

this minor constituent make it uncertain whether the differences are real.

The quantity and types of acyl substituents on the sialic acid residues may also be different in the four orosomucoids studied because the analytical methods used do not yield information on this point. The same reservation applies to glucosamine but in this case the general occurrence of *N*-acetylglucosamine makes such differences less likely.

A comparison with other species (Table 2) shows that orosomucoid from chimpanzee has a carbohydrate composition very similar to the preparations analysed in this investigation whereas orosomucoids from rabbit and rat have distinctly higher and lower carbohydrate content, respectively.

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Ion Binding in Liquid Crystals Studied by NMR IV.* ²³Na NMR of Macroscopically Aligned Lamellar Mesophases

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Recently it was demonstrated^{1,2} that the ²³Na NMR spectrum of two anisotropic lyotropic liquid crystalline phases consists of three equally spaced peaks, reflecting static quadrupolar interactions. In these cases a first order quadrupole splitting was observed. Previously, in a similar liquid crystalline phase, also second order quadrupole effects have been reported.³ Furthermore, first order quadrupole splittings with ⁷Li⁺ and ²³Na⁺ NMR have recently been reported⁴ for hydrated oriented deoxyribonucleic acid (DNA) fibers. We are currently investigating ionic quadrupole splitting and relaxation in lyotropic mesophases in our laboratories with the purpose of getting a better understanding of the binding and motion of small ions in liquid crystals and biological model membrane systems. Quadrupole splittings for a large number of nuclei such as ⁷Li, ¹⁴N (as NH₄⁺), ³⁵Cl⁻, ³⁷Cl⁻, ³⁹K⁺, ⁷⁹Br⁻, ⁸¹Br⁻, and ¹³³Cs⁺ have been observed. Except for F⁻ (¹⁹F has no quadrupole moment) the method is thus generally applicable to the study of alkali and halide ions. A report concerning investigations on unoriented systems will be given shortly. In the present communication macroscopically aligned mesophases will be considered and experimental observations with the lamellar mesophases of the ternary systems sodium octanoate/decanol/water and sodium octanoate/octanoic acid/water will be presented. (Phase diagrams for these systems have been presented by Ekwall⁵.) Previously, proton,⁶ and deuterium^{7,8} magnetic resonance and proton pulsed NMR measurements⁹ have been performed on oriented liquid crystalline lyotropic phases.

The samples were prepared by mixing the appropriate amounts of the components in sealed test tubes above the transition to

*For part III. See Ref. 1.

amorphous liquid state. Macroscopical orientation of the mesophases was accomplished by smearing out small amounts of the unoriented mixture onto pieces of microscope cover glasses (about 12×24 mm). The glasses (25–30 in each sample) were pressed together in moving the glass plates. The samples were then left for at least a week before the measurements were performed. The ^{23}Na wide-line NMR investigations were made using a Varian Associates V-4200 spectrometer equipped with a 12 inch V-3603 magnet and a Varian Mark II Fieldial. The sample temperature was $27 \pm 2^\circ\text{C}$. The derivative of the NMR absorption curve was observed as a function of the angle between the magnetic field and the glass plates. Typical spectra given in Fig. 1 demonstrate the angular dependence of the signal pattern.

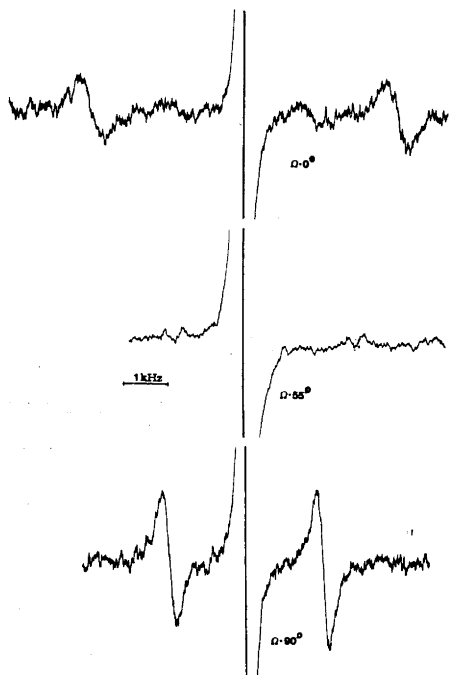


Fig. 1. ^{23}Na NMR spectra of an oriented lamellar mesophase at different angles Ω between the applied magnetic field and a direction perpendicular to the glass slides. The composition of the lamellar mesophase was 48.5 % sodium octanoate, 23.9 % octanoic acid, and 27.6 % water (concentrations in percent by weight). Temperature $27 \pm 2^\circ\text{C}$.

^{23}Na nuclei with spin quantum numbers, I , equal to $3/2$ possess electric quadrupole moments, which can interact with surrounding electric fields. For nuclei located in an asymmetrical environment, this quadrupole interaction splits the NMR signal into an unshifted central ($m = \frac{1}{2} \rightarrow m = -\frac{1}{2}$, m being the magnetic quantum number) resonance at the Larmor frequency, ν_0 flanked at equal intervals by $2I - 1$ satellites. If second order effects are considerable the central line is also shifted.^{3,10} The separation between the outer peaks, Δ in the ^{23}Na NMR spectrum is given for a mesophase by the expression:^{3,10,11}

$$\Delta = p\nu_0 S(3 \cos^2 \Omega - 1) \quad (1)$$

where p is the fraction of sodium nuclei in a site with asymmetrical environment (*i.e.* with static quadrupolar interactions) and ν_0 is given by $\nu_0 = e^2 q Q / 2h$. e is the electron charge, Q the nuclear quadrupole moment, q is the largest of the components of the electric field gradient tensor in the principal axes system and h Planck's constant. Ω is the angle between the external magnetic field, B_0 , and the preferred orientation in the mesophase and S the order parameter.

In Fig. 2 the observed quadrupole splitting, Δ is plotted as a one-parametric function of the angle Ω , the angle between the magnetic field and a direction perpendicular to the glass slides. As may be

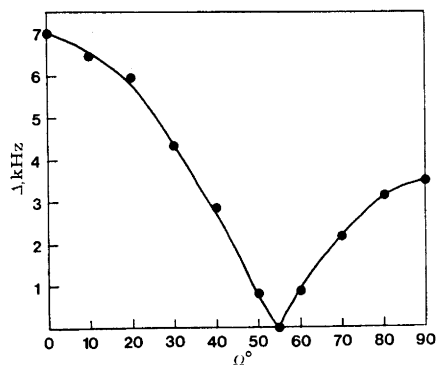


Fig. 2. ^{23}Na quadrupole splitting, Δ as a function of the angle Ω , defined in Fig. 1. The same sample as in Fig. 1 was used. The solid line represents the function $(3 \cos^2 \Omega - 1)$ (*cf.* eqn. (1)).

inferred from this figure, Δ is proportional to $(3 \cos^2 \Omega - 1)$ (solid line in Fig. 2). This has to mean that the lamellae of the mesophase are oriented parallelly with the glass plates, *i.e.* the alignment in the lyotropic mesophase has cylindrical symmetry about an axis (the director¹¹) perpendicular to the glass slides. In this case S can be derived from the theory given by Luckhurst¹¹ to be

$$S = \overline{D_{0,0}^{(2)}} + (1/\sqrt{6}) \eta (\overline{D_{0,2}^{(2)}} + \overline{D_{0,-2}^{(2)}})$$

where the $D^{(2)}$'s are the second rank Wigner rotation matrix elements¹² averaged over the molecular motion and η is the asymmetry parameter defined in the principal axes system. Thus no assumptions about η (*cf.* Ref. 8) have to be made to explain the angular dependence of the quadrupole splitting. The fact that the observed quadrupole splitting must vanish at $\Omega 55^\circ$ and that $\Delta(0^\circ) = 2\Delta(90^\circ)$ is reflected in Fig. 1.

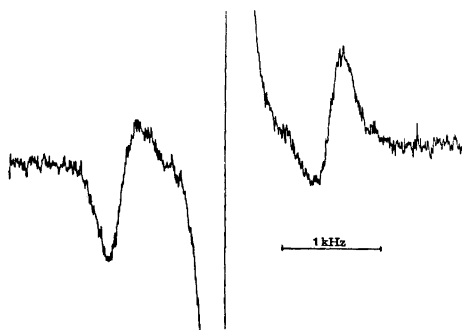


Fig. 3. ^{23}Na NMR spectrum for an unoriented lamellar mesophase (powder pattern). The sample had the same composition as the sample in Fig. 1. Temperature $27 \pm 2^\circ\text{C}$.

The NMR spectrum from an unoriented mesophase sample is a result of the superposition of resonance signals from randomly oriented microcrystallites. Such a spectrum, often called a powder pattern, is traced in Fig. 3. A theory predicts quadrupole splittings from powdered samples¹⁰ to be equal to the splittings obtained from a single crystal oriented with the electric field gradient tensor 90° relative to the applied magnetic field. This appears not to be the case for those liquid crystalline samples examined here by ^{23}Na NMR (*cf.* the data obtained from ^2H NMR in Refs.

7 and 13, where this anomaly was not observed). As a comparison also the water ^2H NMR spectra for the same samples as discussed above, where heavy water was substituted for normal water, were recorded. It was found that the ratio between $\Delta(90^\circ)$ and $\Delta(\text{powder})$ was equal to 1.85 for the deuteron NMR spectra and equal to 1.75 for the ^{23}Na NMR resonance for the same sample. A check was performed to investigate whether any changes in the composition of the sample during the alignment procedure are responsible for the observed difference in the quadrupole splittings. It was found that this cannot be the case, instead a slight decrease in the quadrupole splitting was observed, and in fact it has been shown¹⁴ that ^{23}Na quadrupole splitting decreases when the water and/or decanol contents decrease in this mesophase.

There are two apparent explanations to the difference in $\Delta(90^\circ)$ and $\Delta(\text{powder})$. First, chemical exchange between randomly oriented microcrystallites may affect the spectrum. Second, the order parameter can be different in the two cases, *i.e.* S may be smaller in the unoriented sample due to curved lamellar surfaces. It is not unreasonable to believe that decreases in curvature may occur in the alignment procedure employed. Generally, exchange phenomena are rather temperature-dependent. However, the temperature dependence of the splitting in the two mesophase systems investigated here are extremely different.¹⁴ However, the ratio between $\Delta(90^\circ)$ and $\Delta(\text{powder})$ is about the same in the two systems, so *e.g.* is $\Delta(90^\circ)/\Delta(\text{powder}) = 1.84$ for a sample with the composition 33.5 % sodium octanoate, 32.4 % decanol, and 34.1 % water. Thus it seems more likely that the lamellae are curved and this explanation is also consistent with the fact that the ratios $\Delta(90^\circ)/\Delta(\text{powder})$ obtained for ^2H and ^{23}Na quadrupole splittings are almost the same.

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Note on the Structure of the Gamma Brass Like γ_3 Phase in the Silver Lithium System

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In a research project at this institute the structures of a number of gamma brass like phases have been studied. These phases generally form in systems between a transition metal (T or B^1) according to the nomenclature of Schubert¹) and a non-transition metal from the B^2 – B^4 groups of the periodic table. Several different ordering schemes have been observed for the metal atoms on the atomic sites of the general gamma structure type, which are,¹⁰ in space group $I43m$, those listed in Table I.

A definite tendency has been observed³ for the transition metal atoms to con-

centrate at the OT and OH sites in phases where the transition metal is taken from the T^9 , T^{10} , or B^1 group and the radius ratio $r(B)/r(T$ or $B^1)$ lies in the range 0.95–1.12.

No atomic ordering scheme has, so far, been definitely established for a gamma phase with a non-transition metal component outside the B^2 – B^4 range. In the Ag–Li system there occur three such phases,⁴ all of them cubic. Since silver is a B^1 metal and the radius ratio r_{Li}/r_{Ag} is 1.09, it was deemed to be of great interest to see whether or not the fact that the non-transition metal is in this case taken from another part of the periodic table would lead to the formation of a differently ordered structure.

Experimental. Preparations of the three phases, γ_1 , γ_2 , and γ_3 , homogeneous at room temperature in the approximate ranges⁴ 7–13, 16–23, and 26–36 atomic % Ag, respectively, were synthesized by fusion of the components in argon of atmospheric pressure. Weighed amounts of the materials (Ag, powder, Kebo 99.9 % and Li, granular, Merck, sodium content less than 0.05 %) were melted together in an iron crucible for approximately 15–30 sec, and allowed to cool without quenching. The loss of Li by evaporation was found to be very small, and the final compositions were taken to be equal to those calculated from the amounts of Ag and Li used. The γ_1 and γ_2 preparations were quite sensitive to atmospheric corrosion and were, moreover, soft so that the pellets could not be easily crushed. Thus, the γ_3 -containing charges which were more stable in air, and easier to prepare powder specimens from, were the only ones used for the continued investigation.

X-Ray powder photographs for the determination of lattice parameters were taken in a focusing Guinier-Hägg camera of 80 mm diameter, with strictly monochromatized $CuK\alpha_1$ radiation ($\lambda=1.54050$ Å), and with KCl ($a=6.2919$ Å⁵) as an internal standard.

The diffracted intensities were more accurately determined by means of a powder diffractometer¹¹ employing crystal monochromatized $CuK\alpha$ radiation.

For the calculation of theoretical powder intensities from tentative structure models, Lp-factors were computed according to Sagel,⁶ and the atomic scattering factors and dispersion corrections given by Cromer and Waber,⁸ and Cromer,⁹ respectively, were used.

Results. A preparation which proved to contain γ_3 phase, with only very small