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EPR investigation of phase transitions in amphiphilic systems

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Résumé. — Nous avons étudié trois systèmes amphiphiles utilisant de l'acide palmitique marqué. Deux des systèmes ne présentent pas de changement structural bicouche-monocouche et l'on observe une diminution monotone du paramètre d'ordre lorsque la température augmente. Cependant, dans le troisième système où une telle préstructuration prend place, le paramètre d'ordre présente deux extrema coincidant avec les transitions de phases coagel-gel et gel-cristal liquide.

Une transition supplémentaire est observée dans la phase cristal liquide du système amphiphile eau-palmitate de potassium.

Abstract. — Using spin labelled palmitic acid three amphiphilic systems were investigated. Two of the systems exhibit no bilayer-monolayer structural changes and a monotonous decrease of the order parameter with increasing temperature is found. In the third system, however, where such pre-structuration occurs, the order parameter has two extrema coinciding with the phase transitions coagel-gel and gel-liquid crystal.

In the liquid crystalline phase of the potassium palmitate-water amphiphilic system an additional phase transition is observed.

1. Introduction.

At constant concentration amphiphilic systems form different stable phases at different temperatures. The type of amphiphile chosen might also alter the structure of a particular phase [1].

According to the X-ray data there is a change in the lipid arrangement in the potassium palmitate water amphiphilic system [2] at the transition from the heterogeneous coagel to the homogeneous gel phase. The coagel is composed of hydrated bilayered lipid crystals, in between which is a dilute aqueous solution of lipid in the form of a random distribution of microdroplets. In the gel phase the lipid molecules form monolayers, the hydrocarbon chains being interdigitated and lying in the interior. The monolayers are spaced at equal distances, separated by layers of water. Here the long axes of amphiphilic molecules are perpendicular to the surface while in the coagel bilayers they are tilted. The hydrocarbon chains are rigid in both phases. In the liquid crystalline phase the lipid molecules form equidistant bilayers with melted chains.

On the other hand, sodium soaps [3] and systems with mixed lipids [4] have a bilayered structure in all three phases. At the phase transition from the crystallized coagel to gel there is a loss of tilt and at the gel to liquid crystal phase transition the hydrocarbon chains lose their rigidity.

Changes in the hydrocarbon chain ordering may be expected at the prestructure into the interdigitated phase and can be determined by spin probes. We have, therefore, investigated the chain ordering in three different lamellar systems-potassium palmitate-water (K PW), sodium palmitate-water (NaPW) and an equimolar mixture of potassium oleate and potassium laurate in water (KOLW)-by spin labelled palmitic acid.

2. Experimental.

The lamellar phases of all three systems were studied. The lipid to water ratio in weight % was 70 : 30 in KPW, 86 : 14 in KOLW and 65 : 35 in NaPW. The samples were labelled with the spin probe HFLASL (10, 3), (4-doxyl palmitic acid); its final concentration being $10^{-4}$ M [5].

EPR spectra of the samples sealed in 1 mm capillaries were recorded on a Varian E-9 spectrometer with an added temperature control.
3. Results and discussion.

The EPR spectra of the spin probe HFASL (10,3) dissolved in the three amphiphilic systems are shown in figure 1, 2, 3 and 4. The temperature dependence of the order parameter is presented in figure 5. The spectral lineshapes and spectral splittings were found to exhibit a 3-5 °C hysteresis (Figs. 1 and 2).

In the KPW system the phase transition coagel-gel is at 30 °C ($T_c = 30$ °C) and the gel-liquid crystal phase transition is at 45 °C ($T_e$). For the NaPW system these temperatures are $T_c = 60$ °C and $T_e = 80$ °C, respectively, while for KOLW they are $T_c = -13$ °C and $T_e = 20$ °C as estimated from the EPR spectra [5]. The temperatures of the phase transitions determined with the EPR technique are a few degrees lower than those determined by other methods [7] probably due to the fact that the strongest fluctuations of the newly appearing phase occur around the added impurities — i.e. the spin probe molecules.

The spectra of HFASL in the NaPW system are typical for spin probes in a lamellar anisotropic environment (Figs. 1, 2). The lines narrow with increasing temperature due to the increased rotation rate of the spin probe molecules around their long molecular axes. The narrowing of lines is more abrupt around 58 and 78 °C. These temperatures correspond to the temperatures of the coagel-gel and gel-liquid crystal phase transitions from the phase diagram [7] and the EPR hydrophobic spin probe results [8]. On heating, between 67 and 76 °C, and on cooling between 73 and 63 °C, we observed an additional component superimposed on the spectrum (Figs. 1, 2).

This spectral component can be understood as a result of the exclusion of part of the spin probe molecule(s) from the region with higher order parameter. This can be due to some unknown structural changes in the system or to changes in the ionization of the spin probe molecules [6].

In the KOLW amphiphilic system similar spectra were observed, but due to the lower viscosity of the system the liquid crystalline phase was stable down to room temperature. The intense restrictions on molecular motion begin at $-13$ °C (Fig. 3).

In both systems there is a monotonous decrease of the order parameter, $S$, with increasing temperature, while in the KPW system $S(T)$ has two extrema: a minimum which coincides with the coagel-gel phase transition and a maximum which coincides with the gel-liquid crystal phase transition (Fig. 5). On heating the sample within its coagel state the value of $S$ decreases due to a corresponding increase in the mobility of the system. At the coagel-gel phase transition a bilayer-monolayer prestructuring occurs: lipid chains from each side of the bilayer penetrate into each other merging into monolayers. As a result the spin probes with their sterically disfavoured nitroxide rings are then largely excluded from the monolayers. The spectra observed at these temperatures can be explained as a result of the wobbling of the spin probe molecules anchored with a part of

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**Fig. 1.** — EPR spectra of the spin probe HFASL (10,3) in the lamellar phase of the NaPW system (on the heating cycle).

**Fig. 2.** — EPR spectra of the spin probe HFASL (10,3) in the lamellar phase of the NaPW system (on the cooling cycle).

**Fig. 3.** — EPR spectra of the spin probe HFASL (10,3) in the lamellar phase of the KOLW system.
their tails into the interdigitated monolayers (Fig. 4). If we assume a fast motion regime the expression for the parallel and perpendicular components of the hyperfine interaction tensor $A$ [9] are:

$$\overline{A}_p^w = \frac{1}{2}(A_{xx} + A_{yy}) + [A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})]W$$

$$\overline{A}_\perp^w = \frac{1}{2}(A_{xx} + A_{yy}) + [A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})]\frac{1}{2}(1 - W).$$

Here $\overline{A}_p^w$ and $\overline{A}_\perp^w$ are the observed splittings, $A_{xx}$, $A_{yy}$, $A_{zz}$ are the principal values of the $A$ tensor and $W$ is a measure of the wobbling of the long molecular axes

$$W = \frac{1}{3}(1 + \cos \gamma + \cos^2 \gamma),$$

where $\gamma$ is the angle between the director and the maximal amplitude of wobbling. At the minimum exhibited by the $S(T)$ curve the approximate value of $\gamma$ is 70 degrees. However, the motion at these temperatures is not fast enough and wider lines result. These spectra also show a lower value of $S$. As the temperature increases the spin probe molecules dissolve more and more into the lipid monolayers and $S$ increases. The maximal value of $S$ is obtained when the bilayered liquid crystalline phase is formed. On further heating $S$ decreases as is typical within liquid crystalline phases. The plateau observed between 45 and 70 °C (Fig. 5, box) can be explained by the anomalies in the ordering of the first segments of the hydrocarbon chains (and where the paramagnetic centre is attached to the spin probe) which have been observed in the same system [10, 11].

In this system, at 77 °C, an additional phase transition was observed, as reflected by the change in the mobility of the system (Fig. 6). This process is reversible and can be related to the liquid crystalline polymorphism which was already reported to occur in this system [12-14].

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Fig. 6. — Plot of the ratio of the low field anisotropic \((m = + 1)\) and « isotropic » \((m = + 1)\) lines as a function of temperature for the KPW system.

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