CROATICA CHEMICA ACTA CCACAA 48 (2) 147—154 (1976)

YU ISSN 0011-1643
CCA-924 541.18
Original Scientific Paper

EPR of the Sodium Laurate-Water Lyotropic Mesophases and Micellar Solution

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Received July 7, 1975

The local orientational order of molecules in lamellar and hexagonal mesophases as well as in micellar aggregates of the sodium laurate — water system was studied by EPR. As a paramagnetic probe a fatty acid spin label, dissolved in the hydrophobic environment was used.

It was found that the ordering parameter decreases continously over the whole concentration and temperature range of the mesophases irrespective of the phase transitions.

From the local ordering parameter observed in cylindrical micelles, the variation of cylinder dimensions with temperature and concentration was estimated. In the micellar solution the concentration range where cylindrical micelles were the most stable was determined, and its relation to the maximal stability region in the hexagonal phase was discussed.

The rate of molecular tumbling around the cylindrical axes in the hexagonal phase was found faster than 10^8 sec^{-1} at 100 °C.

INTRODUCTION

Among sodium laurate (NaL) — water system phases the liquid crystalline lamellar and hexagonal phases deserve special attention, since they represent a model for ordered lipid structures[1]. In an isotropic solution the amphiphilic NaL molecules have a tendency to be associated to micelles. Their stability and shape depend on concentration and temperature of the isotropic solution[2].

The mesophase with the highest NaL concentration, the lamellar phase, consists of NaL bilayer sheets with polar heads of the NaL molecules facing the intercalated water layers. At lower NaL concentrations the hexagonal phase is formed. Extended long cylinders of aggregated NaL molecules with polar groups facing the cylinder surface are hexagonally packed and surrounded by water molecules[1]. The neighbouring phase at lower NaL concentrations, the isotropic solution, contains cylindric micelles which can be assumed as precursor building blocks of the hexagonal phase. They transform to spherical micelles at lower NaL concentrations[2].

It has been found that the local ordering of hydrocarbon chains of soap molecules does not change appreciably at liquid crystalline phase transitions, though there are large differences between the long range organization of the mesophases[3]. The local order of hydrocarbon chain segments, in lipid bilayers, was described theoretically by Marčelja[4] with the local order parameter $\eta_i = \left\langle \frac{1}{2}(3 \cos^2 \Theta_i - 1) \right\rangle$ where Θ_i is the angle between the normal to the H—C—H plane of the i-th carbon atom and the bilayer surface normal, and the brackets denote the average over all configurations the hydrocarbon chain can take. The local order parameter in lyotropic systems has been determined by magnetic resonance methods[3,5,6]. In EPR measurements fatty acid type spin labels have been used as paramagnetic probes. They were supposed to reflect the order and dynamics of solvent lipid molecules[7]. Though there was a recent contribution dealing with a similar system[9], we believe that an EPR study through the liquid crystalline and the micellar solution concentration range of NaL has not been done yet.

EXPERIMENTAL

Homogenized samples of sodium laurate and water have been sealed together with 0.05% paramagnetic 2(3-carboxy-propyl)-4,4-dimethyl-2-tridecyl-3-oxazolidinyloxyl ((12.3) FASL) in 1 to 2 mm inner diameter glass capillaries. In order to increase the homogeneity of samples, they were centrifuged through a narrowed capillary section several times at about 80 °C and measured immediately. Samples with different NaL-water concentration ratios were measured in the temperature range between 60—150 °C, on the E-9 Varian EPR spectrometer. The temperature was stabilized to ± 0.2 °C and the temperature gradient was kept below 0.5 °C/cm.

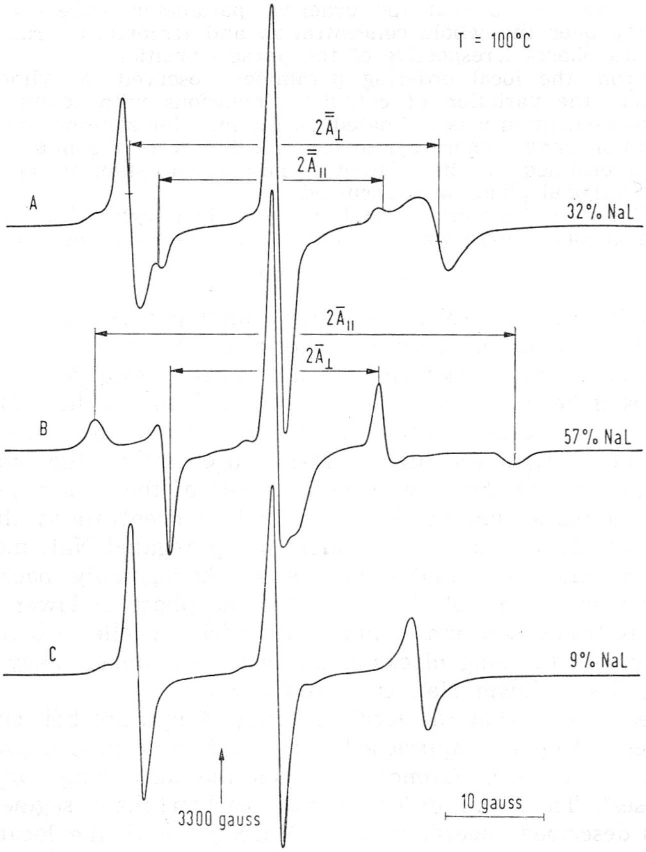

Figure 1. Representative EPR spectra of the (12.3) FASL spin label dissolved in NaL-water system for different concentrations of NaL at 100 °C.

RESULTS AND DISCUSSION

The representative spin label electron paramagnetic spectra in Figure 1 are typical for randomly distributed anisotropic domains with a high local mobility of the paramagnetic probe. The lamellar phase spectra (Figure 1B) agree with other spectra observed in bilayer systems[5,6,8]. The corresponding order parameter can be calculated from the expression[5]

$$\eta_l = (\bar{\mathbf{A}}_{\parallel} - \bar{\mathbf{A}}_{\perp})/(\mathbf{A}_{\parallel} - \mathbf{A}_{\perp}) \tag{1}$$

where $\mathbf{A}_{\parallel}$ and $\mathbf{A}_{\perp}$ are the principal values of the hyperfine coupling tensor (for (12.3)FASL $\mathbf{A}_{\parallel} = 32.4$ Gauss and $\mathbf{A}_{\perp} = 6.1$ Gauss[6]) and $\bar{\mathbf{A}}_{\parallel}$ and $\bar{\mathbf{A}}_{\perp}$ are the experimentally observed hyperfine splittings, derived from the EPR spectra as shown in Figure 1B.

The spectra typical for cylindrical molecular association (Figure 1A) can be explained with a random distribution of cylinder's long axis orientations. The fast molecular motion, in the time scale of the EPR experiment, about the cylinder long axis produces an additional averaging of the hyperfine tensor components[8]. The axially symmetric component $\bar{\mathbf{A}}_{\parallel}$ of the hyperfine splitting tensor is now parallel to the long cylinder axis. Therefore the local order parameter can be calculated from the expression

$$\eta_h = -2(\bar{\bar{\mathbf{A}}}_{\parallel} - \bar{\bar{\mathbf{A}}}_{\perp})/(\mathbf{A}_{\parallel} - \mathbf{A}_{\perp}) \tag{2}$$

The experimental values of the hyperfine splitting components are shown in Figure 1A for hexagonal micelles. It has to be stressed that the expression for η_h is valid only in the approximation of indefinitely long cylinders, resembling those of the hexagonal phase. The order parameter calculated according to this expression is strongly influenced by the cylinder's diameter — length ratio as will be shown later in this paper.

The spectrum in Figure 1C is characteristic for a diluted isotropic solution. From these spectra we can not resolve whether the molecules are aggregated to spherical micelles or dissolved as single molecules.

The hexagonal phase spectrum (Figure 2) differs slightly from the published spectra for the hexagonal phase[8,9]. Our hexagonal phase spectra are supperpositions of lamellar (Figure 1B) and cylindrical aggregate type spectra (Figure 1A). As already shown[8,10], the surface alignment of the lyotropic mesophase influences significantly the EPR spectrum at lower sample tube diameters. Therefore the lamellar type spectrum in the hexagonal phase probably belongs to those spin label molecules which are trapped to the glass surface oriented mesophase regions. In an experiment, where the glass and plastic capillary diameter, as well as the spin label concentration were varied, we found that the amount of surface oriented spin label molecules increases with decreasing diameter and increasing spin label concentration. The surface oriented portion is higher in glass than in plastic capillaries of the same diameter. From this experiment we have concluded that spin label molecules are accumulating in the surface oriented liquid crystal. Therefore a quantitative estimation of the ratio between the randomly distributed hexagonal phase and the surface oriented portion of the liquid crystal molecules was not possible. So, the order parameter was determined only for the unoriented part of the hexagonal phase.

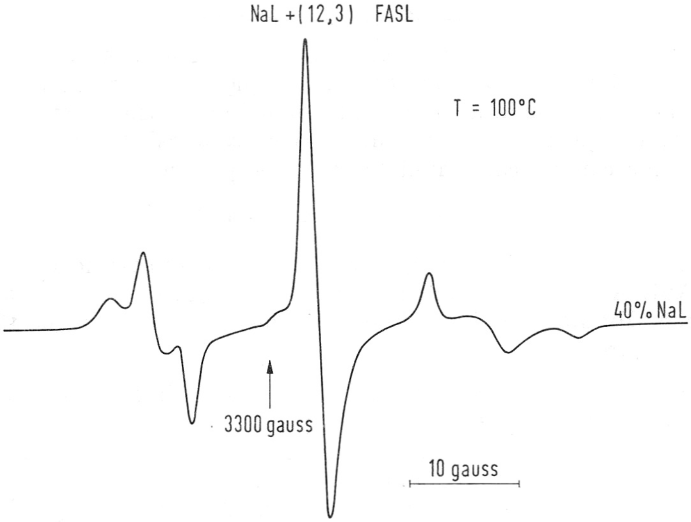

Figure 2. EPR spectrum of (12.3) FASL spin label dissolved in the hexagonal phase of NaL-water system.

From the line shape of the EPR spectra a fast rotational motion of spin label molecules in the anisotropic environment is evident[11]. Therefore the order parameter determined from the absorption line maxima, as shown in Figure 1, can be used as a good approximation, instead of a computer simulated derivation. It should be stressed that the local order parameter evaluated from the spin label spectra does not represent the real order parameter of the hydrophobic environment[7,12]. In spite of this, we can infer that the relative variations of the order parameter are faithfully reproduced.

Figure 3 represents the variation of the local order parameter with NaL concentration. A fast decay of the local order is observed in isotropic solution,

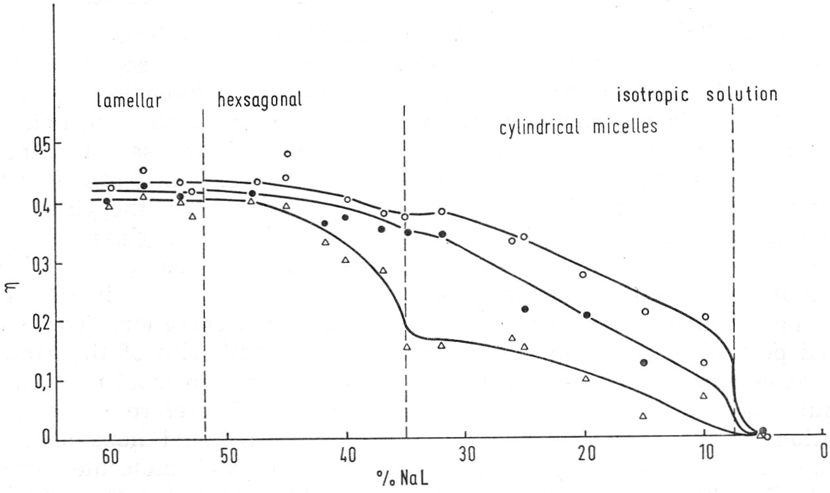

Figure 3. Order parameter variation of (12.3) FASL molecules dissolved in the NaL-water system as a function of NaL concentration (○○○ $t = 80$ °C, ●●● $t = 100$ °C, △△△ $t = 120$ °C)

if the same expression for the order parameter as for the indefinitely long cylindrical micelles is used. Figure 4 shows how temperature influences the order parameter in various phases. Although the local order does not change appreciably with temperature and concentration in the lamellar and hexagonal phase, there is a fast decay observed in the region of isotropic solution. Here the observed order parameter η'_h, evaluated by expression (2), differs from the micellar order parameter η_m, since in expression (2) the dimensions of cylinders were not taken into account. By the assumption that the cylinders

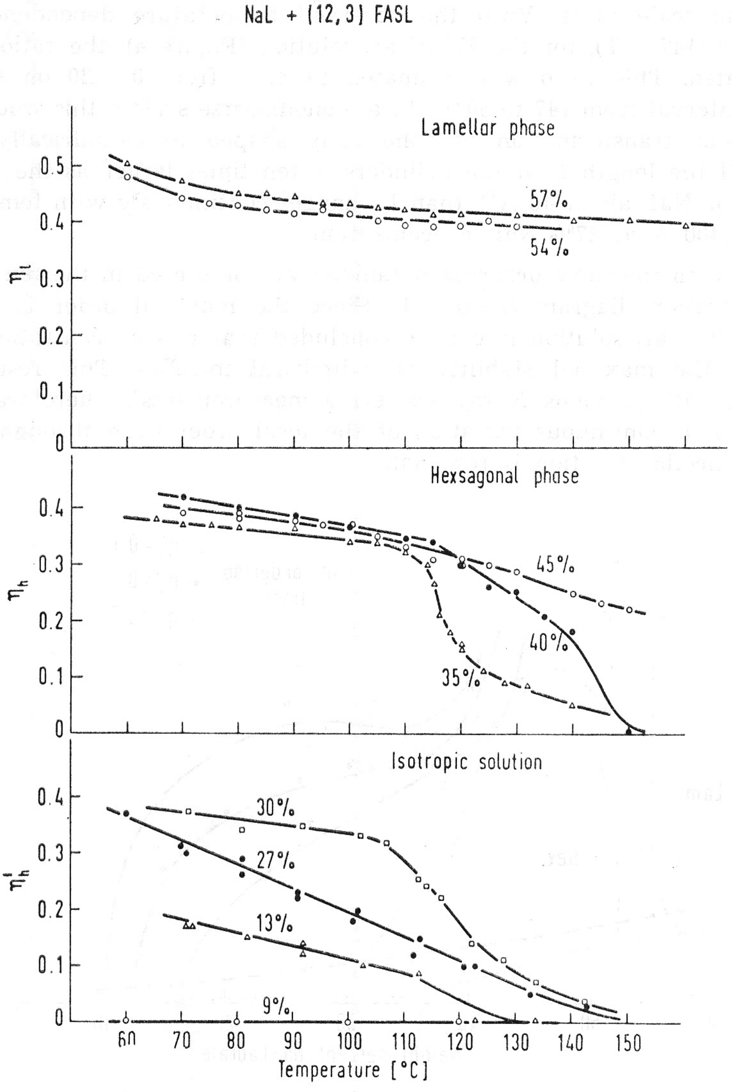

Figure 4. Temperature dependence of the order parameter of (12.3) FASL molecules dissolved in the NaL-water system.

of length L are ended with spherical caps with radius r, the relation between the measured order parameter η'_h, and the micellar order parameter η_m is

$$\eta'_h = \eta_m \frac{L}{2r + L} \tag{3}$$

Assuming that the local order parameter decreases continuously by going from hexagonal to micellar solution, the local micellar order parameter η_m was extrapolated from the hexagonal phase temperature variation of the order parameter (Figure 4). $\eta_m = 1.5 \cdot 10^{-3} (330 - T)$, where T denotes temperature in absolute scale units. With the observed temperature dependence $\eta'_h = 4.2 \cdot 10^{-3} (147 - T)$, for the 27% NaL solution (Figure 4), the ratio L/r can be calculated. This ratio was estimated to vary from 0 — 20 on the temperature interval from 147 to 60 °C. In a monodisperse system this would mean a continuous transformation of spherically shaped to cylindrically shaped micelles. If the length L of the cylinders is ten times larger as the diameter which is for NaL about 40 Å[13], than L changes continuously with temperature from 0 to 400 Å at 27% NaL concentration.

Lines with the same ordering parameter are presented in the temperature — concentration diagram (Figure 5). Since the maximal order is observed for the 27% NaL solution is can be concluded that this concentration region represents the maximal stability of cylindrical micelles. This result is in agreement with previous X ray scattering measurements[2]. Therefore the assumption of a continuous variation of the local order even through the cylindrical micellar solution is reasonable.

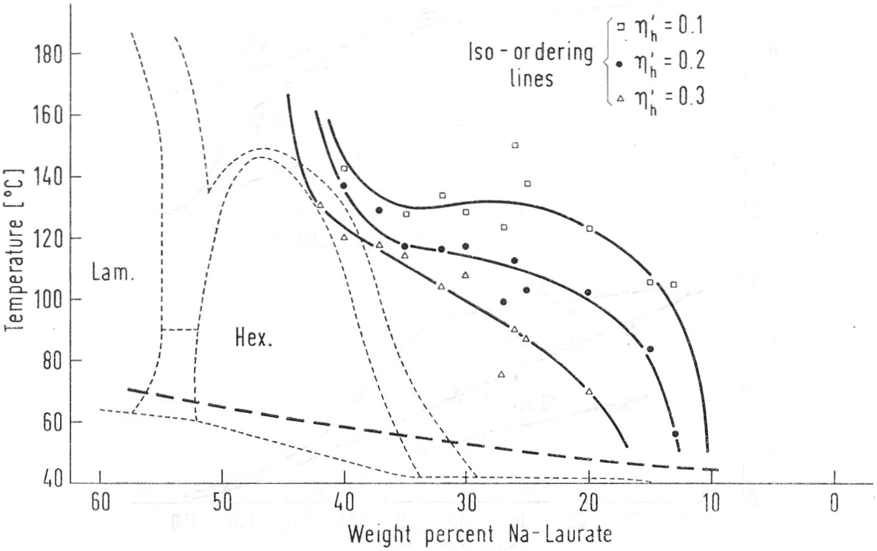

Figure 5. Lines of the same order parameter value η_h represented in the temperature-concentration diagram for the micellar solution. The fine dashed lines show a part of the NaL-water system phase diagram[14]. The strong dashed line denotes approximately the EPR observed transition to the gel phase.

The 27% NaL solutions show a linear dependence of η'_h with temperature (Figure 4). A similar dependence is also found in the hexagonal phase, for 45% NaL solution. From the phase diagram for NaL-water system[14] (dashed lines in Figure 5) we can see that this concentration range of the hexagonal phase is the most stable. A similar hexagonal cylinder length variation with temperature can be assumed at higher temperatures.

It is important to stress that there is a rapid rotational motion of molecules about the cylinder axes in hexagonal and micellar structures as a result of translational diffusion[3]. Molecular motion about the cylinder symmetry axis was found to be faster than 10^8 sec^{-1}. For comparison the hexagonal phase of 37% potasium oleate was measured with the same spin label. Here only the lamellar type spectrum was observed, indicating that, in this case, the rate of molecular motion about the cylinder axis is lower than 10^8 sec^{-1}. The gross features of the long range order determined lyotropic mesophase structure can be resolved only in systems with high lateral molecular mobility in lipid aggregates. It should be stressed that in the case of slow latteral diffusion the cubic phase can not be resolved by the technique used in this work.

CONCLUSION

Nearly continuous local order parameter variation through the whole liquid crystalline concentration range as well as for the cylindrical micellar aggregates was found. This result supports similar observations for liquid crystalline phases of potassium laurate[3], with the exception that no cubic phase spectra were resolved in our NaL measurements.

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IZVLEČEK

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Z metodo elektronske paramagnetne resonance smo študirali lokalno ureditev lamelarne in heksagonalne mezofaze ter micelarnih agregatov sistema natrijev lavrat-voda. Uporabili smo spinski označevalec — nitroksidni radikal, vezan na stearinsko kislino — topen v hidrofobnem področju sistema.

Ugotovili smo, da se ureditveni parametar spreminja zvezno po celem koncentracijskem in temperaturnem območju mezofaz ne glede na fazne prehode.

Iz izmerjenih lokalnih ureditvenih parametrov valjastih micel smo ocenili dimenzije micel pri različnih temperaturah in koncentracijah. Določili smo področje maksimalne stabilnosti valjastih micel in ga primerjali s področjem maksimalne stabilnosti heksagonalne faze.

Ocenili smo, da je hitrost rotacije molekul spinskih označevalcev okrog osi valjev heksagonalne faze pri 100 °C večja od 10^8 sek^{-1}.

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Prispjelo 7. srpnja 1975.