Molecular Dynamics in Lyotropic Mesophases Studied by ^{23}Na NMR and ESR

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The hexagonal phases of sodium octadecanoate–water system NaS and sodium hexadecanoate–sodium tetradecanoate–water system Na(P+M) were studied by sodium-23 NMR and spin label ESR in the temperature range 40—100 °C, covering the transition temperature of isotropic-liquid crystal T_{I-L} and that of liquid crystal-gel T_{L-G}. The ESR spectrum of liquid crystal systems aligned by the magnetic field and the center line of ^{23}Na NMR spectrum were analyzed. The motions of the alkyl chain and sodium ion are reflected on the ESR and NMR spectral shape and width. The NMR line width is predominantly determined by the local motion of the cation attached on the hydrocarbon rod. During the phase separation region its correlation time $\tau_c \simeq 10^{-10}$ s is constant, comparable to that of chain motion. The change in the local motions of these two species is similar, being continuous across T_{I-L} but drastic across T_{L-G}.

Many studies on the lyotropic liquid crystal including biological systems have been carried out by spectroscopic measurements. For example, the properties of the hydrocarbon chain have been studied by ^{1}H, ^{2}H NMR, and spin label ESR.[1a-1j] NMR of sodium-23 and other alkali metal ions has been utilized for the analysis of cation binding in soap–water systems.[2a-2f] Most works have been performed by changing the concentration of components. For the study of molecular dynamics in lyotropic systems around the phase transition or phase separation point, a continuous observation through the transition point is important and variable temperature measurement is essential. Furthermore, a comparison between the dynamical properties of hydrophobic and hydrophilic parts of the amphiphile molecules especially near these transition points will give important information on the mechanisms of biological phenomena. In the present work the dynamical properties of hydrocarbon chain and counter ion in hexagonal phase of lyotropic systems have been studied through phase transition points by means of magnetic resonance.

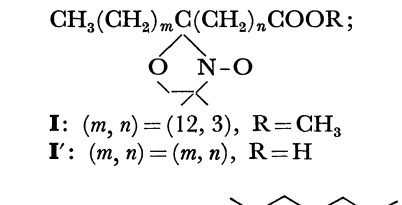
We have observed the temperature dependence of sodium-23 NMR and spin label ESR of lyotropic liquid crystals, sodium octadecanoate–water (NaS) and sodium hexadecanoate–sodium tetradecanoate–water (Na(P+M)) systems, in the range covering the isotropic liquid-liquid crystal and liquid crystal-gel transition temperatures, T_{I-L} and T_{L-G}, respectively. Choice of the soap systems and their phases is made in order to make stable lyotropic liquid crystals of low transition temperatures. The concentrations of the soaps are adjusted to form hexagonal liquid crystals of T_{I-L} below 90 °C so that the liquid crystals can be aligned under the static magnetic field below 100 °C. The use of the systems of low transition temperatures enables us to measure the spin label ESR throughout the transition temperatures including even the liquid crystal alignment by magnetic field with no noticeable label decomposition. Otherwise, the label is rapidly lost in the slightly alkaline medium above 100 °C. The ^{23}Na NMR and spin label ESR of the system through the transition points were observed continuously.

Experimental

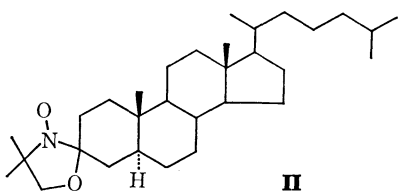
Samples. The soaps (sodium octadecanoate, hexadecanoate, and tetradecanoate) were prepared from reagent grade acids (purity 99%, Wako Chemicals Co.) by NaOH titration and reprecipitated from hot water. The sodium octadecanoate mixture used for NMR measurement was obtained as sodium salt (Kishida Chemicals, Co.) the purity being determined by gas chromatography : 70% octadecanoic, 27% hexadecanoic, and 3% of tetradecanoic and eicosanoic acids.

The sample for NMR measurement was prepared in a 10 mm OD tube with a silicone rubber stopper, being made homogeneous by repeated cooling and heating. The space between the sample mixture and stopper was kept small in order to prevent the evaporation of water. In the case of sodium octadecanoate system, the space above the sample mixture was not small as compared with sample volume so that the homogeneity of the sample might not be satisfactory. The concentration of the mixture was determined by weighing before and after each NMR measurement.

The sample for ESR measurement was prepared in a similar way with appropriate spin probe molecules, **I**, **I′**



I: $(m, n) = (12, 3)$, $R = CH_3$
I′: $(m, n) = (m, n)$, $R = H$



II

(12,3), **I′**(5,10), **I′**(1,14), and **II** (Syva), then sucked up in a capillary tube of about 1 mm diameter, both ends of capillary being sealed. Only the tubes with good sample homogeneity were used. The concentration was determined by means of isotropic-liquid crystal transition points.

The phase transition temperatures T_{I-L} and T_{L-G} were determined by laser light depolarization and scattering. The temperature for both NMR and ESR measurements was initially set above T_{I-L} in order to bring the sample to com-

plete isotropic solution, then slowly changed downwards and spectra were taken 30—60 min after each temperature setting.

NMR Measurement. For the measurement of ^{23}Na NMR signals, a JEOL PS-100 electromagnet with ^{1}H external field lock system was used with 26.45 MHz home made detector systems. Free induction decay (FID) signals were averaged 1000 times and subjected to Fourier transformation with a JEOL EC-6 or EC-100 computer. An average of three observations was taken for each temperature setting. The uncertainty in the shift data for continuous observation was within ± 0.012 ppm over a period of three days. The temperature was controlled by heated air flow (*ca.* 20 l min^{-1}). The temperature distribution across the sample was within ± 0.2 °C.

The half full width of the Fourier transformed signal was taken as the line width and the half full width times the peak height as the measure of intensity. No correction was made for intensity due to the change in the sample density at various temperature nor for the delay time (200 μs) of FID sampling. The maximum line width observable by the present instrumental setting is 500 Hz which has ample allowance for the observed width of the center line of up to 60 Hz. No ^{23}Na satellite for oriented molecules is to be detected under these experimental conditions. ^{23}Na signals of 1.1 M NaCl and 0.8 M sodium acetate aqueous solutions were taken as references.

ESR Measurement. The X-band ESR spectra of nitroxide spin probes were taken with a JEOL JES ME-X spectrometer with temperature control system JEOL JES VT-3. The variation in temperature at each setting was within ±1 °C. The sample capillary was set perpendicular to the magnetic field so that it can easily be rotated around its axis for observation of the effect of magnetic field alignment of the amphiphile systems. Microwave power of 1.0—1.5 mW and 100 kHz field modulation of 1.0 G amplitude were used.

Results

The phase diagram of Na(P+M) system is constructed by laser light depolarization and ESR and NMR spectra (Fig. 1). It is similar to that of NaS system and its analogs such as NaP, NaM, NaL(sodium dodecanoate–water) systems with some depression in

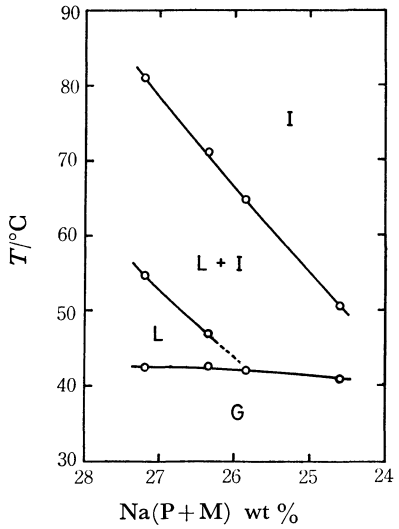


Fig. 1. Phase diagram of Na(P+M) system.

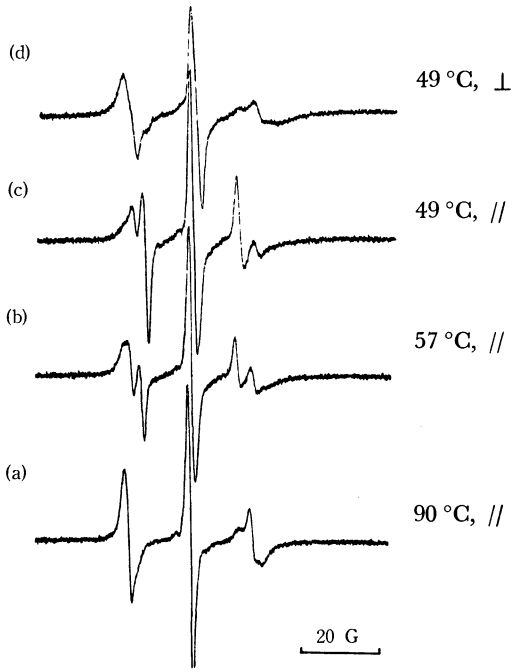


Fig. 2. ESR spectra of label **I** in Na(P+M) 27% system.

the transition point T_{I-L} as compared with that of the corresponding carbon number.

The ESR spectra of label **I** in the system of 27 weight percent aqueous solution of the equal weight mixture of sodium hexadecanoate and sodium tetradecanoate (abbreviation Na(P+M) 27% likewise will be used hereafter) is shown in Fig. 2. The spectrum above T_{I-L} consistes of one triplet due to ^{14}N hyperfine coupling constant of 14.9 G. The spectrum below T_{I-L} seems to be a superposition of two triplets: one with the coupling constant A_{iso} of 14.9 G arising from the isotropic phase and the other with a smaller coupling constant of 11.8 G from oriented molecules. The order parameter of the z axis, the direction of the largest hyperfine splitting (radical axis), for the oriented label **I** can be given by

$$S = (1/2)\langle 3\cos^2\theta - 1\rangle = (A_{//} - A_{\perp})/(A_{zz} - A_{xx})$$
$$= (3A_{//} - 2A_{xx} - A_{zz})/2(A_{zz} - A_{xx}) = -0.19,$$

where $A_{//}$(11.6 G) is the observed coupling constant, A_{xx}=6.1 G, A_{zz}=32.4 G,[1f] and θ is the angle between the radical axis and the static magnetic field. The spectral intensity of the oriented molecules increases and that of the isotropic phase decreases towards T_{L-G}. The line widths of these signals seems to be constant throughout the liquid crystal region. Below T_{L-G}, a sudden signal broadening is observed and the spectrum changes gradually to that of solid towards lower temperature.

The spectrum of label **I** in Na(P+M) 27% system with the sample capillary rotated by 90° in the magnetic field under the conditions of fixed molecular alignment below T_{I-L} shows a larger coupling constant $A_{\perp}$ than isotropic ones (Fig. 2d).

Because of high T_{I-L} of NaS system, the spin labeled compounds decompose when the sample preheating is sufficient enough to equilibrate the system in the

isotropic phase. The ESR experiment of NaS system was carried out only for the purpose of confirming whether the molecular arrangement is of similar type to that of Na(P+M) system in liquid crystal region.

The line widths, intensities, and chemical shifts of ^{23}Na NMR signals of Na(P+M) 25.9, 26.4, and 27.2% systems and NaS 17.1% and 20.0% systems were observed at various temperatures. The results of Na(P+M) 26.4, 27.2, and NaS 20.0% systems are shown in Figs. 3, 4, and 5. The temperature dependence of linewidths and intensities of these five samples are of the same type.

The linewidth in the isotropic region increases towards T_{I-L} with fall in temperature. The Arrhenius plot of the width gives the activation energy for the reorientational motion of ion or the fluctuational motion of the environment of the sodium ion provided that the motional narrowing condition is satisfied in the isotropic region. The activation energie is 18.0—20.0 kJ mol^{-1} for NaS systems and 14.6—16.8 kJ mol^{-1} for Na(P+M) systems. The signal intensity is constant in this region.

In the liquid crystal region, $T_{I-L} > T > T_{L-G}$, the line width remains constant till it starts to increase at T' ($T' > T_{L-G}$). The signal intensity decreases distinctly between T_{I-L} and T' and approaches asymptotically to about 40% of its isotropic value, while the width remains constant, keeping the 40% value till the phase transition temperature T_{L-G} is reached. The effect of sample rotation on the center line width

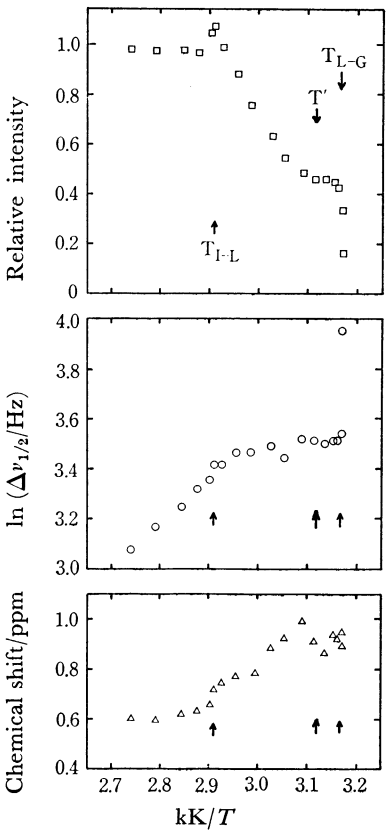


Fig. 3. ^{23}Na NMR parameters plotted against $1/T$ for Na(P+M) 26.4% system. The chemical shift is measured from an arbitrary point and its increasing number means an high field shift.

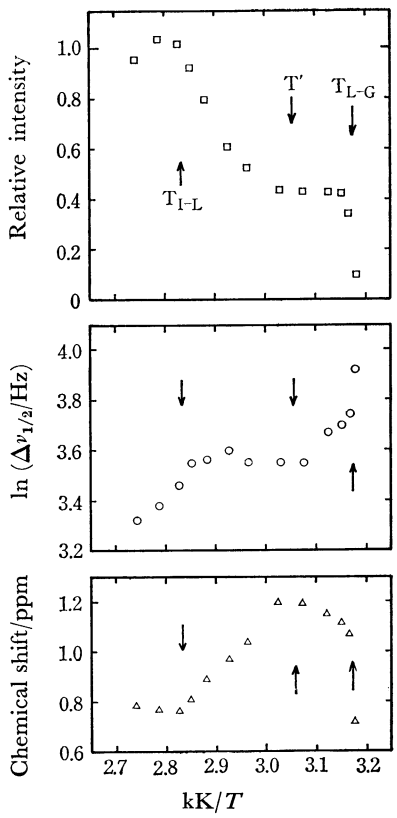


Fig. 4. ^{23}Na NMR parameters plotted against $1/T$ for Na(P+M) 27.2% system.

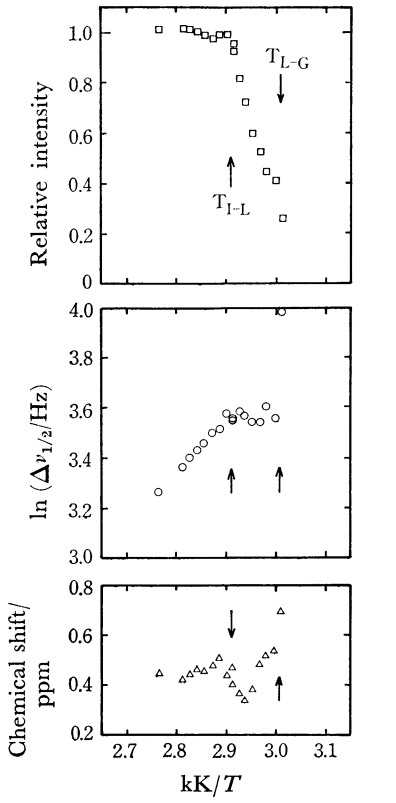


Fig. 5. ^{23}Na NMR parameters plotted against $1/T$ for NaS 20.0% system.

is expected to be negligible, neither linewidth change nor line distortion being observed.

When the temperature is set at T_{L-G}, the line width increases abruptly and the signal becomes undetectable within a few hours as the sample solidifies. No signal in the gel state could be observed.

The temperature dependence of the chemical shift of NaS system and that of Na(P+M) system are not alike. However the data within each system has a similar aspect.

Discussion

ESR Spectrum. The label **I** ESR signal in the isotropic phase is a triplet with the coupling constant A_{iso} of 14.9 G. However, the peak heights of the three lines are not the same, indicating that the phase is a micellar solution as expected. An extra small signal observed at 90 °C in the high field region is probably due to the molecules near the air- and/or glass-sample interface which tends to align while the bulk is still in isotropic state.

Two sets of triplets observed between T_{I-L} and T', one with the coupling constant of isotropic and the other of oriented state, indicates that the system is in the coexistence region of isotropic and liquid crystal phases. The variation in their relative intensities with temperature between T_{I-L} and T' is a further indication of the two phase region. The spectrum of the oriented label is comparable to that of a spin label in shear oriented hexagonal rods observed by Seelig and Limacher.[11] The order parameter S found for the oriented radical axis -0.19 is also that of the molecular axis since the direction of p electrons on N atom in the molecule **I** is parallel to the long axis of the molecule in all its trans configuration. The value $S=-0.19$ can be easily interpreted in terms of the hexagonal phase in which molecules aggregate to form rods with the rod axis parallel to the static magnetic field. The order parameter of a fictitious molecule, with the arrangement $\theta=\pi/2$ and no fluctuational motion of the molecular axis, should be -0.5. The difference between -0.5 and -0.19 is presumably due to the fluctuational motion of the chain and to a slight tilt of the radical axis or that of the molecular axis itself from the normal of the rod surface. The evidence for a magnetic field alignment of rods is obtained from the coupling constant. (1) The coupling constant $A_\perp$ of label **I** observed with sample rotated by 90° is large; $A_\perp(\text{obsd}) > A_{iso} = 14.9\text{ G} > A_{//}(\text{obsd}) = 11.8$ G. The spectrum is consistent with the calculated coupling constant $A_\perp = 16.5$ G for the rod structure with the rod axis perpendicular to the static magnetic field. (2) The spectrum of label **II** whose radical axis is perpendicular to the molecular axis is also consistent. The order parameter of the molecular axis in Na(P+M) calculated from the observed coupling constant 17.5 G and known constants $A_{xx}=6.1$ and $A_{zz}=32.1$ G[1f] is -0.3. The higher order found for molecular axis of label **II** than for label **I** is probably due to more rigid nature of the labeled molecule **II** itself.

The orders observed for the label **I**′(5, 10) and **I**′(1, 14) are lower than that of **I** and **I**′(12, 3), decreasing with the increasing distance between nitroxide group and the carboxyl group. Such a tendency is in line with the liquid crystal structure where the polar group is fixed at the surface of the rods, and resembles that observed in the chain motion in parallel bilayers of lyotropic systems.[1d,g]

The ESR line width is narrow, not changing with temperature in the liquid crystal region. A reasonable interpretation is that the motion of the chain in amphiphilic molecules is rapid enough[3] to average out the θ distribution, leaving only the effective $\langle\cos^2\theta\rangle$ in the spectrum. The increase in line width below T_{L-G} is due to that in rigidity of the chain and in the restriction of molecular rotation around its molecular axis.

No attempt was made to evaluate the equilibrium proportion of liquid crystal *vs.* isotropic liquid in the phase separation region from the apparent intensity of oriented molecules by two reasons. (1) A rather high proportion of molecules is in glass-sample interface of the capillary where the effect of the glass surface on the liquid crystal orientation should be considerable. (2) It is probable that the molecules turning into liquid crystal when their large porportion is already in an array of liquid crystal might not find ample space to form the rod in its preferred orientation along the magnetic field. The following result supports the above argument. No signal for reoriented molecule is detected 1 h after the sample capillary rotation by 90° in the static field at 55 °C while the molecular reorientation is confirmed 10 minutes after the sample rotation at 67 °C, 4 degrees below T_{I-L}, where the liquid crystal is only partly formed.

NMR Spectrum. The factor which determines the NMR line shape and relaxation times of spin 3/2 nucleus ^{23}Na is mainly the interaction between nuclear quadrupole moment Q and the electric field gradient at the nucleus expressed by a tensor $\boldsymbol{q}$.[4] The spin dipolar interaction between ^{23}Na and ^{1}H in the nearby water is negligible unless the system is almost rigid. The following discussion is based on the predominant contribution of the quadrupole interaction to the ^{23}Na spectrum.

Signal Intensities: The constant signal intensity in the isotropic phase has a value similar to that of the free ions in NaCl and in sodium acetate aqueous solutions of corresponding concentrations. No signal intensity is lost in satellites (*vide infra*).

In the liquid crystal region, the signal intensity decreases to 4/10 of isotropic value towards T' ($T' > T_{L-G}$). The phase of isotropic and liquid crystal coexistence has been known for NaS, NaP, and NaM systems in between isotropic and pure liquid crystal phases. The presence of such a phase is also demonstrated for Na(P+M) system by our ESR experiment. Gradual decrease in the NMR intensity is also an evidence of this phase. The loss of intensity is caused by the quadrupole splitting of the signal components m_s: 3/2→1/2 and m_s: −1/2→−3/2 with 3/10 of total intensity for each by the frequency $\pm\nu_Q S$, where $\nu_Q = e^2qQ/2h$, q is the principal value of the electric field gradient tensor $\boldsymbol{q}$ at the ^{23}Na nucleus, and S is the

order parameter for the principal axis of **q**, when the correlation time for the rod tumbling motion becomes longer than $(2\pi\nu_Q S)^{-1}$ by the liquid crystal formation.[4] The satellite would be out of our experimental frequency range. Evaluation of micelle tumbling rate necessary to collapse the quadrupole splittings may be helpful. The observed quadrupole splittings $\nu_Q S$ for lamellar NaL[2f] and NaP[2e] systems are 25—30 KHz. The splitting for hexagonal phase can be a half of these values[2c] or less, since the area per polar group is larger in hexagonal phase than in lamellar phase, suggesting a lower ordering. Thus $\nu_Q S$ can be estimated to be 15 kHz or less. The calculated correlation time for tumbling motion $\tau_\perp$[5] of a rod with its short axis $a=20$ Å[6] at 60 °C is 5×10^{-6} s, if the long to short axis ratio $b/a=25$, which is just short enough to average out the splitting of 30 kHz. A rod motion under the same conditions except for $b/a=50$ gives $\tau_\perp=4\times10^{-5}$ s, which satisfies $2\pi\nu_Q S\tau_\perp\simeq1$ for $\nu_Q S=4$ kHz. The rotational motion of a rod around the rod axis is also effective to collapse the splitting if the rod is not aligned parallel to the magnetic field, the motion being faster than the tumbling motion. Therefore, Na ion attached to the rod in free state, *i.e.* in the isotropic part, has a motion sufficiently fast to give a single signal even below T_{I-L}, while the ion on the rod in the aligned domain gives satellite signals.

The constant intensity 4/10 of the total in the range $T'>T>T_{L-G}$ indicates that the phase is purely liquid crystalline.

Spectrum Analysis: The line width remains constant while the liquid crystal is equilibrated with isotropic liquid($T_{I-L}>T>T'$). The intrinsic widths of both liquid crystal and isotropic parts should be indistinguishable since the width of the superposed signal is constant irrespective of a drastic composition change. A rapid local motion[2d] should be effective for determining the line width in both cases in order to meet the requirement that the width is the same regardless of the presence of a rod motion. In this case the line width is determined by the relation[1d,4]

$$\begin{aligned}1/T_2 &= (8\pi^2\nu_Q^2/5)f(\tau_c)\\ &= (8\pi^2\nu_Q^2/5)[\tau_c+(5/3)\tau_c(1+\omega_0^2\tau_c^2)^{-1}\\ &\qquad +(2/3)\tau_c(1+4\omega_0^2\tau_c^2)^{-1}],\end{aligned}\tag{1}$$

where τ_c is the correlation time for the local motion which changes the direction of the principal axis of **q**. The estimated value $\nu_Q=100$ kHz[7] is used to evaluate $f(\tau_c)$ for the observed width of 25—40 Hz. The result of $f(\tau_c)=1.4$—2.5×10^{-10} s and $\omega_0=1.6\times10^6$ s^{-1} leads to the extreme narrowing condition $f(\tau_c)=\tau_c$. The rapid local motion seems to be a wobbling motion of the principal axis of **q** for the following reasons. First, the correlation time for the local chain motion is of the same order as determined by deuterium NMR of β-CD_2 group in potassium hexadecanoate-water lamellar phase[1d] ($\tau_c\simeq10^{-10}$ s) and by the present ESR experiment ($10^{-10}\simeq\tau_c<10^{-9}$ s). Second, the observation that the order parameters and their temperature dependence of chain part and of Na^+ ion are comparable[2e,f] suggests that the Na^+ ion whose hydrated water is hydrogen bonded to carboxyl group moves as the chain moves around its equilibrium direction. The reported values of the quadrupole splittings 28—36 kHz for α-CD_2 deuterium NMR and 18—27 kHz for ^{23}Na NMR of unoriented lamellar NaL[2f] and NaP[2e] systems give the order parameters 0.11—0.14 with $\nu_Q(D)=(3/2)e^2qQ/h=250$ kHz[1d] for α-CD_2 and 0.18—0.27 with $\nu_Q(Na)=100$ kHz for Na^+. The former is about 1/3 of calculated value 1/2—1/3[2e] and the latter is about 1/4 of the calculated maximum value 1. The values of order parameters for D and Na are comparable and the observed to calculated ratios for both cases can be regarded to be similar.

The ion exchange phenomenon between rod sites or between a rod site and free state can also be considered as a mechanism of nuclear relaxation.[2a] However, the same ion exchange rate should be assumed for free and aligned rods in the liquid crystal domain in order to explain the common width for both states. This is not appropriate. The exchange phenomena, although not completely ruled out, can not be taken as an important mechanism.

Before concluding that the fast local motion contributes to the line width of the center line predominantly, it should be pointed out that the comparison of T_2 with T_1(Na) would confirm this point since the contribution of local motion to T_1 is dominant.

The broadening of the center line in the region $T'>T>T_{L-G}$ may be caused by the decreased local motion and to a certain extent by the onset of second order shift of the center line expressed by

$$\nu^{(2)} = (3/16)(\nu_Q^2/\nu_L)(\cos^2\theta-1)(9\cos^2\theta-1),\tag{2}$$

where ν_L is the Larmor frequency and θ is the angle between the principal axis of **q** and the direction of static magnetic field. The second order shift can contribute to the line width when there is appreciable distribution in θ. The constant term of (2) is 70 Hz when ν_Q is 100 and 1.8 kHz when it is 500 kHz.[2b] Since there is no observable line distortion, the signal must be the results of a time average of $\nu^{(2)}$ under the decreased local motion of **q** principal axis around θ_0, the ensemble average of θ, which is 90° for hexagonal phase unless the ion binding is in bridged form or there is some chain tilt. The average value of $\nu^{(2)}$ should appear on the chemical shift. A simple trial calculation of the θ dependent term of (2) under the conditions of uniform θ distribution[8] around θ_0 (90°) in the range between $\theta_0-\alpha$ and $\theta_0+\alpha$ shows that $\nu^{(2)}$ is a sharp function of ordering:

$$\delta(\alpha) = \langle(\cos^2\theta-1)(9\cos^2\theta-1)\rangle_\alpha,\tag{3}$$

$\delta(0)=1$(distribution around θ_0 is 0), $\delta(37°52')=0$, and $\delta(90°)=-0.53$, as shown in Fig. 6. The observed temperature dependence of chemical shift of Na(P+M) and NaS systems are not monotonous, showing no resemblance to each other at low temperature. A possible explanation for the different behavior in the two systems can be found in a slight difference in the ordering. At $T\simeq T_{L-G}$, where the local motion started to be highly restricted, the difference in shift behavior shoud be amplified. The equilibrium position $\theta_0=90°$, which gives the highest order for the hexagonal phase, takes $\nu^{(2)}=(3/16)\nu_Q^2/\nu_L$ giving rise to a low field shift. The present result

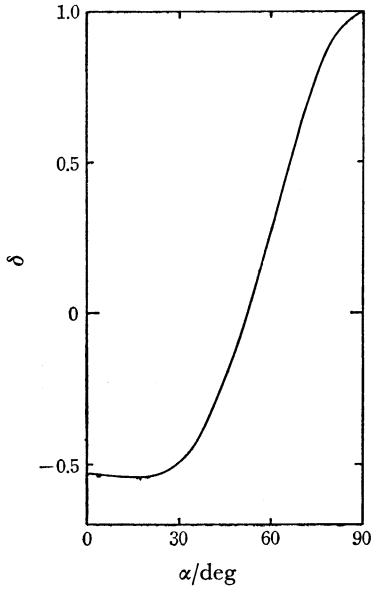


Fig. 6. Plot of $\delta(\alpha)$ against α.

	observed shift near T_{L-G}	ordering detected by ESR
Na(P+M)	low field shift	good
NaS	high field shift	poor

is explained by the difference in the ordering.

It is of importance to point out the possibility of evaluation of $\langle\cos^4\theta\rangle$ from shift data since a comparison of $\langle\cos^4\theta\rangle$ and $\langle\cos^2\theta\rangle$ can give information on the orientational direction θ_0 and the amplitude of orientational fluctuation separately, while $\langle\cos^2\theta\rangle$ available from the first order splitting of ^{23}Na satellite lines or from ESR parameter, alone gives the combined effect of these two factors.

In the gel phase, $T_{L-G} > T$, the θ distribution in (2) may be effective under the diminished time averaging effect of local motion, a contribution of the dipolar interaction bringing about further broadening.

The behavior of Na^+ ions in the Na(P+M) and NaS systems is obviously different from that of free ions even in the isotropic region, $T > T_{I-L}$. The widths of hydrated free Na^+ ions in 1.2 M NaCl and 0.8 M sodium acetate solutions are 3 and 4 Hz at 70 °C, respectively, being much narrower than those of Na(P+M) and NaS systems, 22—30 Hz (70—92 °C) and 26—36 Hz (72—89 °C), respectively. The apparent activation energies obtained by simple Arrhenius plots of these widths are 8 and 11 kJ mol^{-1} for NaCl and sodium acetate solutions while they are 16 and 19 kJ mol^{-1} for Na(P+M) and NaS systems, respectively. It is thus not probable that all or even the large portion of the counter ion is free in the isotropic region. Since there is no jump in the width at T_{I-L} in changing from isotropic to liquid crystal region, the origin of the line width and its temperature dependence should be found in the model in which all or most of the cations are attached to the micelles. The tensor q of hydrated Na^+ is not susceptible to an appreciable change in this narrow temperature range because of the high charge density at Na^+ ion.[9] The local molecular motion as in the liquid crystal region together with some contribution from a micelle tumbling motion should be responsible for the width. The increasing exchange rate (exchange between micelle sites and between micelle and free ion) at higher temperature might contribute to the apparent activation energy.

Concluding Remarks. The phase diagram of Na(P+M) system, which has not been given so far, is found to be similar to that of NaS, NaP, NaM in the concentration 26—28%. It is shown that the motions of the individual molecules and ions are reflected on the magnetic resonance spectra, and their motions change similarly across the phase trnasition points: the cation has fluctuational motions as the chain in the liquid crystal region. This observation is consistent with that of Abdolall *et al.* observed in the lamellar phase of NaP system.[2e]

The models we present for the observed phases are not completely based on concrete evidence, but they give the only interpretation consistent with both NMR and ESR data. It is desirable to have a better signal to noise ratio for further argument of line widths and shapes. T_1 data and the observation of the satellite signals are also important.

References

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8) The time average of $\cos^n\theta$ is better represented by the form $\int \cos^n\theta \cdot \exp[-V(\theta-\theta_0)/RT]\sin\theta d\theta$ where the potential function $V(\theta-\theta_0)$ takes its minimum value at the equilibrium position θ_0.

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