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# N.M.R. in Amphiphilic Solutions

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## *Résumé.*

On présente une étude préliminaire des spectres de résonance magnétique des protons en haute résolution pour des systèmes de deux et trois composants de molécules amphiphiliques organiques et d'eau. On a observé les déplacements chimiques dans les phases liquides et on a montré que lorsque des phases mésomorphes apparaissent, on observe une réduction de l'intensité du signal des protons de l'eau, tandis que le signal protonique des chaînes hydrocarbonées est complètement supprimé.

Ceci suggère que le degré d'ordre dans la portion hydrocarbonée des couches cristallines liquides est dans ces systèmes est plus grand qu'on ne le pensait.

## *Summary.*

A preliminary study has been made of the high resolution proton magnetic resonance spectra of two and three component systems of amphiphilic organic molecules and water. Chemical shifts have been observed in the liquid phases and it has been found that where mesomorphic phases are formed there is a reduction of the intensity of the water proton signal while that from the hydrocarbon chain protons is completely suppressed.

This evidence suggests that there is a greater degree of order in the hydrocarbon portion of the liquid crystal layers in these systems than has heretofore been suspected.

## INTRODUCTION.

Several of the physical properties of three component systems of soap-amphiphile-water have been studied in recent years [1] and a striking regularity of behaviour is evidenced by the fact that most of the systems conform to the phase diagram shown in Fig. 1. The soaps used have been sodium alkyl sulphates and alkyl ammonium chlorides with additives of aliphatic alcohols, amines and acids having a minimum chain length of five carbon atoms.

Up to A the soap is assumed to be largely in the form of Hartley ionic micelles (aggregates of about fifty soap ions with their ionic heads on the circumference of a sphere and the aliphatic chains turned into the centre, the whole surrounded by an equilibrium number of oppositely charged gegenions,  $S_1$  in Fig. 2). The arrangement of soap ions in this fluid structure will be completely random and the long hydrocarbon tails of molecules free to bend and twist in all directions at will. If, as we suspect, the polar group of the added amphiphile adjoins that of the soap and the carbon chains lie together, then an increase in concentration of the amphiphile will enforce an increasing amount of regularity in the positioning of the molecules.

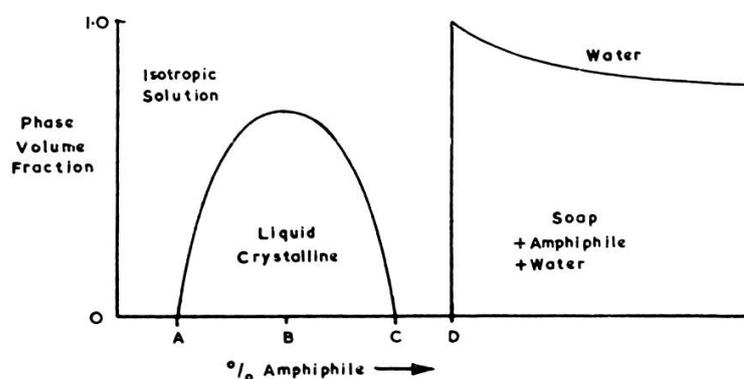


Fig. 1.

This explains the formation of the liquid crystalline phase which is observed in these systems in the same way as in concentrated aqueous solutions of single amphiphiles such as octylamine and dodecylamine [2], the sodium and potassium carboxylate soaps [3], and polypeptides [4]. The structure of this phase as shown by Winsor [5] seems to be a lamellar arrangement of soap and amphiphile molecules with alternate layers of water molecules (L.C. in Fig. 2).

Hydrogen bonding between the polar groups and the water layer has been proposed but there is no conclusive evidence on this point.

Further addition of amphiphile beyond C on the phase diagram dissolves the liquid crystals and gives a clear solution briefly before water begins to separate out at D. It is suggested by Winsor [5] that the clear isotropic solution between C and D consists of water dissolved in oleophilic micelles ( $S_2$  in Fig. 2) which then break down as the dilution is increased with consequent separation of the water as a second phase.

The only N.M.R. work on the mesomorphic state up to the present has employed wide line techniques in the study of single substances such as p-azoxy anisole and its homologues [6, 7, 8, 9, 10, 11].

Records of the proton resonance at a number of temperatures over the melting range of these substances have shown that the 3-4 gauss wide line of the solid anisoles splits into three components, with a similar total width, on passing through the liquid crystalline phase and then gives a single line 0.1 gauss wide on melting to the liquid phase. By deuteration of the methyl group in p-azoxy anisole, Jain, Lee and Spence [10] showed that the middle component of the liquid crystal spectrum is the alkoxy proton line and the outer doublet must therefore be ascribed to the benzene ring protons.

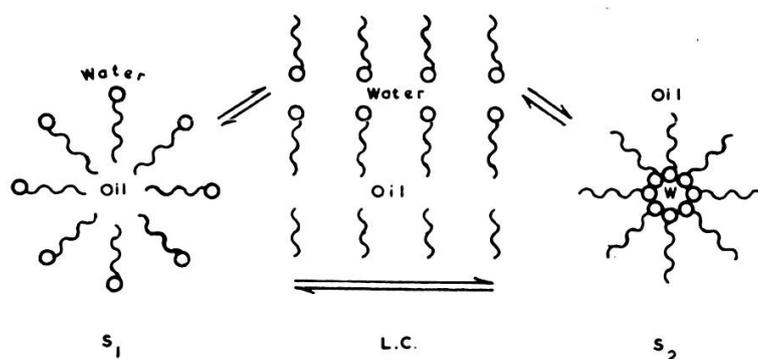


Fig. 2.

Studies of line shapes by Lippman and Weber [11] have shown that this middle peak is only resolved in the compounds containing odd numbered alkoxy chains. Temperature dependence of line form in the nematic liquid crystalline phase are not yet theoretically explicable and although there is a slight change in line shape from nematic to smectic states of the azoxy-heptyl ether, Lippman and Weber found no measurable change in second moment. This suggests that the rotation of the molecules in the direction of their longitudinal axes is the mechanism governing the proton resonance line shape.

The work detailed in this paper is the beginning of an N.M.R. study of aqueous amphiphilic solutions with a view to observing structural effects in the mesomorphic state and also investigating the possibility of hydrogen bonding in these solutions since the N.M.R. technique has already been found to give very clear indications of this phenomenon [12, 13, 14, 15, 16].

## EXPERIMENTAL.

All chemicals were supplied by L. Light and Co.

B.P. grade sodium dodecyl sulphate (SDS) was recrystallized from absolute alcohol. Octylamine, octanol, and caprylic acid were used as supplied.

A sample of the octylamine was titrated with a standard hydrochloric acid in alcoholic solution and found to be 99% pure.

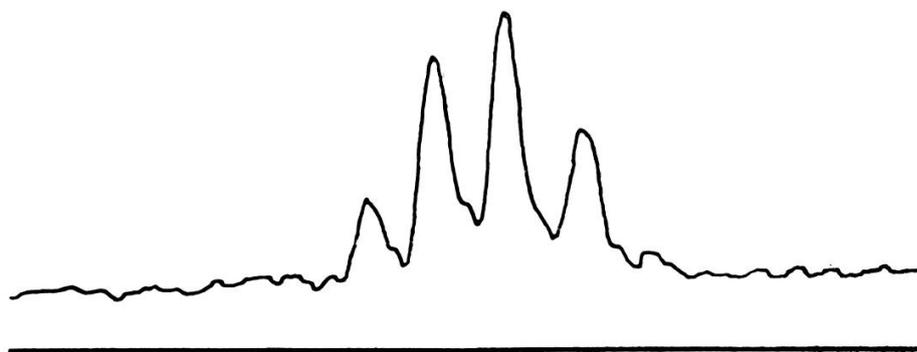


Fig. 3.

H' resonance at 17.2 mc from the — CHO of acetaldehyde spectrum — separation of peaks 2.85 cycles.

The N.M.R. spectra were obtained on the pre-prototype of the Fairey Spectrometer. This comprises a permanent magnet with 4 inch diameter pole faces, a gap of 0.72 inch giving a field of approx. 4,000 gauss at which the  $H^1$  frequency is 17.2 mc/s. The samples were contained in Jena glass tubes of 5 mm o.d. and 3 mm i.d. containing a capillary of benzene as an external reference. All absolute chemical shifts ( $\delta$ ) are related to a water zero reference and expressed in parts per million. No correction has been made for bulk diamagnetic susceptibility differences.

Sample spinning at 4,500 r.p.m. was employed and Fig. 3 shows the homogeneity of field attained under these conditions.

The side bands (marked X) occurring in some of the spectra are due to the existence of a linear gradient in the magnetic field during these observations [17]. They were in fact used as calibration points in the spectra instead of the usual 50 c/s modulation.

The N.M.R. spectrum of each sample was observed initially at 40° C and then at intervals down to 15° C.

## RESULTS.

(a) *Octylamine-water.*

Mesomorphism has been observed at room temperature by Ralston and co-workers [2] in solutions of octylamine containing between 0.6 and 0.99 mole fraction of water. A number of samples were made up within this concentration range in order to first examine the proton magnetic resonance in a two component liquid crystal system.

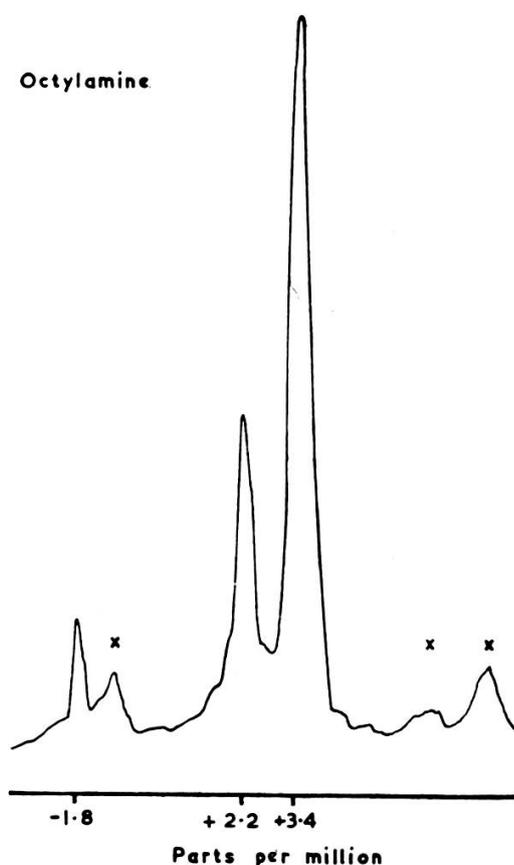


Fig. 4.

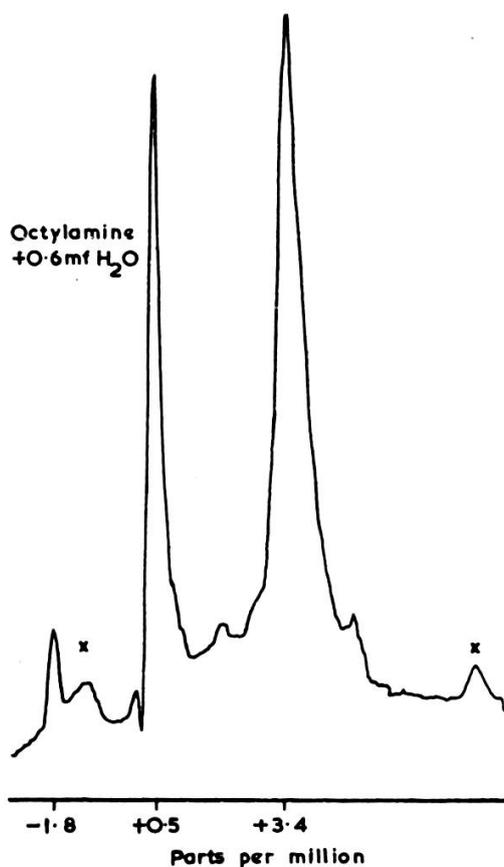


Fig. 5.

First additions of water cause a negative shift of 1.7 parts per million in the amino proton line (Fig. 4 and 5) and a single line appears at  $\delta = +0.5$  which indicates exchange between the OH and  $\text{NH}_2$  protons at such a rate that they cannot be distinguished. At a mole fraction of 0.6 water the solution remains isotropic and both lines remain unchanged over the whole temperature range.

Further addition of water ( $x = 0.7-0.8$ ) gives at  $20^\circ\text{C}$  "a highly dispersed mixture of amine and hydrated amine molecules in a mesomorphic

state" [2]. The N.M.R. spectrum at 40° C differs from the first case only in the intensity of the labile proton line but on cooling the alkyl proton line slowly dwindles and disappears at about 20° C while the water line splits (0.1 parts per million) and then broadens slightly overall as the whole mass cools. (Fig. 6 and 7.)

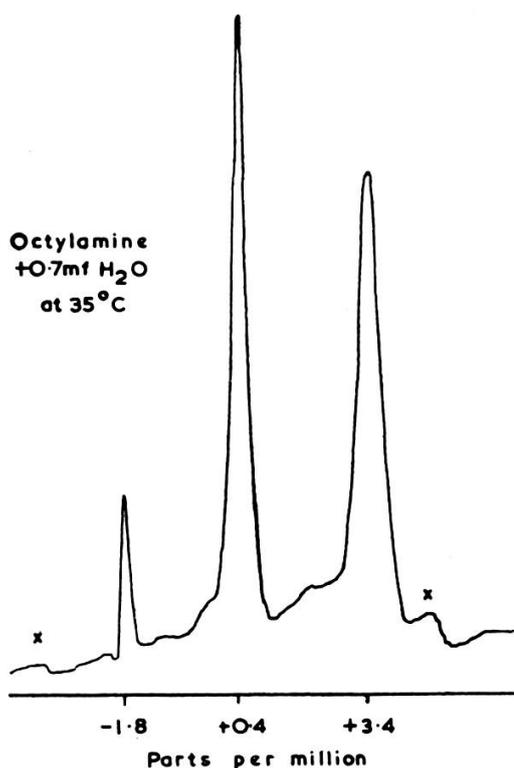


Fig. 6.

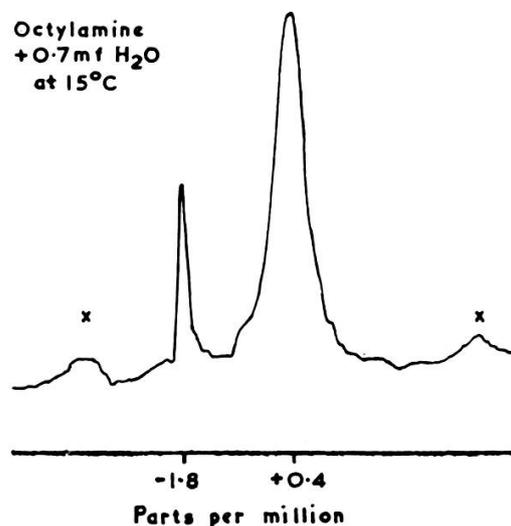


Fig. 7.

Greater concentrations of water ( $x = 0.9-0.95$ ) give two phase systems at 40° C, one of which is liquid and the other liquid crystalline. When these two phases are observed simultaneously at the higher temperature there are two distinct proton lines in the amino hydroxy region at  $\delta = 0.0$  and  $\delta = +0.5$ . A line at the alkyl position ( $\delta = 3.4$ ) is obtained from the liquid layer (Fig. 8).

The isotropic liquid crystalline gel is only stable below 20° C and then gives a single line at  $\delta = 0.0$ .

(b) *Sodium dodecyl sulphate-octanol-water.*

A series of mixtures of 0.5 M SDS and octanol were made corresponding to the different systems of the phase diagram Fig. 1.

The spectrum of the 0.5 M SDS solution is composed of a large water proton line at  $\delta = 0.0$ . and a smaller composite line in the alkyl position from the protons of the dodecyl chain at  $\delta = + 3.5$ .

When liquid crystals are formed on addition of octanol the alkyl line again diminishes and eventually disappears while the water proton line broadens and also diminishes in intensity.

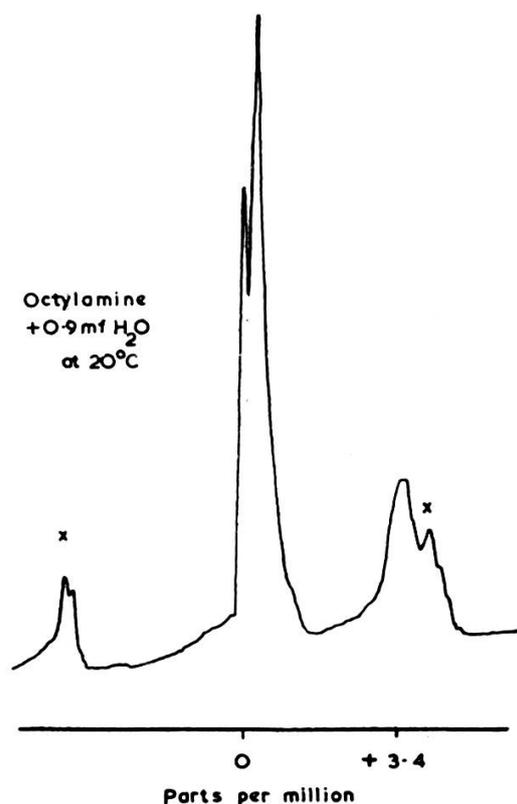


Fig. 8.

Samples were taken from the clear S<sub>2</sub> layer and the undissolved liquid crystalline layer of a solution of equal parts 0.5 M SDS and octanol. The clear top layer shows a spectrum similar to that of octanol with slightly enhanced alkyl and hydroxyl proton lines and the liquid crystal layer gives a single peak at  $\delta = 0$ .

(c) *Sodium dodecyl sulphate-caprylic acid-water*

A series of mixtures of caprylic acid and 0.5 M SDS showed similar spectra to those of the previous system. A sample of the top layer of S<sub>2</sub> solution gave only two lines, one in the alkyl position and the other at

$\delta = -2.7$ . A further completely isotropic  $S_2$  solution made by dissolving 5 gm SDS in 5 ml caprylic acid with the minimum amount of water showed the second line at  $\delta = -0.8$ .

#### DISCUSSION.

The disappearance of the alkyl proton lines in the liquid crystalline phases of all the systems seems to indicate a restriction in the freedom of motion of the hydrocarbon chains similar to that found in the mesomorphic state of the *p*-azoxy ethers studied by previous workers. It seems probable that the restriction on the movement of these protons is caused by an increasing regularity of structure as shown in Fig. 2 so that the chains take up ordered positions in liquid crystalline lamellae.

This conclusion is at variance with most of the results obtained on the structure of liquid crystalline phases in other similar systems. It is claimed by Winsor [5] that the arrangement of the alkyl chains in liquid crystals is completely random and fluid and this is supported by the X-ray results of Marsden and McBain [18].

The amalgamation of the amine and water lines implies that the protons in these positions are exchanging rapidly even in the mesomorphic state. The intensity of the line is seen to diminish by about one half as the liquid crystals are formed from isotropic solution and so it is possible that a large number of water molecules are effectually removed from the liquid state to be used in holding together the lamellar structure by hydrogen bonding between polar groups and/or through a pseudo-crystalline structure within the water layer as suggested by Winsor [5].

Since the reduction in signal is approximately the same in octylamine-water and SDS-octanol-water it seems likely that a similar mechanism operates in both cases. It is known [2] that octylamine hexahydrate is the main constituent of the liquid crystalline phase in mixtures of octylamine and water so it is possible that multi-hydrates are also formed in this phase in the three component amphiphilic systems.

The negative shift of 0.5 p.p.m. in position of the single liquid crystal line in more dilute solutions is probably due to the increased formation of hexahydrate and explains the two lines 0.5 p.p.m. apart, obtained from the two phases of these solutions at higher temperatures.

The slight broadening of the water line in the mesomorphic state may be due to an increase in viscosity of the water as a result of closer packing

of the molecules between the liquid crystal lamellae. It seems more probable however that the broadening is a result of proton exchange between water molecules in the liquid state and those in the form of multi-hydrates. This type of explanation was proposed for the similar effects observed in the case of aqueous solutions of deoxyribonucleic acid by Jacobson (19) and of aluminium chloride by Shoolery and Alder (20).

Solutions of the  $S_2$  type containing water dissolved in SDS + amphiphile show again only one hydroxy proton line which means that the polar heads of the amphiphile must be in true solution in the aqueous centre of the oleophilic micelle. As would be expected, the line is shifted negatively in the case of the caprylic acid system but tends to return towards higher fields as the proportion of water increases and the average time spent by each proton on an acid site decreases.

The results of these preliminary observations indicate that the application of N.M.R. spectrometry to the study of amphiphilic solutions can provide useful information, and it is hoped to employ both high resolution and wide line techniques in a more detailed study of these and other amphiphilic and mesomorphic systems.

## REFERENCES

1. HYDE, A. H., D. M. LANGBRIDGE and A. S. C. LAWRENCE, *Discussions Far. Soc.*, 1954.
2. RALSTON, A. W., C. W. HOERR and E. J. HOFMANN, *J. Amer. Chem. Soc.*, **64**, 1516 (1942).
3. LUZZATI, V., H. MUSTACCHI and A. SKOULIOS, *Discussions Far. Soc.* (1958), p. 43.
4. ROBINSON, C., J. C. WARD and R. B. BEEVERS, *Discussions Far. Soc.* (1958), p. 29.
5. WINSOR, P. A., Solvent properties of amphiphilic compounds (1954), *Butterworths Scientific Publications*.
6. SPENCE, R. D., H. A. MOSES and P. L. LAIN, *J. Chem. Physics*, **21**, 380 (1953).
7. JAIN, P. L., H. A. MOSES, J. C. LEE, R. D. SPENCE, *Physic. Rev.*, **92**, 844 (1953).
8. SPENCE, R. D., H. S. GUTOWSKY, C. H. HOLM, *J. Chem. Physics*, **21**, 1891 (1953).
9. EWING, R. and J. C. LEE, *Physic. Rev.*, **94**, 1411 (1954).
10. JAIN, P. L., J. C. LEE and R. D. SPENCE, *J. Chem. Physics*, **23**, 878 (1955).
11. LIPPMANN, H. and K. H. WEBER, *Ann. Physik* (6), **20**, 265 (1957).
12. GUTOWSKY, H. S. and A. SAIKA, *J. Chem. Physics*, **21**, 1688 (1955).
13. HUGGINS, C. M., G. C. PIMENTEL and J. N. SHOOLERY, *J. Chem. Physics*, **23**, 1244 (1955).
14. HUGGINS, C. M., G. C. PIMENTEL and J. N. SHOOLERY, *J. Phys. Chem.*, **60**, 1311 (1956).

15. COHEN, A. D. and C. REID, *J. Chem. Physics*, *25*, 790 (1956).
  16. BECKER, E. D., U. LIDDEL and J. N. SHOOLERY, *J. Mol. Spectroscopy*, *2*, 1 (1958).
  17. WILLIAMS, G. A. and H. S. GUTOWSKY, *Physic. Rev.*, *104*, 278 (1956).
  18. MARSDEN, S. S. and J. W. MCBAIN, *Nature, London*, *165*, 141 (1950).
  19. JACOBSON, B., ANDERSON, W. A., ARNOLD, J. T., *Nature, London*, *173*, 772 (1954).
  20. SHOOLERY, J. N. and ALDER, B. J., *J. Chem. Phys.*, *23*, 805 (1955).
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