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Nuclear Magnetic Resonance Studies of Surfactant Mesophases

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Abstract—Nuclear magnetic resonance (n.m.r.) spectroscopy has been used to study smectic and waxy mesophases occurring in surfactant systems. The measurement of n.m.r. line widths as a function of temperature and surfactant concentration in a system containing crystalline, mesomorphic and isotropic phases produces information about the phase diagram of the system. The different kinds of phases are easily distinguished by their line widths but it is not always possible to distinguish different phases of a given type. Line widths of waxy type mesophases in saturated soaps have been found to be sufficiently characteristic of the phase to allow transition temperatures to be determined. Transition temperatures determined by n.m.r. agree well with those determined by other methods. Studies of the neat and middle phases in several systems indicate that the phase structures are probably identical for members of a homologous series of compounds. Neat phase lines are in general wider than middle phase lines and are more sensitive to changes in molecular structure. The length of the hydrocarbon portion of the surfactant molecule appears to be the primary factor determining the widths of the lines from middle phase. Mesophase line widths are found to be only slightly temperature and concentration dependent. N.m.r. lines from mesophases appear to have a characteristic shape. The shape can perhaps best be described as "super-Lorentzian". The widths of n.m.r. lines from mesomorphic phases appear to be almost independent of the bulk viscosity of the systems.

Introduction

The application of nuclear magnetic resonance (n.m.r.) spectroscopy to studies of mesomorphic phases has largely been directed toward systems containing nematic type mesophases.[1] Only a few investigations of smectic[2] and waxy type mesomorphic phases have been made.[3] The lack of structure in the n.m.r. lines arising from the smectic and waxy mesomorphic phases is probably partially responsible for the lack of interest shown them.

This paper discusses some n.m.r. results obtained from surfactant systems which contain both smectic and waxy mesomorphic phases.

Experimental

Standard procedures were used both in the preparation of the systems used in these studies and in the method of obtaining the n.m.r. spectra. In any case where the identification of a mesomorphic phase was in question the identification was made by microscopy.[4] Partial phase diagrams are available for some of the systems included in this investigation.[5]

The method of preparation of one of the surfactants, dimethyldodecylamine oxide, has been described elsewhere.[6] The purity of the batch used in these studies is comparable. The other surfactants were over 98% pure as determined by standard analytical techniques. The mesophases were prepared by weighing the desired amount of surfactant into 15 mm o.d. tubes, constricted in the center to about 2 mm, adding the desired amount of D_2O or H_2O, and then sealing the tubes. A nitrogen atmosphere was used in some cases to avoid pickup of moisture from the air. After sealing, the samples were homogenized by centrifuging them back and forth through the constrictions at slightly elevated temperatures. The mesophase conversion was checked by observing the samples through crossed polaroids. After conversion the samples were transferred to standard 5 mm n.m.r. tubes and again sealed under nitrogen.

The n.m.r. spectra were obtained from either a Varian A-60 spectrometer equipped with a variable temperature probe or from a wide-line spectrometer which has previously been described.[7] In most cases the lines from the mesophases were recorded under the modulation conditions $\nu_m \gg \gamma \Delta H$ and $H_m \gg \Delta H$. Here ν_m and H_m are the frequency and amplitude of the modulation field respectively, ΔH is the line width, and γ is the magnetogyric ratio of hydrogen expressed in units of Hz/gauss. These conditions produce the absorption curve directly.

A polarizing microscope was used for the microscopic observations.

Results

I. Phase Studies

The width of a n.m.r. line is inversely proportional to the amount of motion present in the system producing the line. A typical organic solid usually has a line width somewhere between 10 and 20 G[8] while a liquid such as water has a line only a few milligauss in width. It is obvious then that liquid and solid phases can be distinguished from each other by n.m.r. line width measurements. Mesophases, which are generally believed to be somewhere between solids and liquids in degree of order and perhaps in degree of molecular motion, should have lines which are intermediate in width. If true, it should be possible to distinguish mesophases from liquid and/or solid phases and thereby have a method of determining phase diagrams of systems containing the three kinds of phases.

A. *Sodium Palmitate–Water System.*

The sodium palmitate ($C_{15}H_{31}COONa$)–water system contains not only solid and liquid phases but several different mesomorphic phases. In addition to several waxy type mesophases[9] the system contains both neat and middle phases.[10]

In Fig. 1 the n.m.r. line widths of the sodium palmitate–deuterium oxide (NaP–D_2O) system are shown as a function of the concentration of NaP and of the temperature between 0° and 200° C. The line widths are represented on the vertical axis.

Three primary levels of line width are apparent. These levels can be associated with the various phases in the system. The upper level (widest lines) comes from the crystalline phases. The lowest level, widths about 10–20 mG, comes from the isotropic liquid phase. The intermediate line widths, outlined by the light dashed line, arise from the neat and middle phases. These widths are in the 125 170 mG range.

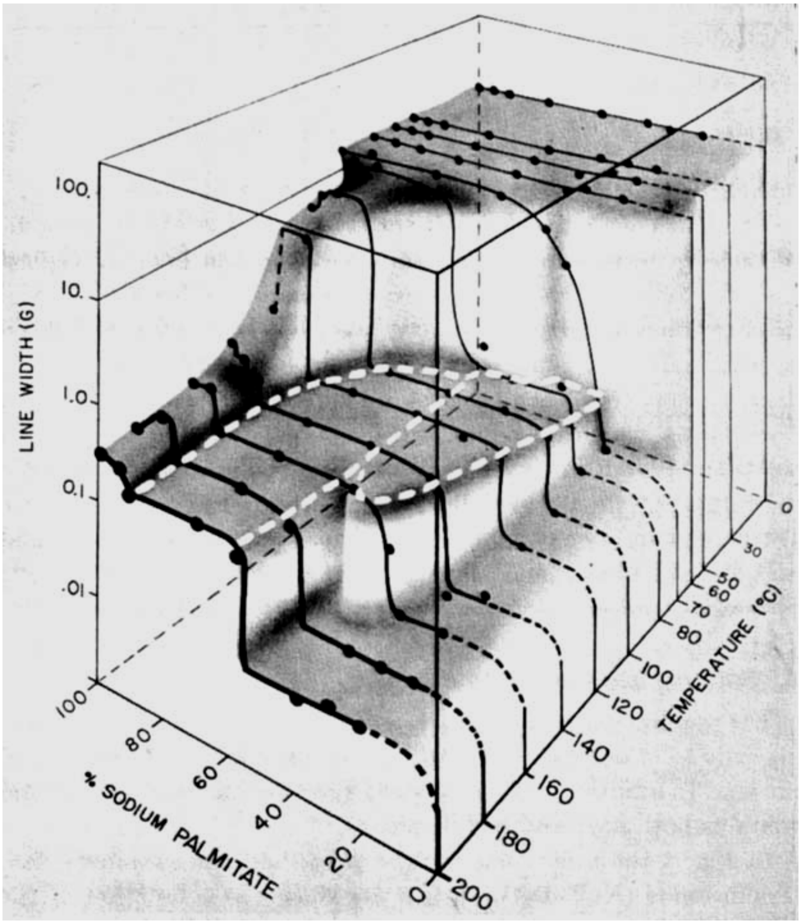


Figure 1. The line width of sodium palmitate in D_2O as a function of temperature and concentration.

In addition to the three primary levels there are widths intermediate between those of the solid phases (10–12 G) and the neat and middle phases. These lines, occurring at high temperature and high concentration of NaP, arise from the waxy type mesomorphic phases. The widths of these lines vary from about 200 to about 550 mG and are in the order: subwaxy > waxy > superwaxy.

Figure 1 indicates quite clearly that n.m.r. line width measurements can be used as an aid in determining the phase diagram of a system containing crystalline, mesomorphic and/or liquid phases. However, it should be pointed out that the similarity in the widths of the lines from neat and middle phases dictates that extreme care be exercised if the line width measurements alone are used to distinguish between the two phases. Other line parameters such as the second moment and perhaps the shape function should be used to support the width measurements.

B. *Dimethyldodecylamine Oxide–WaterSystem* ($DC_{12}AO$)

Dimethyldodecylamine oxide [$CH_3(CH_2)_{10}CH_2N(O)(CH_3)_2$] is a nonionic surfactant which exists in at least five different phases. In addition to the isotropic liquid phase and the crystalline phase (or phases) there is a middle phase, a neat phase and a third phase which we will designate as viscous isotropic. Neat and middle phases are easily identified by their microscopic textures[4] and were detected in this system by this method. The viscous isotropic phase appears to be similar to a phase found in saturated potassium soaps[11] and in other surfactant–water systems.[12] This phase exists at room temperature in the concentration range from about 60 to about 70% $DC_{12}AO$, which is between the middle and neat regions. It is clear in appearance, stiff and somewhat brittle; in fact, more viscous than either the neat or middle phase.

The n.m.r. lines produced by the non-crystalline phases in the amine oxide system are shown in Fig. 2. The neat and middle phases again have lines which are similar in width, the neat phase lines being slightly wider than the middle phase lines. Both the widths and shapes of the lines from the neat and middle phases are similar to those found in the sodium palmitate system. Crystalline $DC_{12}AO$ line widths are an order of magnitude wider than the lines from the neat and middle phases.

Both the fluid isotropic and the viscous isotropic phases show high-resolution n.m.r. spectra. This type of spectrum is expected, of course, from the fluid phase but in view of the high viscosity of the viscous isotropic phase such spectra are surprising. In another material, diethyldodecylammoniopropanesulfonate, the viscous isotropic phase also shows a normal high-resolution spectrum. Also in this system the phase is very viscous. Evidently in this kind of phase the bulk viscosity of the medium has little effect on the line width. On the molecular level there is apparently sufficient motion to average out dipole–dipole interactions which produce the widths found in other mesophases.

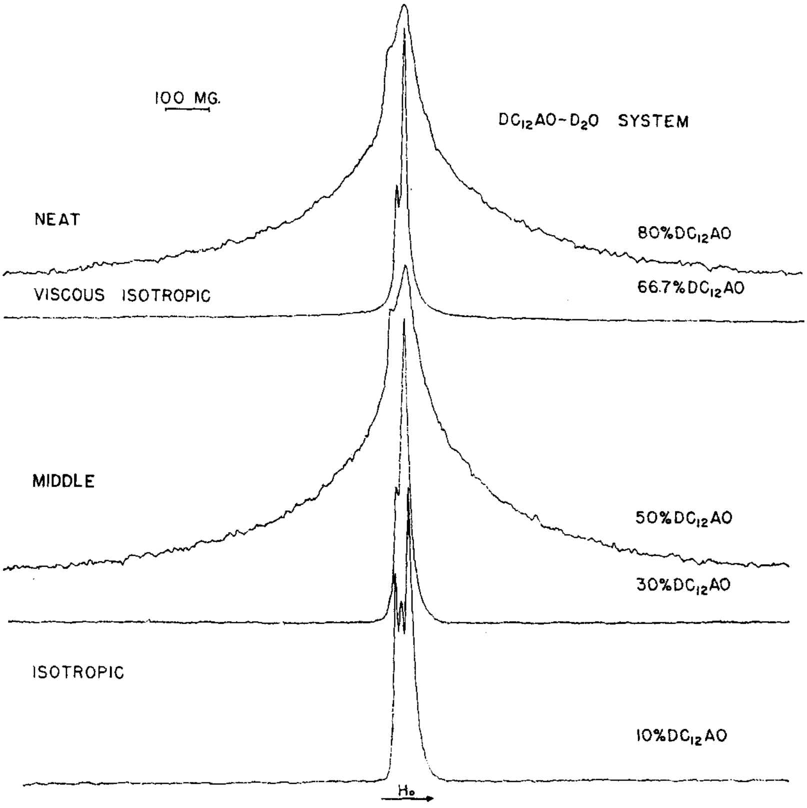


Figure 2. The n.m.r. lines found in the $DC_{12}AO-D_2O$ system at 30° C.

In Fig. 3 the n.m.r. line widths are shown as a function of the percent of $DC_{12}AO$ in D_2O. The phase boundaries are easily identi-

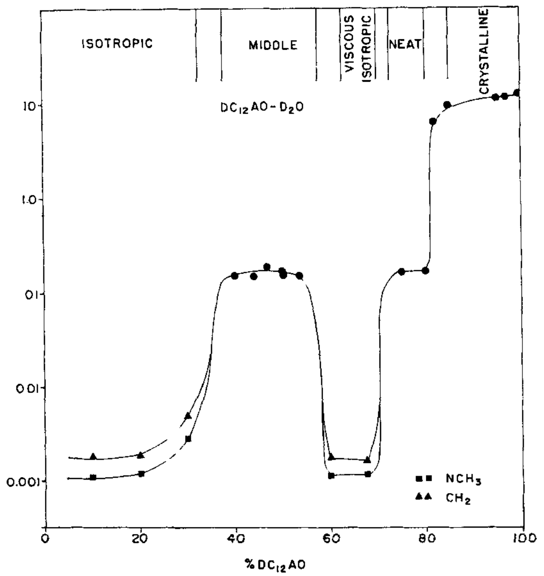


Figure 3. The n.m.r. line widths of $DC_{12}AO$ in D_2O at 30° C.

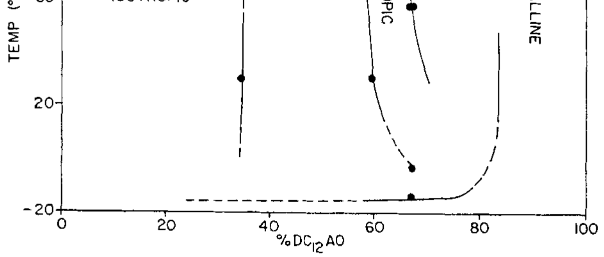


Figure 4. The phase diagram of the $DC_{12}AO–D_2O$ system as determined by n.m.r.

fied. The various phases are indicated at the top of the figure. In the phases in which high-resolution spectra are produced, the widths of only the lines from the methylene groups and the -*N*-methyl groups are shown.

In Fig. 4 the phase diagram derived from the n.m.r. data is shown. The detection of phase transitions between mesomorphic and isotropic phases can be done in two ways. The wide lines arising from the mesophases can be observed as a function of temperature or concentration and the transitions determined by the abrupt changes in the widths. This method is illustrated in Fig. 5. An alternate method is illustrated in Fig. 6. The high-resolution spectrum produced by the isotropic phase is observed and the disappearance of the sharp lines indicates the phase transition. All

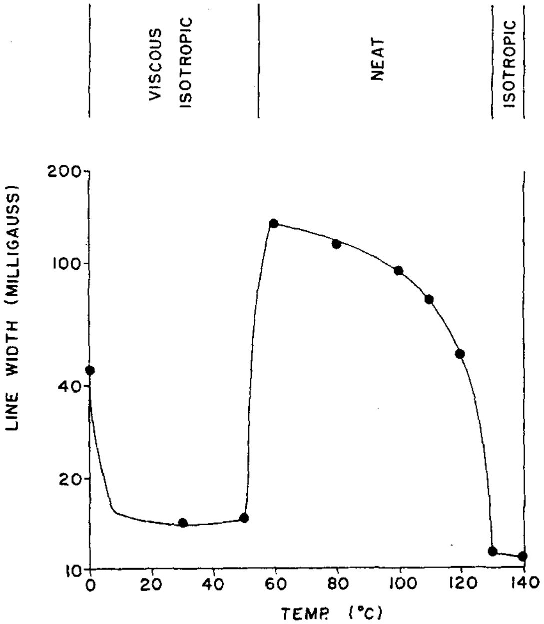


Figure 5. The line width of a 66.7% $DC_{12}AO$–33.3% D_2O system as a function of temperature.

the spectra in Fig. 6 above 32° C were obtained with the same instrumental conditions. The decrease in the amplitudes of the lines indicates that the isotropic-neat transition occurs over a range of temperatures.

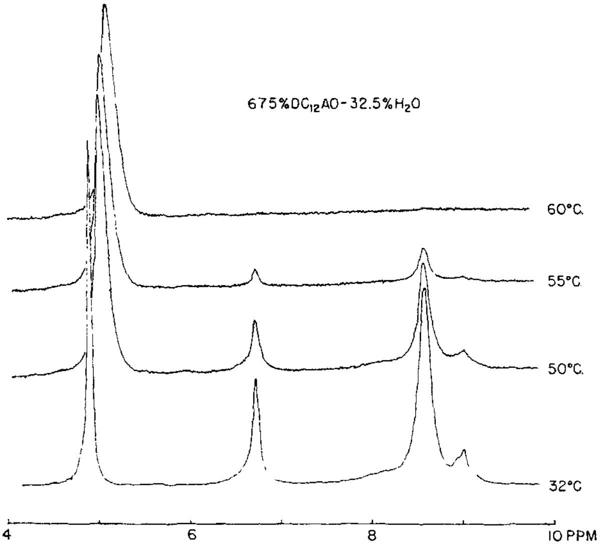


Figure 6. N.m.r. spectra (60 mc) of a 67.5% $DC_{12}AO$–32.5% H_2O system as a function of temperature.

II. Detection of Phase Transitions in Waxy Phases

The investigations of anhydrous saturated soaps by Grant and Dunell[3] indicated that crystalline–mesomorphic and crystalline–liquid transitions in these soaps could easily be detected by the n.m.r. method. Mesomorphic–mesomorphic transitions, however, were not generally detected in these studies. We have found that with improved instrumentation and techniques such transitions are observable. One of the most valuable improvements in technique has been to determine the line widths directly from the absorption curves rather than from derivatives of the absorption curves.[7] The method of obtaining the derivatives can introduce artificial broadening[13] and therefore can make it difficult to obtain true line

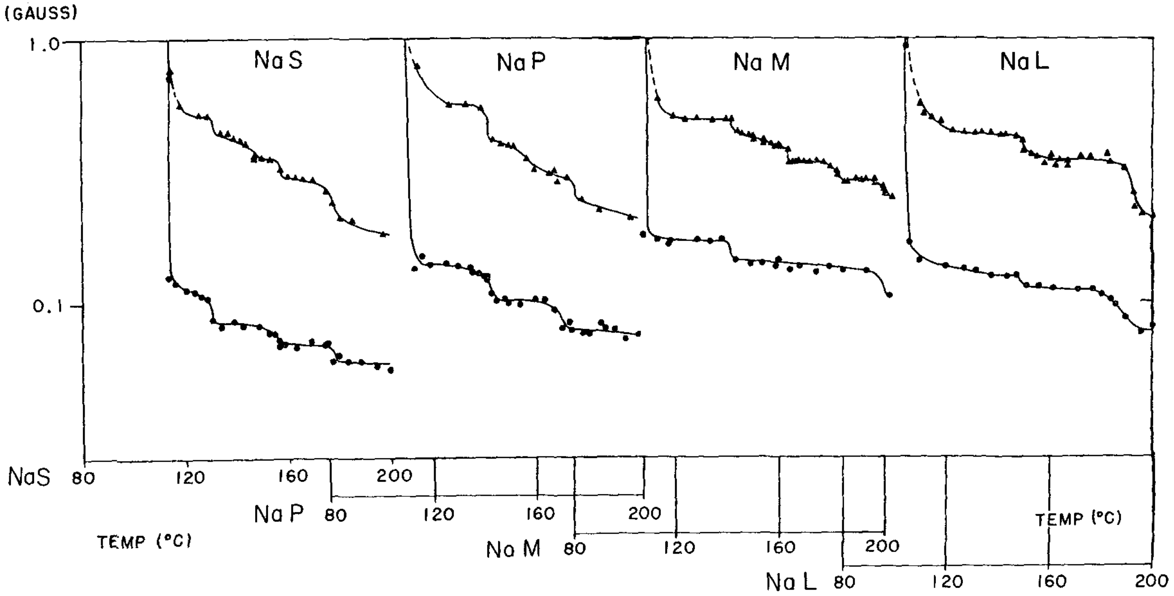


Figure 7. The n.m.r. line widths of the waxy phases in anhydrous sodium soaps as a function of temperature. (▲—measured at half-height; ●—measured between the maxima and minima points of the derivative curves.)

TABLE 1 Phase Transitions in the High -Temperature Mesophases of Anhydrous Sodium Soaps

	Transition temperature (° C)							
	C_{18}		C_{16}		C_{14}		C_{12}	
Phase transition	N.m.r.	Other†	N.m.r.	Other†	N.m.r.	Other†	N.m.r.	Other†
Subwaxy–Waxy	131	129–34	143	134–40	141	133–42	148	130–42
Waxy–Superwaxy	158	165–80	174	172–76	182	175–82	191	182–87
Superwaxy–Subneat	180	188–210	> 200	195–200	203	204–18	> 200	200–20

† These values have been reported in the literature and have been determined by microscopy, dilatometry, calorimetry and other methods.[14]

widths and to detect small changes. Measurements on the derivative curves can produce the same results, however, if extreme care is taken to make the modulation amplitude small.

The n.m.r. line widths have been measured in anhydrous sodium stearate, sodium palmitate, sodium myristate and sodium laurate from the crystalline–mesomorphic transitions ($\approx 100°$ C) to 200° C. All four of the soaps have lines which are very similar in shape but have different widths. The line widths are shown in Fig. 7 as a function of temperature. The widths measured from the absorption curves are represented by the filled triangles (upper curves) and the widths determined from the maxima and minima points of the derivative curves are represented by the filled circles (lower curves). The former method of determining the widths appears to be the most sensitive to changes in the systems. The phase transitions indicated by the abrupt changes in the line widths are tabulated in Table 1. Also tabulated in Table 1 are transition temperatures determined by microscopy, dilatometry, X-ray diffraction and several other methods.[14] In general the agreement between the n.m.r. values and the other values are quite good. Some of the line width changes occur over a 4–5° range making it difficult to select a single value for the transition temperature. The values listed in Table 1 are the temperatures in the center of the ranges.

The order of the line widths in the waxy phases (see Fig. 7) deserves some comment. There appears to be some relation between the line widths and the length of the hydrocarbon portions of the molecules. Sodium laurate is the one exception. The widths are in the order myristate > laurate > palmitate > stearate at most temperatures. The longer chains should possess the most motion and thus produce sharper lines. The order of the widths for a given soap is: subwaxy > waxy > superwaxy > subneat. As expected, the widths decrease with increasing temperature.

III. SHAPES AND WIDTHS OF N.M.R. LINES IN MESOPHASES

A. *Line Shapes*

The shapes of the lines from all the mesophases studied are similar. Since the lines are much more intense in the wings than are

Lorentzian curves (normally found in liquid systems), they may be described by the term "super-Lorentzian".

In Fig. 8 a line from the superwaxy phase of sodium stearate is reproduced as obtained at 169° C. The lines from the subwaxy and waxy phases are similar in shape to this one. In Figs. 9 and 10 lines from the neat and middle phases of sodium palmitate are shown along with calculated Lorentzian line shapes. A Lorentzian line has a ratio between the widths measured at half-height and at the inflection points ($\Delta H_{1/2\,\max}/\Delta H_{\mathrm{inf}}$) of 1.73. The ratios for the waxy type phases vary from about 5 to about 2.5 depending upon temperature and upon chain length. The lines from neat and middle

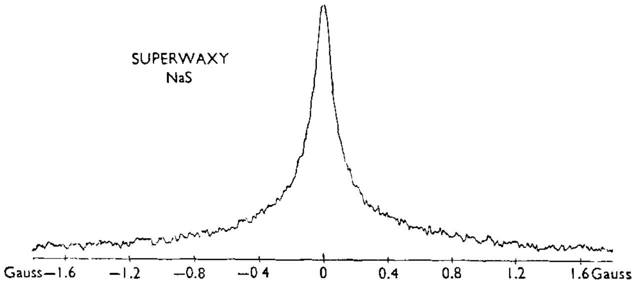


Figure 8. The n.m.r. spectrum of anhydrous sodium stearate at 169° C.

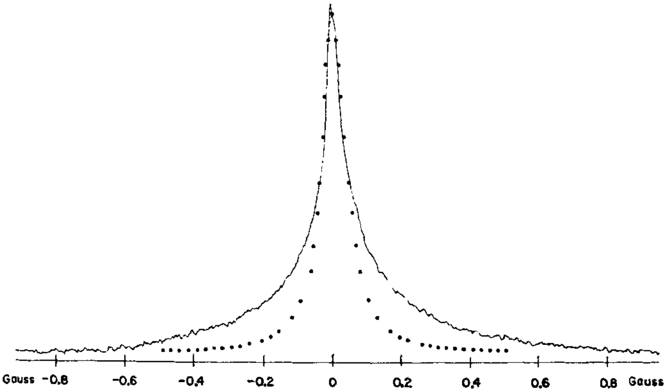


Figure 9. The n.m.r. spectrum of a 70% sodium palmitate–30% D_2O system (neat phase) at 110° C.

phases appear to differ from a Lorentzian shape by about the same amount as indicated in Figs. 9 and 10, the dots representing Lorentzian lines of the same width at half height.

Some insight into the origin of the experimental shapes of the neat phase and middle phase lines can perhaps be obtained by considering the structure of the two phases as proposed by Luzzati, *et al.*[10, 11] These structures are schematically illustrated in Fig. 11. In both structures the motion of a given methylene group in the chain may depend to some extent upon its distance from the ends of the chain. Those groups near the polar end may possess little motion while those near the free end of the chain may be relatively mobile. The observed n.m.r. lines are, of course, made up of components arising from the individual protons on the hydrocarbon chains. If there is a distribution of motion along the chain, then there will be a distribution of widths among the resulting line components. A distribution of lines having a distribution of widths, each line being perhaps Lorentzian or Gaussian in shape, could produce the observed shape.

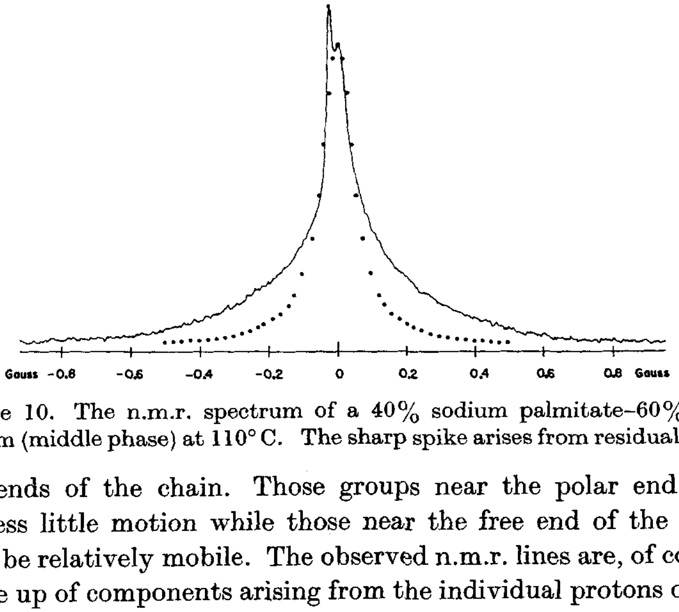
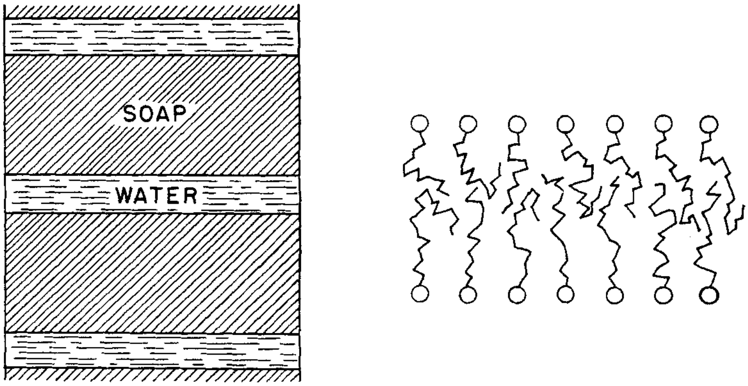


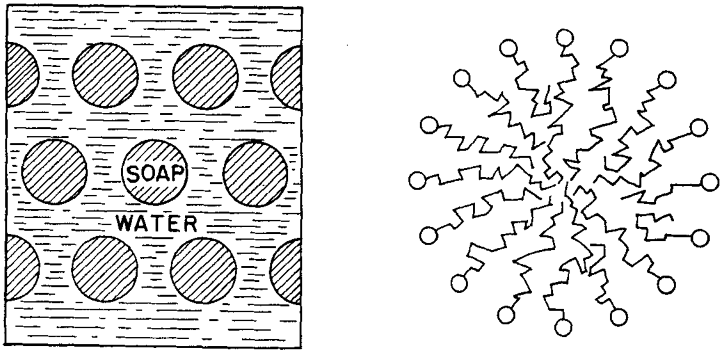
Figure 10. The n.m.r. spectrum of a 40% sodium palmitate–60% D_2O system (middle phase) at 110° C. The sharp spike arises from residual H_2O.

The structures of the waxy type mesophases are similar to those of the neat and middle phases in the sense that one end of the molecule can be fixed in place by the binding action of the polar groups while the other end can be mobile.[15] As in the neat and middle phases such an arrangement could produce a distribution of correlation times and thus a distribution of line widths.

The shapes of the neat and middle lines also change with temperature. As the temperature is raised the lines become more nearly Lorentzian, lending support to the suggestion that the shapes result from a distribution of molecular motion in the hydrocarbon



a. NEAT SOAP



b. MIDDLE SOAP

Figure 11. Schematic structures of neat and middle soaps. After Ref. 10.

chains. Data from sodium stearate, sodium palmitate, sodium myristate and sodium laurate indicate that the temperature dependence increases with increasing chain length, that is, the longer the chain the faster the lines approach a Lorentzian shape, also supporting the above idea.

B. *Line Widths*

The n.m.r. spectra of several neat and middle mesophases have been recorded. In Figs. 12 and 13 are shown the lines from neat and middle phases, respectively, in the homologous series of soaps, sodium laurate, sodium myristate, sodium palmitate and sodium

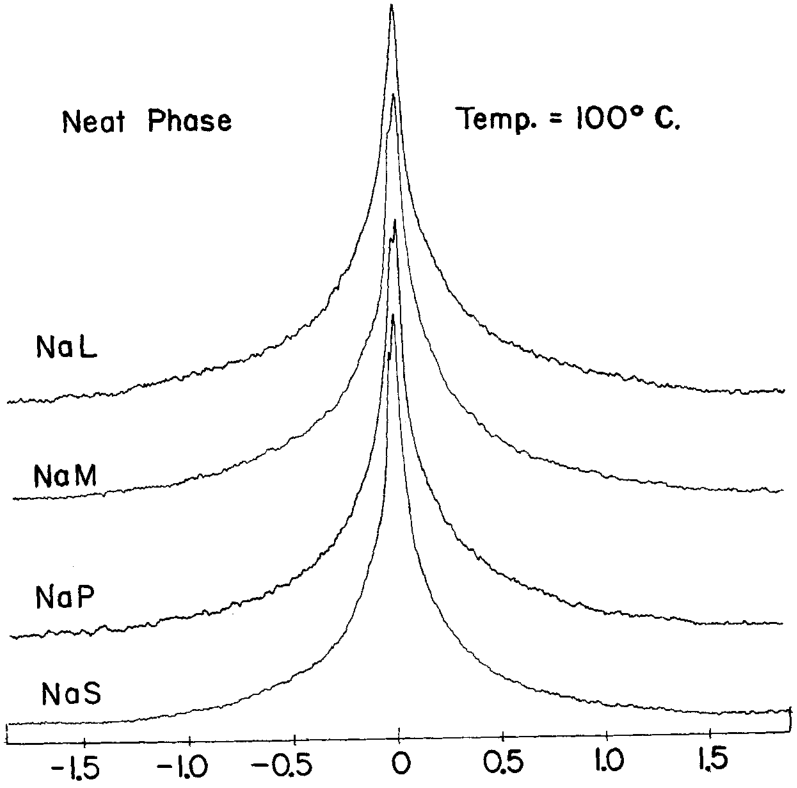


Figure 12. N.m.r. lines of neat phase saturated sodium soaps at 100° C.

stearate. The neat phase is displayed by 70% soap in D_2O at 100° C. The middle phase is displayed by 40% soap in D_2O at 100° C. On some of the spectra a small peak produced by the residual HOD in the solvent can be seen on the low-field side of the soap signals.

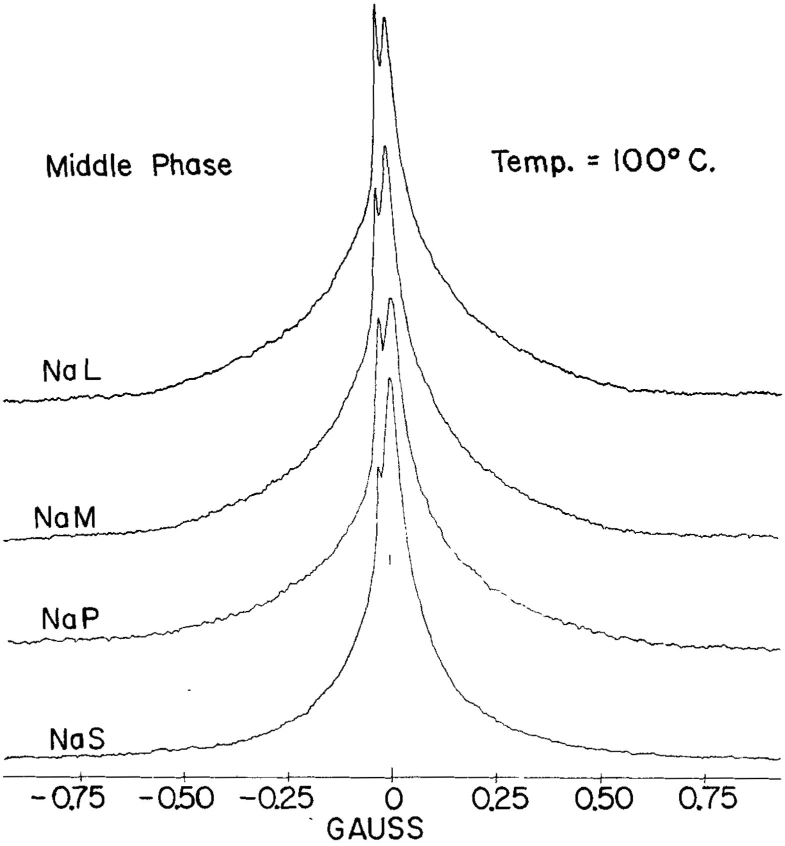


Figure 13. N.m.r. lines of middle phase saturated sodium soaps at 100° C.

In Table 2 are tabulated the widths measured in several systems at 100° C. All widths were measured at one-half maximum intensity. In all cases the middle phase line widths are less than the neat phase line widths. Evidently in the neat phase, where the amount of solvent is less, the surfactant molecules are packed closer together thus producing wider lines. With the exception of the amine oxide the difference between the line widths of the two phases is about 20–30 mG. The series of soaps, stearate through laurate, have lines which become sharper with increasing chain lengths at this temperature; however, this may not be true at all temperatures. In Figs. 14 and 15 are shown the line widths as a function of temperature for some members of this series in the neat and the middle phase, respectively. The small arrows indicate the boundaries of the mesophases. These data indicate that the order of widths might depend upon the temperature at which the measurements are made. Perhaps an "equivalent" temperature should be chosen, based upon the temperature of formation of the phase, and the comparison made there. In addition, an "equivalent" concentration should

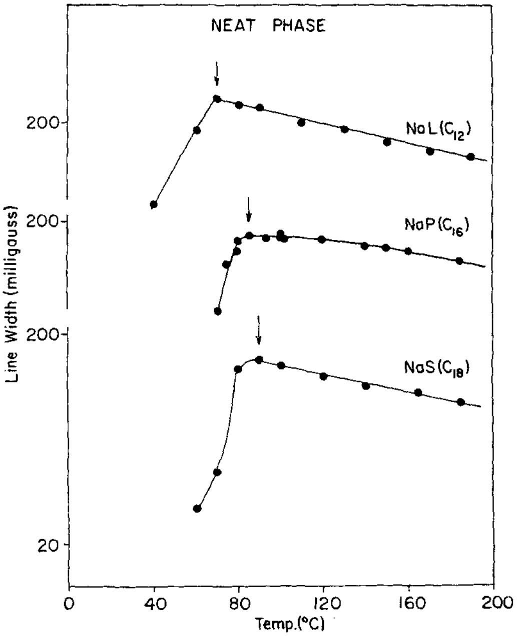


Figure 14. The temperature dependence of the line widths of saturated sodium soaps in the neat phase.

perhaps be used. A slight concentration dependence of the line widths was found in the sodium palmitate data illustrated in Fig. 1.

The data in Table 2 indicate that the widths of the n.m.r. lines in the middle phases are much less dependent upon the molecular structure than are the neat phase widths. The middle phase line widths appear to be determined largely by the length of the hydrocarbon chains. In neat phase, however, the existence of a double bond with a *cis* configuration (sodium oleate) produces a width which is typical of a much shorter chain such as sodium laurate or sodium myristate. The *trans* configuration (sodium elaidate) on the other hand produces a width about the same as the saturated material sodium stearate. The configuration about the bond does not affect the middle phase line width to any great extent. Evidently the layered neat structure can accommodate the *cis* con-

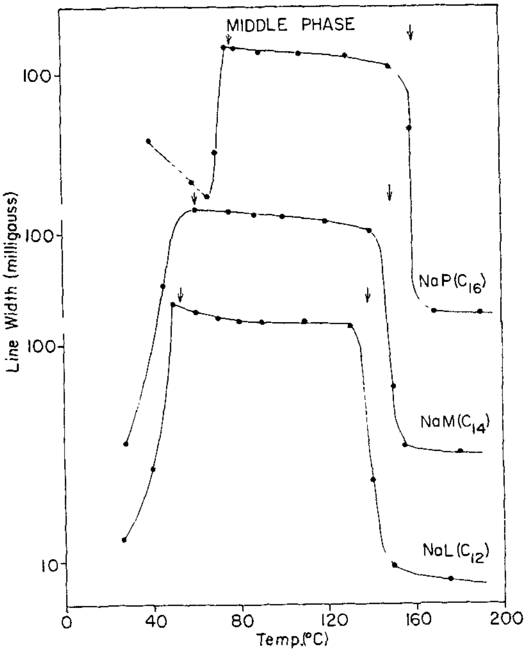


Figure 15. The temperature dependence of the line widths of saturated sodium soaps in the middle phase.

figuration without producing an expansion of the structure. The hydrocarbon chains in sodium oleate are probably not as free to rotate as those in the saturated materials because of the *cis* configuration. This could account for the larger-than-expected line width. Another possibility is that there may be a partial folding of the chains in the neat phase. Neither of these processes would significantly affect the middle phase structure.

TABLE 2 N.m.r. Line Widths in Neat and Middle Phases in Surfactants

System	Concentration (% in D_2O)	Line width (mG)	Number of carbons in chain
	Neat phase (100° C)		
Dimethyldodecylamine Oxide	75	134	12
Sodium Laurate	70	197	12
Sodium Myristate	70	167	14
Sodium Palmitate	70	162	16
Sodium Stearate	70	139	18
Sodium Oleate	70	183	18 (*cis*)
Sodium Elaidate	70	140	18 (*trans*)
	Middle phase (100° C)		
Dimethyldodecylamine Oxide	50	120	12
Sodium Laurate	40	128	12
Sodium Myristate	40	117	14
Sodium Palmitate	40	112	16
Sodium Stearate	40	105	18
Sodium Oleate	40	113	18 (*cis*)
Sodium Elaidate	40	106	18 (*trans*)

The smaller-than-expected width of the neat phase line in dimethyldodecylamine oxide probably results because the head group is not as polar as those in the soaps, thus allowing more motion in the molecules.

Summary

The data illustrated and discussed in this paper have shown that nuclear magnetic resonance spectroscopy is a valuable tool for studying systems containing mesophases. Crystalline, mesomorphic, and isotropic liquid phases can easily be distinguished from each other through line width and line moment measurements. Careful and detailed measurements of the same parameters allow certain kinds of mesomorphic phases to be distinguished from each other. Because of the ability to distinguish different phases in a system the phase diagram can be easily determined.

The measurements of line widths and line moments along with a consideration of line shapes allow certain conclusions to be drawn about the structures of mesomorphic phases. Changes in line widths, line moments, and line shapes produced by changes in the molecular structure of the surfactant produce additional information about the phase structures and about the molecular motions.

Note added in proof

The phase diagram of dimethyldodecylamine in H_2O has recently been determined by microscopic techniques. (Lutton, E. S., *J. Am. Oil Chem. Soc.* **43**, 28 (1966)). The n.m.r. and microscopic data are in good agreement.

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