in anisotropic media such as a hexagonal or lamellar phase is anisotropic, which causes a complicated ESR spectrum and difficulties with its interpretation.[2,3]

The translational diffusion coefficients have been calculated from the concentration-dependent line broadening of the ESR spectra using the spin exchange theory[3,6] for the hydrophobic regions of the bilayer and hexagonal mesophases.[3,4,6-10] It has been found that diffusion of the probes in the bilayers of the gel ($P_{\beta'}$) phase is orders of magnitude slower than in the bilayers of the lamellar liquid crystalline phase of phospholipid-water systems.[4,11]

Hydrophilic probes (R = NH_2, OH) have been seldom exploited in the study of lyotropic liquid crystals. Their molecules have a nearly spherical shape[2] and cannot be oriented by the mesophase, which does not allow to determine the mesophase order parameters.[12] Hydrophilic spin probes are considered to be localized in aqueous or intermediate (on the border between aqueous and hydrophobic) regions of the lyotropic system. The obtained ESR spectra are well-resolved and easily interpreted, which makes application of hydrophilic spin probes in the study of lyotropic phases easier from the methodological point of view than application of the amphiphilic probes. Local viscosity of the environment of the probe molecule and diffusion in the hydrophilic regions can then be investigated.[2,13-15] It appears to be important to study the rotational and translational diffusion of the hydrophilic probe as it can help to obtain an insight into the mobility of low-molecular polar organic substances in biological systems.

In previous studies[14,15] translational and rotational rates of diffusion of a hydrophilic spin probe tanol (R = OH) in the isotropic liquid and hexagonal phases of sodium dodecyl sulfate (SDS)-water system have been determined. High mobility of the probe in the aqueous regions of both micellar solution and hexagonal phase has been observed. The ratio of the translational and rotational rates of diffusion in SDS-water system has been found to be much higher than this ratio for Newtonian liquids.[16]

Phase behaviour of nonionic surfactants is in many respects different from the phase behaviour of ionic surfactants.[17] Alkyl polyoxyethylene ethers make the most studied class of nonionics. The polar part of their molecules consists of a long polyoxyethylene chain which may be larger than the nonpolar part. However, for the reasons of comparison with ionic surfactants it might be appropriate to investigate the properties of nonionic surfactants with compact polar head groups (such as PO or other oxides of the elements of V and VI groups of the Periodic Table).

In this work rotational and translational diffusion of tanol in hexagonal (Hex), lamellar (Lam) and isotropic (*I*) phases are studied in a wide temperature range for the system containing water and a nonionic surfactant with a compact polar head group,

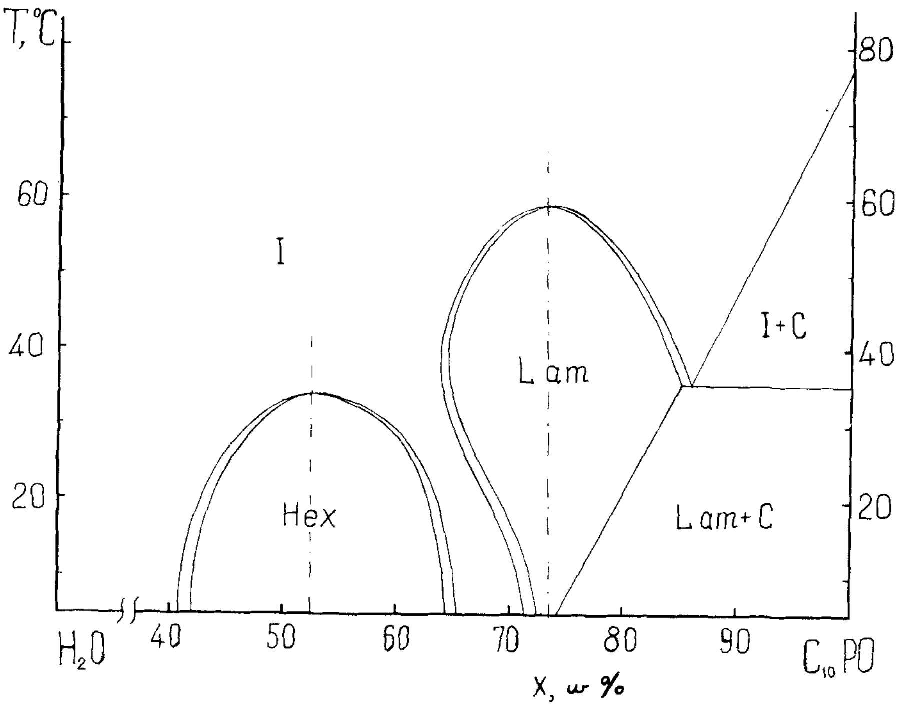


FIGURE 1 Phase diagram of the decyldimethylphosphine oxide ($C_{10}PO$)-water system.[18]

decyldimethylphosphine oxide. The phase diagram for this system has been investigated by differential scanning calorimetry (DSC) and polarising microscopy[18, 19] (Figure 1). So far ESR with a hydrophilic spin probe has not been used in the study of lyotropic systems containing nonionic surfactants.

MATERIALS AND METHODS

Decyldimethylphosphine oxide ($C_{10}H_{21}P(CH_3)_2O$, abbreviated $C_{10}PO$) purified by sublimation in vacuo and twice distilled water were used.

Mixtures with the surfactant content 52.5w% (mixture 1) and 72.7w% (mixture 2) were weighed into a hermetically closed microvessel and thermostatted for 30 min at 50°C and 59°C, respectively. Crystals of the spin probe tanol (2,2,6,6-tetramethyl-4-oxypiperidine-1-oxyl) with the probe content in the range $C = (0.4 - 8.0) \cdot 10^{-2}$ M were introduced and the mixtures were kept at the same temperatures for 30 min more. An aliquot was taken into a capillary with $d < 1$ mm and the capillary was sealed.

The ESR spectra were recorded with the help of a commercial RE-1306 radiospectrometer with the frequency 9 GHz in the temperature intervals 0–60°C for mixture 1 and 30–80°C for mixture 2. A variable temperature accessory provided temperature stability within 0.3°C.

ESR SPECTRA CHARACTERISTICS

ESR spectra typical for the case of low spin probe content $C < 5 \cdot 10^{-3}$ M are reproduced in Figure 2. The results have been processed by a computer, and average values of the linewidth (ΔH), shift (δ), asymmetry (As), hyperfine splitting constant (HFS) and probe rotation frequency (ν) were obtained from 5 records of a spectrum.

The value of ΔH was measured as a peak to peak distance. Asymmetry was calculated as the ratio of the positive amplitude to the total amplitude of the third component. Line shift was found as the difference of distances between the second and third components at low and high probe concentrations. HFS was calculated as half of the distance between the first and third components at low probe content, with the accuracy 0.03 G.

The ESR spectra at low probe concentration characterize the process of the probe rotational diffusion, measured parameters being rotation frequency (ν) and probe rotational correlation time (τ_c). The value of τ_c is related to the local viscosity (η_{loc}) of the system.

The values of ν were determined according to formula:[2]

$$\nu = \tau_c^{-1} = \{B \cdot \Delta H_2 [(I_2/I_3)^{1/2} - 1]\}^{-1} \tag{1}$$

where ΔH was the width of the ESR spectrum second component and I_2, I_3 were peak amplitudes of the second and third components, $B = 6.73 \cdot 10^{-10}$ s/G.

The values of η_{loc} were calculated from the Debay relation[3]

$$\eta_{loc} = \tau_c \cdot 3\kappa T / 4\pi r^3 \tag{2}$$

where k was Boltzmann constant, T was temperature, K, and r was the radius of interaction of the probe molecules (for tanol $r = 4$ Å).[2]

Characteristics of the translational diffusion can be obtained at high spin probe concentration ($C > 5 \cdot 10^{-3}$ M) when binary molecular collisions take place. These collisions lead to spin exchange processes which affect the width, the dynamic shift and the asymmetry of the ESR line.[6]

The spin exchange theory is well elaborated[3,6] and allows to calculate the spin exchange rate constants by two ways: from the concentration-dependent broadening of the linewidth ΔH (the constant $K_e^{\Delta H}$) and from the shift δ (the constant K_e^{δ}) of the ESR line. The concentration dependence of ΔH is given by[6]:

$$\Delta H_2 = \Delta H_0 + \sqrt{3}/2(1 - \varphi) \cdot K_e^{\Delta H} \cdot C \tag{3}$$

where ΔH_0 is obtained by extrapolation of the dependence $\Delta H(C)$ to zero probe concentration and φ is the statistical weight of the spectral line (equal to 1/3 for nitroxyl radicals).

The constant K_e^{δ} can be calculated from[20]

$$K_e^{\delta} = \{-A \cdot \Delta H_3 + [(A \cdot \Delta H_3)^2 + \mathrm{HFS} \cdot \delta]^{1/2}\}/C \tag{4}$$

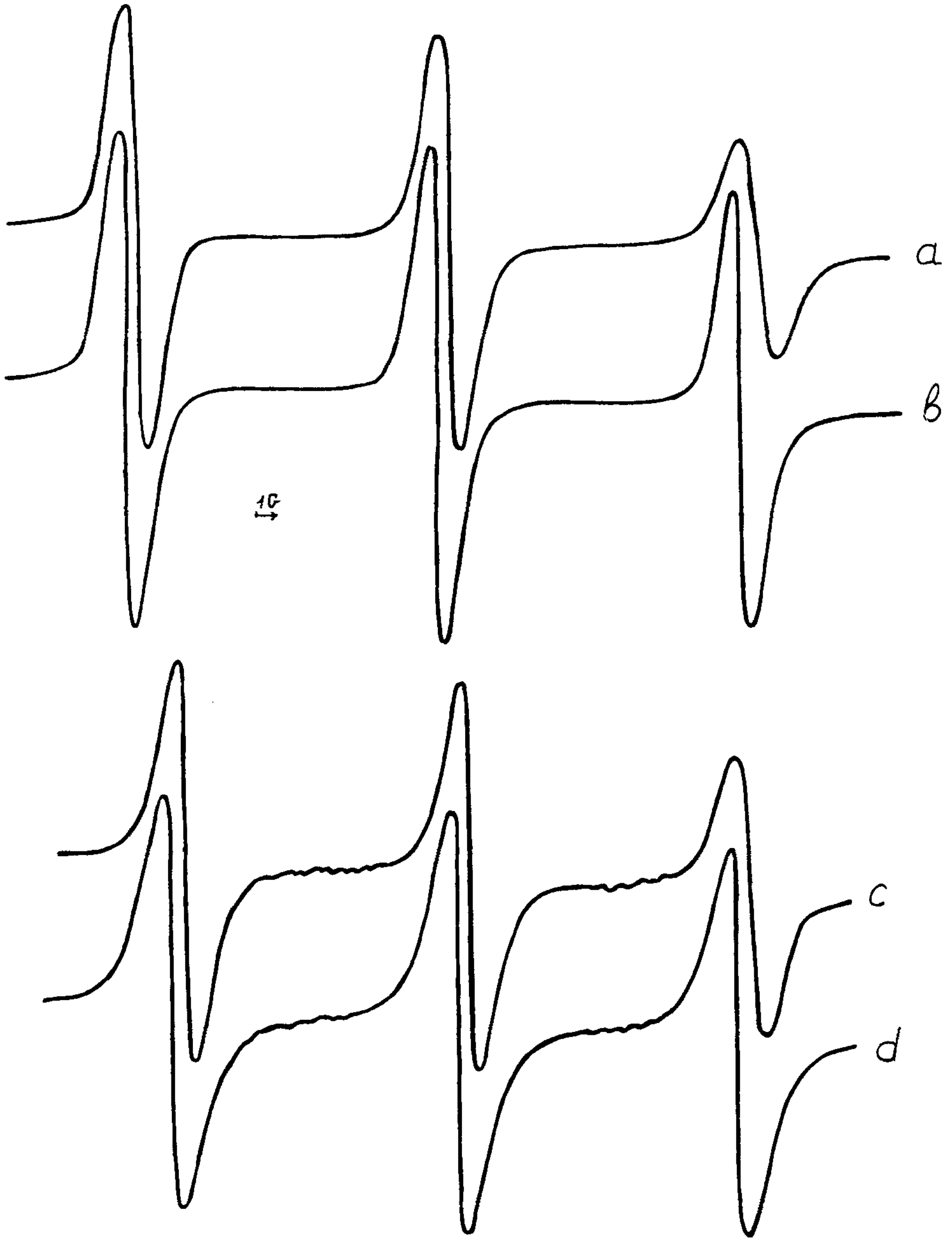


FIGURE 2 ESR spectra of tanol ($C = 0.37 \cdot 10^{-2}$ M) in mixture 1 at 5°C, Hex phase (a) and at 60°C, I phase (b); of tanol ($C = 0.5 \cdot 10^{-2}$ M) in mixture 2 at 40°C, Lam. phase (c) and at 60°C, I phase (d).

where $A = 0.65$ is a numerical constant and ΔH_3 is the linewidth of the third component.

Spin exchange is the only mechanism of phase relaxation of the probe in systems with viscosity not higher than 50 cP.[6] It is known that in the liquids with the viscosity higher than 50 cP the dipole-dipole interactions take place which lead to additional broadening of spectral lines.

This effect displays itself in the fact that the experimental values of $K_e^{\Delta H}$ are higher than those of K_e^{δ}.

Procedures of separation of the contributions of spin exchange and dipole-dipole interactions have been developed in Ref.[1,6,21] We used the procedure of separation according to Ref.[21] as it did not require knowledge of macroscopic viscosity:

$$(K_e^{\delta} - \beta K_d)\cdot C = -A\cdot\Delta H_3 + [(A\cdot\Delta H_3)^2 + \mathrm{HFS}\cdot\delta]^{1/2} \tag{5}$$

where K_d was the dipole-dipole interactions rate constant, β was a numerical coefficient dependent on the nature of diffusion. Thus, $\beta = 0.107$ for the Brownian diffusion model and $\beta = 0.0444$ for the model of jumping diffusion.[22]

The translational diffusion coefficient (D_{tr}) can be calculated with the help of the Stokes-Einstein formula (sterical factor is not taken into account):[6]

$$D_{tr} = K_e/8\pi r \tag{6}$$

where K_e is the average value of $K_e^{\Delta H}$ and K_e^{δ}.

RESULTS

Lyotropic hexagonal and lamellar phases are known to exist in C_{10} PO-water system.[18,19] In the binary system the mixtures considered (52.5 and 72.7w%) correspond to the concentrations for which the Hex/I and Lam/I transition take place at 34.0° and 59.1°C, respectively, according to the DSC data (Figure 1).[18] The question is whether these transitions would display themselves in the characteristics of the ESR spectra of the hydrophilic spin probe.

In Figure 2 ESR spectra are presented for mixture 1 (a, b) and mixture 2 (c, d) containing $0.37\cdot10^{-2}$ M and $0.5\cdot10^{-2}$ M of tanol, respectively. One can see that at temperatures both before and after the phase transition the spectral lines are simple Lorentzian type. This indicates the absence of the superposition of the spectra and, consequently, a homogenous distribution of the probe in a single region of every phase. In Table I the values of rotational correlation time and local viscosity are given for mixtures 1 and 2. ESR spectra characteristics for tanol in pure water are presented for comparison in Table II.

The ESR spectra have been found to be symmetric in the whole temperature range: As equals 0.495 ± 0.002 for the Hex phase and 0.498 ± 0.002 for the I phase of mixture 1 and 0.493 ± 0.004 for the Lam phase and 0.488 ± 0.001 for the I phase of mixture 2. These results are very close to those for tanol in water where As = 0.502 ± 0.003 (Table II). These data and the values of τ_C indicate that rotation of tanol is isotropic and rapid both in isotropic and anisotropic phases, which is expected for a radical with a nearly spherical shape.[2]

The temperature dependences of the HFS values for both mixtures are reproduced in Figure 3. In Figure 4 the Arrhenius dependences of the rotation frequency of tanol are given. The values of the linewidth and the shift of the ESR spectral line have been measured for 8 concentrations of tanol in the range $C = (0.4-8.0)\cdot10^{-2}$ M. The

TABLE I

Temperature dependences of the rotational correlation time (τ_c) and of the local viscosity (η_{loc}) in mixtures 1 and 2 of $C_{10}PO$-water system

T, °C	$\tau_c \cdot 10^{11}$, s	η_{loc}, cP	T, °C	$\tau_c \cdot 10^{11}$, s	η_{loc}, cP
Mixture 1			Mixture 2		
0	79.3	11.1 ± 0.1	30	23.8	3.71 ± 0.08
5	46.2	6.59 ± 0.09	40	22.2	3.58 ± 0.08
15	24.2	3.56 ± 0.09	46	21.3	3.50 ± 0.08
20	18.9	2.87 ± 0.08	48	20	3.31 ± 0.08
29	11.8	1.87 ± 0.07	50	18.9	3.14 ± 0.08
31	10.8	1.72 ± 0.07	52	8.3	1.39 ± 0.06
33	9.9	1.58 ± 0.07	54	6.3	1.21 ± 0.06
34	8.9	1.42 ± 0.06	60	6.1	1.05 ± 0.06
35	8.3	1.31 ± 0.06	70	6.0	1.06 ± 0.06
37	8.1	1.29 ± 0.05	80	5.1	0.92 ± 0.06
40	7.2	1.16 ± 0.05			
50	5.1	0.85 ± 0.05			
60	4.2	0.72 ± 0.04			

TABLE II

Temperature dependences of the hyperfine splitting constant (HFS), rotational correlation time (τ_c), local viscosity (η_{loc}), translational diffusion coefficient (D_{tz}) and of the ratio of translational and rotational diffusion rates (K_e/v) for tanol in pure water

T, °C	HFS, G	$\tau_c \cdot 10^{11}$, s	η_{loc}, cP	$D^0_{tr} \cdot 10^6$, cm^2/s	K_e/v, G·s/M
0	17.17	23.2	0.90 ± 0.08	1.05 ± 0.05	3.1 ± 0.3
10	17.14	4.9	0.63 ± 0.04	1.03 ± 0.03	3.5 ± 0.5
20	17.11	3.9	0.60 ± 0.04	2.35 ± 0.03	4.1 ± 0.4
30	17.09	3.3	0.52 ± 0.05	3.08 ± 0.06	4.2 ± 0.5
40	17.05	3.2	0.51 ± 0.04	3.93 ± 0.06	5.1 ± 0.5
50	17	2.6	0.43 ± 0.03	4.33 ± 0.07	4.8 ± 0.4

dependences $\Delta H(C)$ have been found to be linear at $C > 10^{-2}$ M for both mixtures for all the temperatures studied. At lower probe content deviations from this linear dependence have been observed which can be explained by the inhomogeneous exchange broadening due to superhyperfine spin-proton interaction inside the probe molecule.[6] The tangents of the slopes of the dependences $\Delta H(C)$ have been used in calculations of the spin exchange rate constants $K_e^{\Delta H}$ with the help of Equation (3). These values and the spin exchange rates constants K_e^{δ} calculated from the shift according to Equation (4) are presented in Table III.

It can be seen from Table III that for mixture 1 the values of $K_e^{\Delta H}$ and K_e^{δ} are rather close to each other in the temperature range 31–60°C. Analogously, these constants almost coincide for mixture 2 in the temperature range 52–80°C (Table III). This means that the only mechanism of the phase relaxation of tanol in isotropic liquid phase in both mixtures is the spin exchange, as the equality of these constants is an experimental criterion of the absence of the dipole-dipole interactions.[6] The average

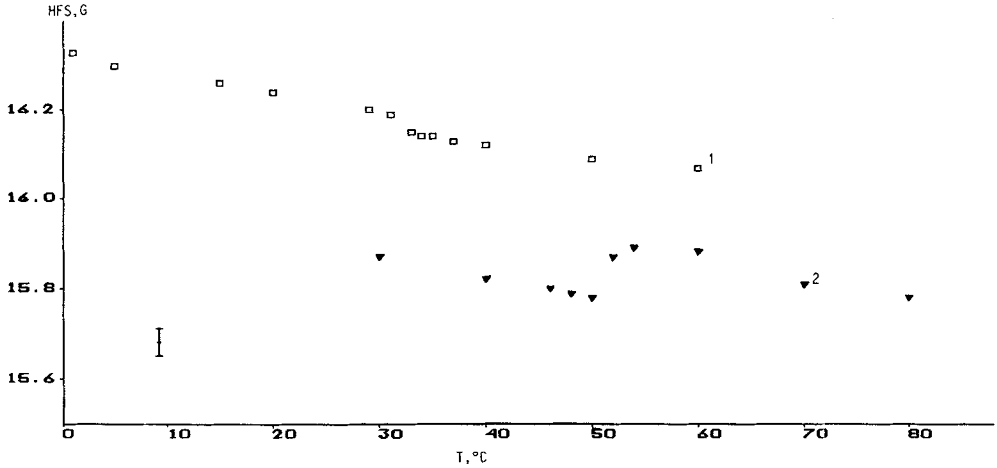


FIGURE 3 Temperature dependences of the hyperfine splitting constant (HFS) of tanol in mixture 1 (curve 1) and in mixture 2 (curve 2).

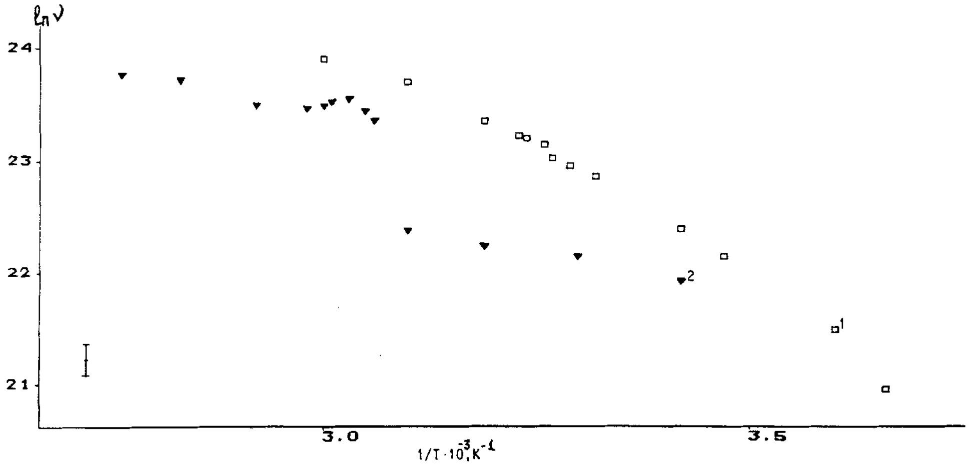


FIGURE 4 Arrhenius dependences of rotation frequency (ν, s^{-1}) of tanol in mixture 1 (curve 1) and in mixture 2 (curve 2).

values of $K_e^{\Delta H}$ and K_e^{δ} at 31–60°C for mixture 1 and 52–80°C for mixture 2 yield the values of the spin exchange rate constants for isotropic phases. In the temperature range 0–29°C for mixture 1 and 30–50°C for mixture 2 the values of $K_e^{\Delta H}$ differ from those of K_e^{δ}, which indicates the presence of two mechanisms of phase relaxation of tanol in Hex and Lam phases: spin exchange and dipole-dipole interactions. As described above, it is possible to separate the contributions of these mechanisms and to calculate the rate constants of the spin exchange (K_e) and of the dipole-dipole interactions (K_d) according to Equation (5). Results of this separation are given in Table III.

TABLE III

Temperature dependences of spin exchange rate constants $K_e^{\Delta H}$, K_e^{δ}, K_e, of dipole-dipole interactions rate constant K_d and of the ratio of translational and rotational diffusion rates (K_e/v) for tanol in mixtures 1 and 2 of C_{10}PO-water system. D_{tz} and D_{tz}^0 are translational diffusion coefficients in the C_{10}PO-water system and in pure water, respectively

T, °C	$K_e^{\Delta H}$, G/M	K_e^{δ}, G/M	K_e, G/M	K_d, G/M	K_e/v, G·s/M	D_{tr}/D_{tr}^0
Mixture 1						
0	35 ± 3	16 ± 4	21 ± 7	51 ± 2	25.0 ± 6.0	0.52 ± 0.001
5	35 ± 3	19 ± 4	23 ± 7	43 ± 2	17.0 ± 3.0	—
15	39 ± 3	24 ± 4	28 ± 7	41 ± 2	10.0 ± 2.0	0.43 ± 0.001
20	40 ± 3	31 ± 3	33 ± 5	30 ± 1	9.0 ± 1.0	0.36 ± 0.02
29	44 ± 5	33 ± 5	36 ± 5	26 ± 1	6.0 ± 0.6	0.29 ± 0.01
31	44 ± 5	40 ± 5	42 ± 5	—	6.4 ± 0.5	—
33	44 ± 3	38 ± 6	41 ± 4	—	5.6 ± 0.6	—
34	44 ± 3	40 ± 6	42 ± 4	—	5.3 ± 0.6	—
35	47 ± 6	41 ± 6	44 ± 5	—	5.1 ± 0.5	—
37	50 ± 5	44 ± 5	47 ± 5	—	5.3 ± 0.5	—
40	55 ± 5	47 ± 6	51 ± 5	—	5.0 ± 0.4	0.30 ± 0.01
50	65 ± 6	58 ± 6	62 ± 5	—	4.4 ± 0.3	0.33 ± 0.02
60	84 ± 5	70 ± 9	77 ± 7	—	4.3 ± 0.3	—
Mixture 2						
30	26 ± 2	17 ± 5	20 ± 5	44 ± 5	7.2 ± 0.1	0.16 ± 0.01
40	32 ± 2	19 ± 4	23 ± 4	35 ± 4	7.6 ± 0.2	0.15 ± 0.01
46	35 ± 3	25 ± 4	28 ± 4	26 ± 2	8.3 ± 0.3	—
48	36 ± 5	29 ± 5	31 ± 5	19 ± 2	8.9 ± 0.5	—
50	35 ± 2	31 ± 4	32 ± 4	9 ± 1	8.8 ± 0.4	0.17 ± 0.01
52	41 ± 3	45 ± 4	43 ± 4	—	5.3 ± 0.3	—
54	42 ± 2	46 ± 5	44 ± 4	—	4.7 ± 0.3	—
60	48 ± 2	52 ± 5	50 ± 5	—	4.5 ± 0.3	0.23 ± 0.02
70	57 ± 6	60 ± 6	59 ± 6	—	5.3 ± 0.4	0.24 ± 0.01
80	72 ± 5	71 ± 5	72 ± 6	—	5.4 ± 0.4	—

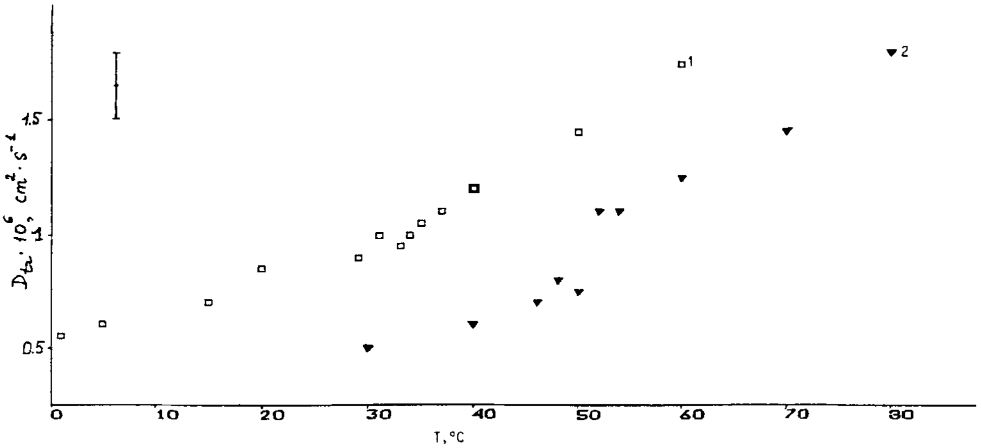


FIGURE 5 Temperature dependences of the translational diffusion coefficient (D_{tr}) for tanol in mixture 1 (curve 1) and in mixture 2 (curve 2).

Using formula (6) the coefficients of the translational diffusion of tanol have been obtained as a function of temperature (Figure 5). In Table III the values of the ratio of translational and rotational rates of diffusion for tanol are given.

DISCUSSION

Hydrophilic nature of tanol makes it natural to assume that the spin probe is localized in the aqueous regions of the phases. Analysis of ESR spectra demonstrates fast molecular motion of the probe in both lyomesophases and in isotropic liquid. Rotational correlation time and local viscosity data for mixtures 1 and 2 (Table I) indicate that rotation of tanol in the aqueous regions of the lyomesophases and of the micellar solutions is only to a small extent hindered in comparison with its rotation in pure water (Table II).

The values of the local viscosity for the lyomesophases are higher than in water only by a factor of.[5-8] This is a remarkably small difference taking into account that macroscopical viscosity of lyotropic liquid crystalline phases is not less than 3 orders of magnitude higher than viscosity of water.[23]

The values of the local viscosity for the hydrophobic regions of the lyomesophases in ionic surfactant-water systems studied with the help of amphiphilic probes are close to the values of η_{loc} in Table I: η_{loc} equals 3cP at 20°C for the Hex phase in potassium palmitate-water system[2] and 4cP at 22°C for the Hex phase in sodium octanoate-decanol-water system.[3] Rotational correlation time of a cholestane spin probe in the Lam phase of a dipalmitoylphosphatidylcholine(DPPC)-water system was reported to be 10^{-10}s[11] which is of the same order of magnitude as τ_C for the lyomesophases in the system studied (Table I). Thus, the obtained characteristics of the rotational diffusion of tanol provide complementary evidence on the similarity of the local molecular properties of different lyomesophases noted in Ref. 24. The local molecular environment of hydrophilic and amphiphilic probes appears to be similar in liquid crystalline phases formed by ionic and nonionic surfactants and by lipids.

The values of the hyperfine splitting constant of tanol for mixtures 1 and 2 (Figure 3) significantly differ from those in water (Table II) and approach HFS in hexane: for example, at 30°C HFS for tanol is equal to 16.2 G in the Hex phase and to 15.9 G in Lam phase whereas it is equal to 17.09 ± 0.03 G in water and 14.95 G in hexane. For several stable spin probe radicals dissolved in various solvents a linear dependence of HFS upon the dipolar moment of the molecule of the solvent was found.[25] However, if the solvent is able to form a hydrogen bond with the radical such a linearity is not observed. It is clear that a molecule of water is able to form a hydrogen bond with the OH group of tanol. It is known that the phosphine oxide group is able to form a hydrogen bond with the OH group of phenol.[17] It is reasonable to suggest that in the C_{10} PO-water system tanol can be solvated both by the water molecules and by the surfactant molecules and a competition between the processes takes place. Solvation of the OH group perturbs the electron shell of the radical and changes HFS. Interaction of tanol molecules with the polar head groups of the surfactant, however, does not lead to any long-range ordering of the radical as follows from the shape of the ESR spectra.

One can suggest that a rapid exchange between the molecules of the radical interacting with PO groups of the aggregates and the molecules of the radical interacting with the water molecules takes place. The hydrogen bond formation increases HFS.[25] Ability to form a hydrogen bond is greater for a water molecule than for a PO group of the surfactant, which is consistent with the fact that HFS in both mixtures is lower than in water and HFS in mixture 2 with a higher $C_{10}PO$ content is lower than in mixture 1.

The rate of translational diffusion of the spin probe is also rather high in both mixtures. It follows from Figure 5 that the values of D_{tr} are several times lower than those for water (Table II) and are of the same order as D_{tr} for tanol in the Hex phase of the SDS-water system.[15] At the same time they are much higher than the value of D_{tr} for the amphiphilic spin probes in the bilayers of Lam liquid crystalline phase of phospholipid-water systems. For example, at 30°C the values of $D_{tr} \cdot 10^8$ cm^2/s are equal to 308 in water (Table II), 89 in the Hex phase and 49 in the Lam phase of $C_{10}PO$-water system (Figure 5), 70 in the Hex phase of SDS-water system[15] (spin probe tanol); 12 in the Lam phase of dimyristoylphosphatidylcholine (DMPC)-water system (phosphatidylcholine spin probe)[10], 8 in the Lam phase of DMPC-water system (fluoresence probe)[4], 7 in the Lam phase of DMPC-water system (25°C, androstan spin probe).[7] Relatively high values of D_{tr} for tanol in Lam and Hex phases in $C_{10}PO$-water system confirm the concept of high mobility of water molecules in lyomesophases.[5]

Translational diffusion of a small molecule in the colloidal system has been theoretically described in the cell model of Jönsson e.a.[26] The observed change in the diffusion of the molecule in the colloidal system relative to its diffusion in water can be schematically attributed to two mechanisms: first, the colloidal particle excludes a certain fraction of the total volume for the diffusing molecule and this leads to a lengthening of the diffusion paths; second, the direct specific interaction between the particle and the small molecule can further decrease D_{tr}. It follows from the cell model[26] that the minimum limiting value of the D_{tr}/D_{tr}^0, the ratio of translational diffusion coefficients in the system and in water, is 2/3 in the presence of the first mechanism only. The values of the D_{tr}/D_{tr}^0 for tanol vary for the Hex phase from 0.5 to 0.3 and for the Lam phase from 0.15 to 0.16 (Table III). From the point of view of the cell model the values of D_{tr}/D_{tr}^0 lower than 2/3 give evidence of the existence of the second mechanism of the diffusion change. Explanation of the reduction of translational diffusion of tanol in lyomesophases of C_{10} PO-water system relative to its diffusion in water as due to the direct specific interaction of tanol with micelles is consistent with the above discussed suggestion about the formation of a hydrogen bond between the OH group of tanol and PO group of surfactant.

The ratio of translational and rotational rates of diffusion of tanol for isotropic solutions varies from 5.6 to 4.3 for mixture 1 and from 4.7 to 5.4 for mixture 2 (Table III) and is close to the value of $K_e/v = 5.0 \pm 0.5$ for Newtonian liquids (in G·s/m).[16] The values of this ratio for lyomesophases of C_{10} PO-water system are higher (Table III). The frustration of the proportionality between rotational and translational diffusion of tanol has been observed previously for micellar solutions and Hex phase of SDS-water system[14] and can been interpreted as being due to the different influence of the mesophase structure on translational and rotational mobilities of the probe.

Our data show that the spin probe method is able to detect transitions from lyotropic liquid crystalline phases to isotropic liquid, but various ESR spectra characteristics react upon these phase transitions in a differnt way. The Hex/liquid phase transition displays itself only as a change of the slope in the temperature dependence of D_{tr} and in the Arrhenius dependence of ν while detectable jumps are observed in these plots for the Lam/I transition (Figures 4, 5). A small jump in the temperature dependence of HFS corresponds to the Lam/I transition whereas for mixture 1 this dependence is practically linear in the whole temperature range (Figure 3).

The spin probe technique yields somewhat lower transition temperatures than those obtained for $C_{10}PO\text{-}H_2O$ system with the help of DSC.[18] A special DSC experiment for the sample of mixture 1 containing 0.025 M of tanol demonstrated that the spin probe acts as an impurity decreasing the Hex/I transition temperature by 2.7°C and making the transition temperature interval broader.

The transition from the hexagonal phase to the isotropic liquid is accompanied by subtle changes in the ESR spectra parameters. The changes at the Lam/I transition are more pronounced (Figures 3–5) but still much smaller than changes in the diffusion parameters at the transitions from a gel to the Lam liquid crystalline phase in phospholipid-water system. For example, there is a twofold decrease in τ_c (Table I) and a ~ 50% increase in D_{tr} at the Lam/I transition in mixture 2 (Figure 5) whereas τ_c and D_{tr} for the Lam phase differ by several orders of magnitude from τ_c and D_{tr} for the gel phase of DPPC-water system investigated with the help of amphiphilic probes.[4, 11]

One can compare these results with the data on the enthalpies of phase transitions measured with the help of DSC technique for the mixtures studied in this work which equal 0.043 ± 0.001 kJ/mole (mole of mixture) for the Hex/I and 0.129 ± 0.002 kJ/mole for the Lam/I transition.[18] The enthalpy of the main phase transition $P_{\beta'} + H_2O \leftrightarrows \text{Lam}$ for DPPC-water system was reported to be 2.7 kJ/mole of mixture.[27] One can see that breaking of the hexagonal arrangement of the cylindrical aggregates and formation of the micellar solution is accompanied by only subtle changes in the state of the aqueous region and in thermodynamic parameters of the system. Transformation of bilayers of the Lam phase into finite micelles of the isotropic liquid requires more energy and leads to a noticeable increase in rotational and translational diffusion of a hydrophilic molecule in the aqueous region of the system studied. The most considerable heat effects and changes in diffusion in the hydrophobic regions accompany the transition $P_{\beta'} + H_2O \leftrightarrows \text{Lam}$ in lipid-water systems. Thus, one can observe a certain similarity in the changes of thermodynamic and diffusion parameters at phase transitions in lyotropic systems.

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