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Infrared and far-infrared spectroscopic studies on the structure of water in lyotropic liquid crystals

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Studies on the infrared and far-infrared spectra of water in lyotropic liquid-crystalline phases of dodecyltrimethyl ammonium chloride (and related materials) have shown the existence of at least two severely perturbed types of water molecule—both very different from bulk water. Band shifts, half-widths and relative intensities change rapidly over the concentration range, but show no discontinuities at phase boundaries (including the gel/lamellar boundary). The water molecules therefore probe only the short-range interactions between head group and counterion and do not reflect changes in long-range micellar interactions in the different mesophases. These data support the equilibrium binding model for water-surfactant interactions at polar organic interfaces and tend to refute the existence of different polarized layers. As such, they may eventually help to cast light on the nature of hydration forces between the bilayers in lamellar phases.

1. Introduction

The binding of water at polar charged organic interfaces has been a topic of considerable interest among surface chemists, spectroscopists and biochemists (and biophysicists) for the past 20 years. The state or structure of water in ordered phases (micelles, mesophases, microemulsions) has been perceived to be important: for example, for the stabilization of the bilayer structures (lamellar phases) from which biomembranes are formed [1-11] and for the adhesion [8] and fusion [7] of such membranes. Accordingly, there have been a range of spectroscopic measurements aimed at distinguishing biological (i.e. perturbed or bound) water from bulk water. The most extensive studies have been made using N.M.R. techniques, notably ^2H and ^{17}O quadrupolar splitting [12-22] and ^1H , ^2H , ^{17}O nuclear relaxation times [15-18, 23-30]. These have been employed to monitor the ordering and motional freedom of the water molecules at organic interfaces, through the well-known order and relaxation parameters [18, 19]. However, there have also been microwave (dielectric) [31-35], far-infrared [36-38], mid-infrared [39-54] and Raman [55] spectroscopic measurements aimed at finding structural and motional changes caused by water molecules interacting at either head group or counterion (or both). It is clear from the literature that the interpretation of such spectra is far from straightforward or conclusive and often different models will apparently fit the same data. Certainly, a consensus of opinion on the crucial question as to whether water molecules in mesophases form perturbed and distinct layers [10, 11], or whether there is simply an *equilibrium*

between differently perturbed molecules near the polar groups [12, 56, 57], has been elusive.

Vibrational spectroscopy has, at least in principle, an advantage over N.M.R. methods in seeking to distinguish different kinds of water molecules at an interface. This results from the very short observation times (10^{-12} – 10^{-14} s) which match the rapid time scales on which water molecules are expected [24] to interchange with each other. Thus, water molecules finding themselves in different environments will (if the difference in vibrational energies is great enough) show up as separate bands in the infrared (or Raman spectra). This paper describes a study of the mid-infrared and far-infrared spectra of water in mesophases produced at high concentrations of the cationic surfactants dodecyl and hexadecyl trimethyl ammonium chloride, ($C_{12}N^+(CH_3)_3Cl^-$ or $C_{12}TACl$, $C_{16}N^+(CH_3)_3Cl^-$ or $C_{16}TACl$), and the corresponding bromides. These systems have the advantage that the behaviour of the C_{12} surfactant with water is relatively well-known [58], while the $C_{16}TACl$ system, currently under investigation [67], has some interesting intermediate phases of high viscosity whose structures are not well understood [59]. No work on the structure of water in these systems has been reported previously.

2. Experimental

Cationic surfactants were either obtained from Eastman Kodak or were available within Unilever Research. They had been recrystallized from acetone and were used without further purification. Deuterium oxide (D_2O) was purchased from Fluorochem Ltd (99.83 per cent 2H) and it was mixed with distilled H_2O (~ 4 per cent by volume, D_2O). Samples of surfactant (previously dried over P_2O_5) were weighed into 10 mm vials with the required amount of water (either 1H_2 or the isotopic mixture) and the components were mixed by prolonged incubation at about $60^\circ C$ over periods of several weeks. Sample homogeneity was ensured by periodic centrifugation at 4000 rpm and was checked by polarized optical microscopy for each phase studied.

The material was sampled by spreading a thin film ($\sim 50 \mu m$) between infrared transmitting plates (CaF_2 or silicon) and then clamping the plates in a standard, variable temperature cell holder. At elevated temperatures some loss of water from the edges of the cell is expected. This was minimized by wrapping tape around the cell perimeter. There is, however, certain to be some water lost (at, for example, $50^\circ C$) during the measurements. Nevertheless, a check on the viscosity after the spectroscopic measurement always revealed the correct phase. Since some of the phases studied are highly viscous, definition of the cell path length was difficult. We attempted to measure the path length of material at the cell edge using a reflecting microscope with a graduated scale. This was only partially successful and up to 50 per cent variation in the path length was sometimes observed. Thus, in the spectra we report here, only *relative* intensities are significant.

In the mid-infrared region we employed a PE 580 dispersive spectrometer equipped with an air drier and computerized data collection. In the far-infrared a modified Beckman-RIIC interferometer was used. A Golay cell (50 – 350 cm^{-1}) or a helium cooled germanium bolometer (20 – 180 cm^{-1}) was used to detect radiation from a high pressure mercury arc source. Phase modulation was used to improve signal-to-noise ratios. In both cases the temperature was controlled between 30 and $70^\circ C$ to within $\pm 1^\circ C$ using a Beckman RIIC temperature controller. $50^\circ C$ was chosen as the principle temperature of investigation for a $C_{12}TACl$ because it allowed the lamellar phase to be studied (figure 1) with minimum water loss.

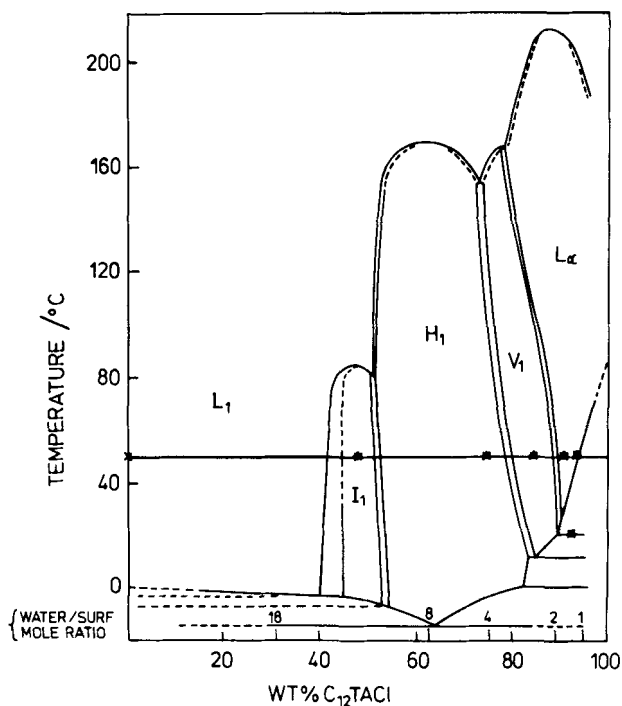


Figure 1. The phase diagram of C₁₂TACl with water (taken from [58]). The concentrations (at 50°C) studied in this work are marked * and the water/surfactant mole ratios are also indicated above the concentration axis.

3. Results and discussion

The infrared and far-infrared spectra of pure water are, of course, well-known [60] as is the mid-infrared spectrum of HDO, whose decoupled $\nu(\text{OD})$ stretching vibrations occur at 3400 cm^{-1} and 2500 cm^{-1} respectively (at 22°C). We concentrate in this paper on the regions between 1800 cm^{-1} and 2700 cm^{-1} and between 20 cm^{-1} and 350 cm^{-1} where the external vibrations (hindered rotation, ν_L and translation ν_T) of the hydrogen bonded liquid network occur [60]. In the mid-infrared we have studied changes in the $\nu(\text{OD})$ band and in the combination of band of liquid H₂O. $\nu_A(\text{H}_2\text{O})$, at $\sim 2120\text{ cm}^{-1}$. The latter is usually referred to as the association band [60] because of its original assignment to the transition ($\nu_2 + \nu_L - \nu_T$). More recent work on solid water in crystalline hydrates [61] would indicate that $\nu_2 + \nu_R$ (R, librational modes) may be preferred. A summary of the bands involved is given in table 1. These regions have been chosen partly for their convenience, being in the most important windows of the liquid H₂O spectrum; but partly also because these are the modes which are expected to be most sensitive to the interactions and perturbations at the organic interface. Figure 2 shows the mid-infrared portion of the spectrum of 4 per cent D₂O in H₂O which provides a baseline against which to compare spectra in the different mesophases. Figure 3, A–F, shows the changes which occur as the concentration of C₁₂TACl increases. The corresponding points A–F are marked (with an asterisk) on the phase diagram (cf. figure 1) which also shows the surfactant/water mole ratios. Several important changes in band shapes, relative intensities and maxima occur as shown in figures 4–7 and now documented.

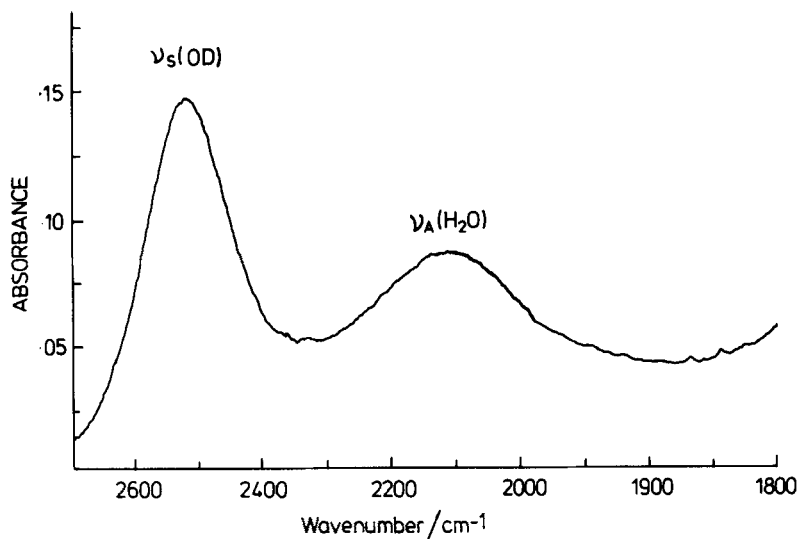


Figure 2. The mid-infrared spectrum of water liquid (at 50°C) with (4 per cent D₂O added) in the range 1800–2650 cm⁻¹.

Table 1. Band assignments for HDO (in H₂O).

	$\bar{\nu}_{\max}/\text{cm}^{-1}$	$\Delta\bar{\nu}_{1/2}/\text{cm}^{-1}$
$\nu_s(\text{OD})$	2520	156
$\nu_A(\text{H}_2\text{O})(\nu_2 + \nu_R)$	2106	221
$\nu_{\text{Lib}}(\nu_R)$	~ 685 (300–900)	—
$\nu_{\text{Trans}}(\nu_T)$	~ 200	—

(1) First, all the water spectrum is indistinguishable from that of bulk water until the order/disorder transition near the L_1/I_1 boundary is approached. Thus, for liquid micellar solutions at H₂O/C₁₂TACl ratios ≥ 12 any perturbed water is present at low relative concentrations and is not seen in our spectra.

(2) As the H₂O/C₁₂TACl ratio is increased from 12 to a ratio of 1 the $\nu_A(\text{H}_2\text{O})$ band at 2106 cm⁻¹ becomes *relatively* more intense and distinctly narrower (cf. figures 4 and 7 respectively). There are clear signs of a low frequency shoulder near 2050 cm⁻¹ (which seems to disappear again at the highest concentrations) and a high frequency shoulder at ~ 2146 cm⁻¹ which is probably responsible for the apparent shift in the $\nu_A(\text{H}_2\text{O})$ band maximum to higher frequencies (see figures 3 F and 5). It would appear that this band gets narrower despite the fact that bands due to perturbed water are increasing in relative intensity. At the highest surfactant concentrations in the lamellar phase L_α (cf. figure 3 F) it is evident that the $\nu_A(\text{H}_2\text{O})$ band comprises two components.

(3) The $\nu(\text{OD})$ band also narrows considerably as the water concentration decreases and it also has shoulders, especially one to low frequency at ~ 2500 cm⁻¹ which is particularly obvious in the L_α phase (cf. figure 3 D, E). (Note that the structure of the sample 3 D is L_α + solid rather than V_1 + solid as expected from figure 1. This is because the equilibrium phase structure forms slowly (taking several hours after heating.) The relative intensity of this band drops dramatically as the L_α phase is approached (cf. figure 7) and at about 94 per cent surfactant (and 50°C) it *disappears*

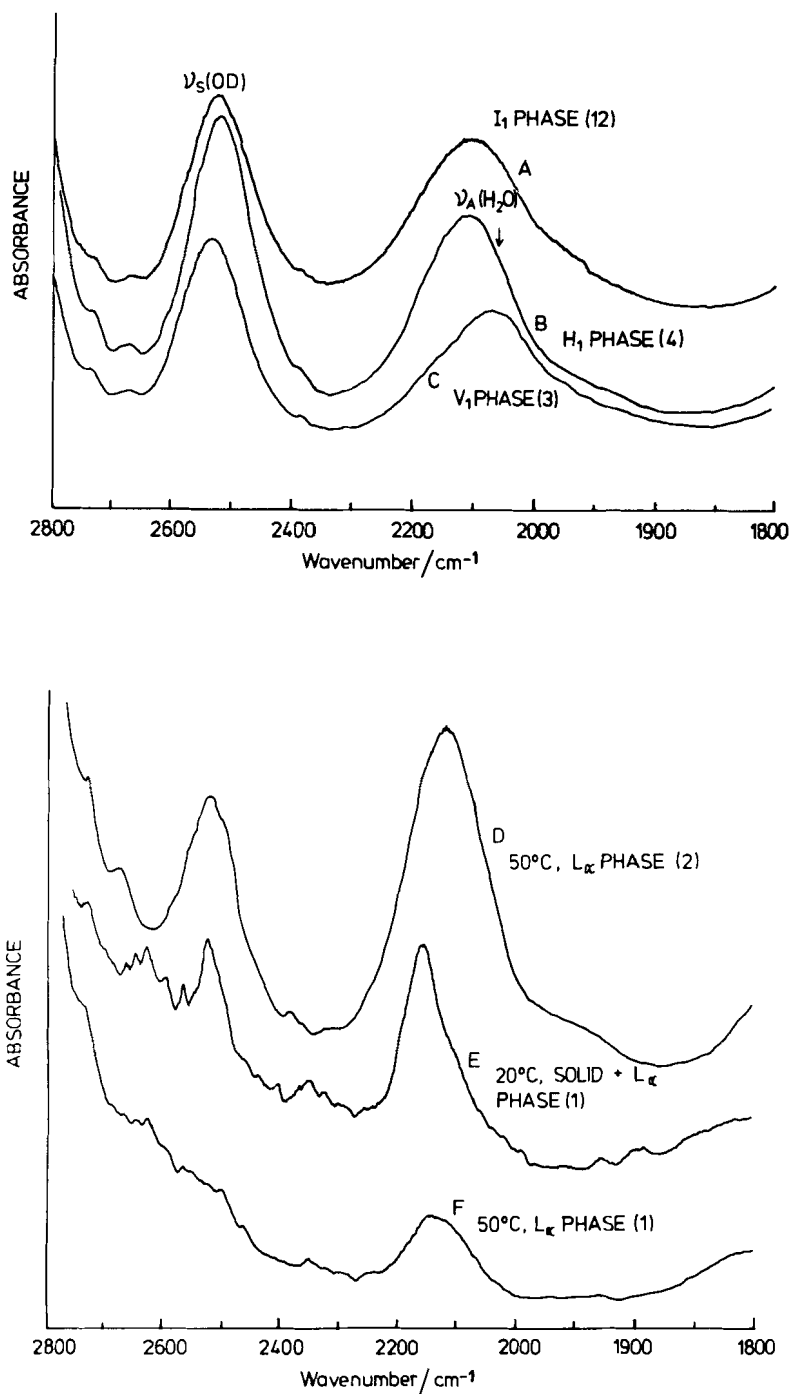


Figure 3. The mid-infrared spectra of thin films of each of, A, the I_1 (cubic), B, the H_1 (hexagonal), and C, the V_1 (cubic) phases of $C_{12}\text{TACl}$ with water (at 50°C) in the 1800–2800 cm^{-1} region. Figure 3D, E and F show the spectra of the L_α (lamellar) phase at two different concentrations (D, 90.7 per cent; F, 93.8 per cent) and also the spectrum, E, of a mixture of solid and L_α phase at 20°C (93.8 per cent) (the water/surfactant mole ratio is given in brackets for each phase).

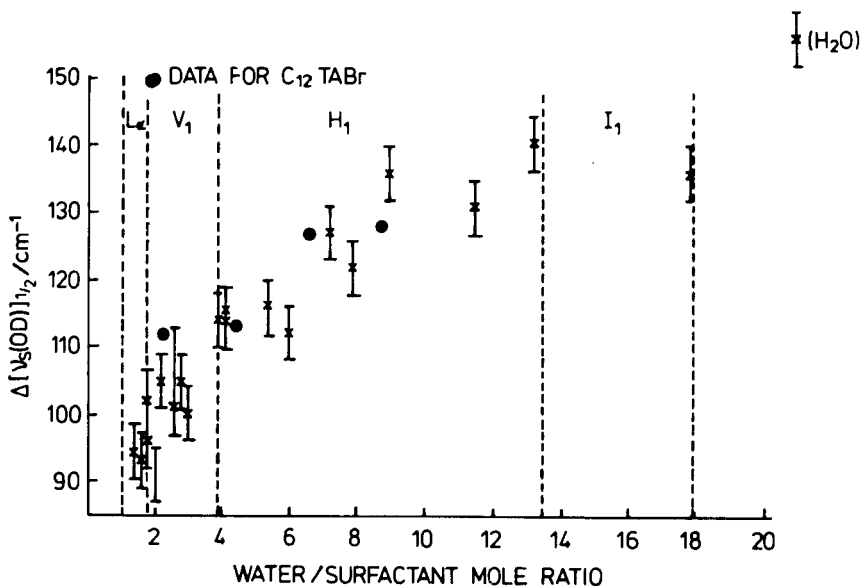


Figure 4. Variation of the half-width of the $\nu_s(\text{OD})$ band as a function of water/surfactant mole ratio at 50°C .

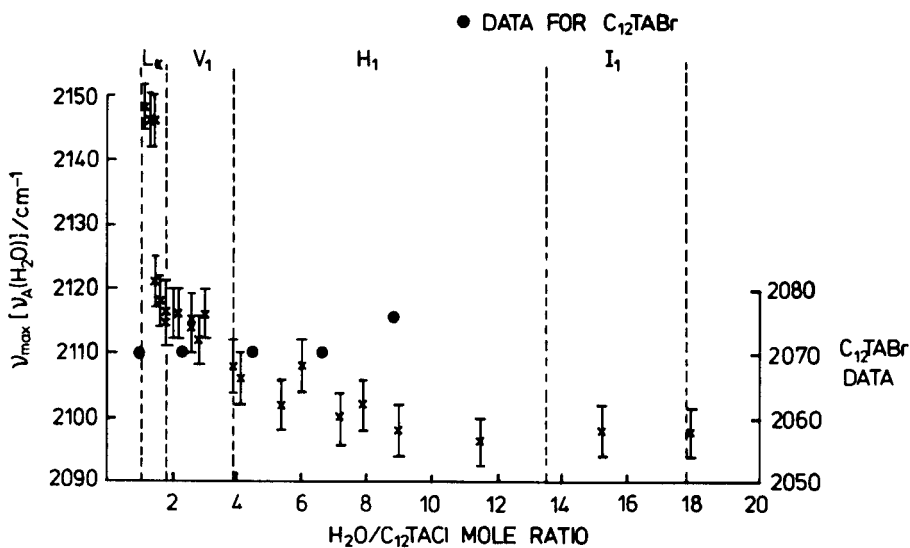


Figure 5. Variation of the apparent position of the $\nu_A(\text{H}_2\text{O})$ band as a function of water/surfactant mole ratio at 50°C .

completely (cf. figure 3 F). It should be noted that, at this concentration, the meso-phase contains only one water molecule for every head group present. Furthermore, of these water molecules only about 4 per cent are HDO molecules. Thus HDO molecules are separated on average (and on a 10^{-14} s time scale) by relatively large distances. There is, therefore, the possibility of a reduction in intensity, through a near cancellation of $\partial\mu/\partial Q$ of this mode due to the severe perturbation from bulk HDO properties.

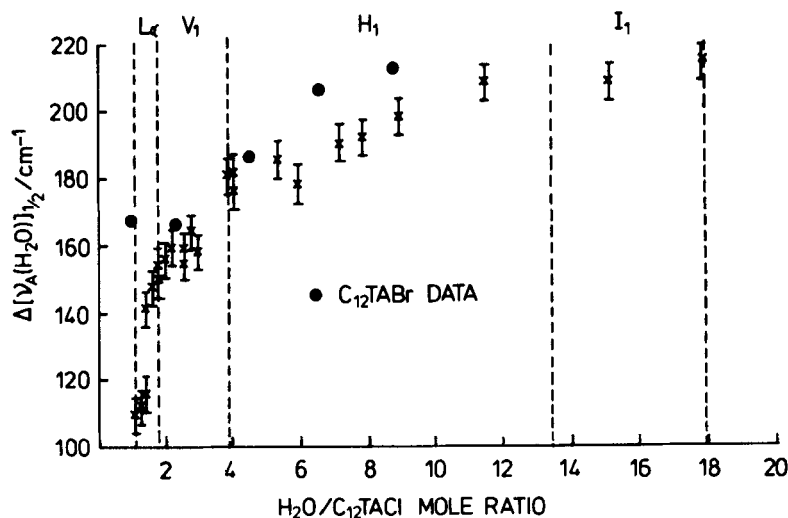


Figure 6. Variation of the half-width of the $\nu_A(\text{H}_2\text{O})$ band as a function of water/surfactant mole ratio at 50°C .

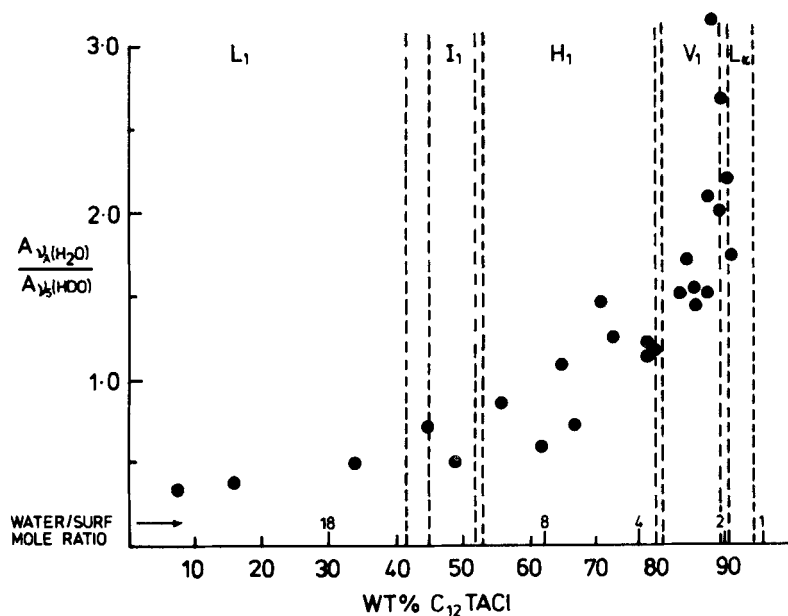


Figure 7. The intensity ratio of $\nu_A(\text{H}_2\text{O})/\nu_s(\text{HDO})$ band intensities as a function of concentration of C_{12}TACl .

We have to be rather careful about the interpretation of shoulders in these spectra as being due to distinctly different water molecules. Figure 8 shows that, quite conceivably, shoulders observed on the $\nu(\text{OD})$ band at higher concentrations of surfactant could be weak solid state vibrational bands of the organic component. However, some of these shoulders do become evident at much lower concentrations of surfactant and are, in all probability due to the perturbation of water molecules due to cation or anion binding [61, 62].

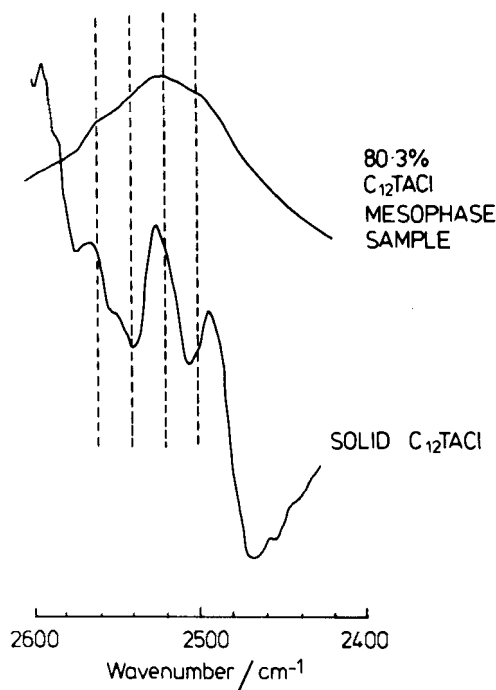


Figure 8. Comparison of the spectra of the second cubic phase (V_1) of $C_{12}TACl$ with that of the solid surfactant. (Investigation of possible solid phase bands in the mesophase spectrum.)

It is worth noting that, despite the strong perturbation of the water spectrum, the band shifts observed are rather small compared with the $\sim 200\text{ cm}^{-1}$ shifts [62] expected if water is strongly hydrogen-bonded to a base, for example, to the Cl^- counterions. The $-N^+(CH_3)_3$ head groups do not, of course, have obvious sites for hydrogen-bonding interaction. They are, however, expected to have strong ion-dipole interactions with water. These are known to lead to spectral shifts [64 (b)] of the order of $20\text{--}50\text{ cm}^{-1}$ which is the kind of shift observed in this work. The initial implication is therefore that changes in our spectra are caused by short range head group-water interactions. There is, however, at least some evidence that H_2O/X^- interactions may also be important (see later).

A number of rather important conclusions arise from this part of the work. Firstly, although water is in a very different environment in these mesophases from what it is in bulk water, there is no distinct break in the water molecule properties at the phase boundaries. Thus the infrared spectra are relatively insensitive to changes in phase structure and therefore to the long range packing of micelles in the different mesophases. Secondly, there is evidence in the $\nu_A(H_2O)$ band (cf. figure 3 F) of *at least two* different water environments. In at least one of these environments the HDO molecules appear to be so severely perturbed that their $\nu(OD)$ intensity is lost. Shifts of the water $\nu(OH)$ bands due to binding with the chloride ion are usually to high frequency but only by $\sim 10\text{ cm}^{-1}$ [63] so this seems an unlikely alternative. Incidentally, this does not occur when the bromide counterion is used; an indicator that binding to the counter-ion *may* be important. Thirdly, both bands suffer considerable loss of breadth on incorporation into highly polar and motionally restricted,

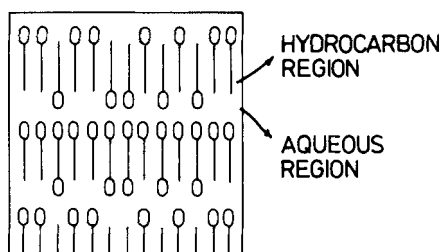


Figure 9. Interdigitated structures of the gel phase of $C_{16}TACl$.

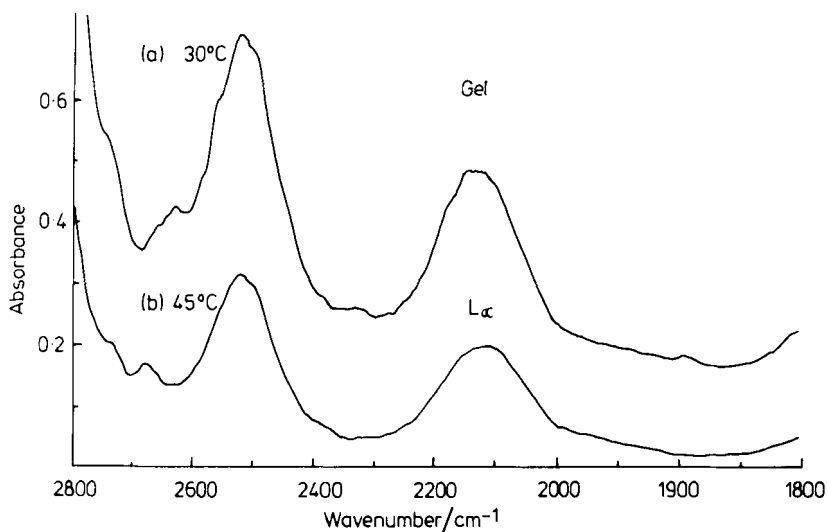


Figure 10. Comparison of the spectra of the gel and lamellar phases of $C_{16}TACl$ showing the basic similarity of bound water in the two phases (84.2 per cent solid surfactant in each case).

environments. The breadth of hydrogen bonded $\nu_s(\text{OH} \cdots \text{B})$ bands has often been attributed [64] to an overlapping of many different environments of $\nu(\text{OH})$ bands caused by a distribution of hydrogen bonding lengths and angles (the effect is known as inhomogeneous broadening [65]). Thus, it follows that water molecules in these lyotropic phases are subject to a narrower range of interactions than they are in bulk water. Since in liquid-crystalline phases, water molecules are involved in strong interactions with cations or anions (or both), this is to be expected. By the same token, their freedom to rotate and translate is also expected to be reduced—as found from the reduced self-diffusion coefficients for water in other lyotropic mesophases [13, 24, 29, 30]. Infrared spectra contain both rotational and vibrational components [66] (i.e. motional and interaction dependent parts). Hence we cannot be certain that the rotational motions are slowed down. Such a phenomenon could contribute to band narrowing if ps motions were restricted at the interface. It is also worth mentioning here the gel phase of $C_{16}TACl$ which is thought to consist of interdigitated surfactant molecules in a monolayer arrangement (cf. figure 9) where the chains are in a solid-like all-trans conformation [67, 68]. Comparison of mid-infrared spectra of the gel and lamellar phases (cf. figure 10) obtained at 84.2 per cent surfactant shows that the differences in water environment are very small (within the experimental

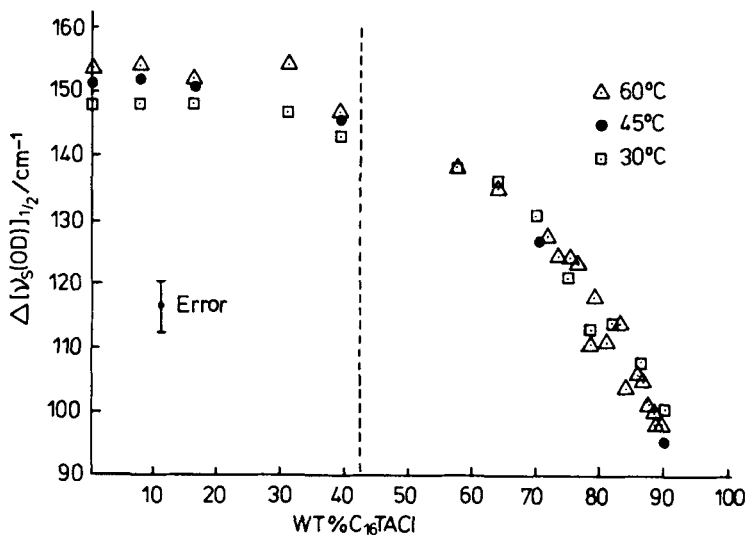


Figure 11. Changes in the $\nu_s(\text{OD})$ band halfwidth as a function of temperature and concentration for C_{16}TACl . The dotted line marks the order/disorder boundary. Conversion from gel to lamellar phase occurs at ~ 85 per cent surfactant from 30°C to 40°C .

error). This means that interactions other than water binding are responsible for the differences in phase organization. The behaviour of the $\nu(\text{OD})$ bandwidth shows that a very similar pattern for C_{16}TACl (cf. figure 11) demonstrating again that the water environment changes gradually across the phase diagram and confirming that our spectra detect only differences in short-range interactions in the head group region. The microscopic state of water is independent of phase structure.

As mentioned previously (cf. table 1), the far-infrared spectrum of water is expected to be sensitive to changes in water environment because the overall spectral profile reflects the intensity and position of the librational and translational bands of the hydrogen-bonded network. We have examined the spectrum of H_2O in C_{12}TACl mesophases at the points shown on figure 1. The signal-to-noise ratios are necessarily rather poor—the level of reproducibility being demonstrated in figure 12. The water spectrum (cf. figure 12 A) is not changed to any significant extent until the first cubic phase is reached at 47 per cent surfactant. At this concentration (cf. figure 12 B) the well-known shoulder at 200 cm^{-1} (due to ν_T) begins to shift to lower frequency and another band near 115 cm^{-1} begins to grow. At about 56 per cent surfactant (also I_1 phase) the two bands are clearly seen and are accentuated in the H_1 phase at about 71 per cent surfactant (cf. figure 12 C). In the second cubic (V_1) and in the lamellar phases (L_α) the band at 115 cm^{-1} increases in intensity (relative to that at $\sim 160\text{ cm}^{-1}$) and a band between 65 cm^{-1} and 85 cm^{-1} begins to emerge (cf. figure 12 D). The almost solid surfactant (at 93.7 per cent) also shows two bands at about 120 cm^{-1} and 85 cm^{-1} (cf. figure 12 E). In order to demonstrate more fully the spectral changes involved we show in figure 13 a schematic representation of the mesophase far-infrared spectra.

It is clear in the first instance that beyond the $\text{L}_1 \rightarrow \text{I}_1$ phase transition the water is no longer bulk water. Furthermore, it is equally clear that ν_T bands due to $(\text{O}^{\delta-}-\text{H}^{\delta+}-\text{O}^{\delta-})$ or $(\text{O}^{\delta-}-\text{H}^{\delta+}-\text{X}^-)$ or $(\text{N}^{\delta+}+\text{O}^{\delta-}-\text{H}^{\delta+})$ (or some combination

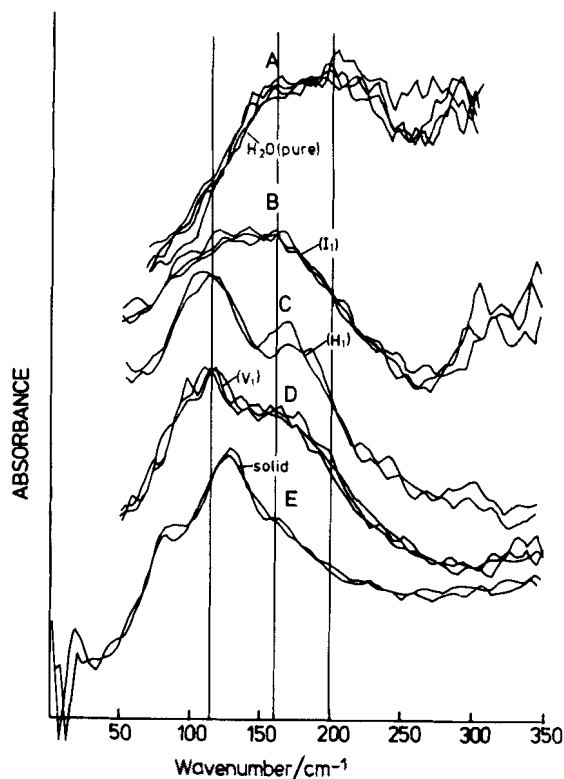


Figure 12. Far-infrared spectra of the various mesophases of $C_{12}TACl$ with water (the temperature is $20^{\circ}C$).

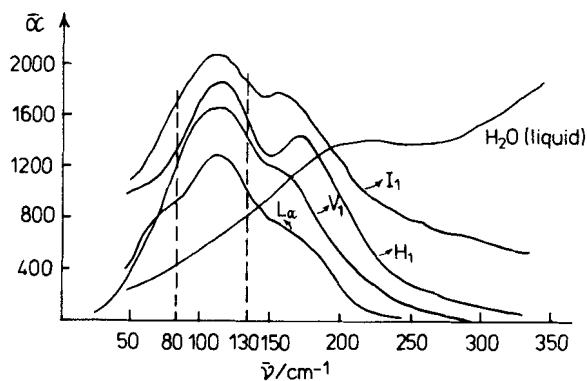


Figure 13. Schematic diagram showing the gross changes in far-infrared spectra of $C_{12}TACl$ as a function of concentration ($T = 20^{\circ}C$).

of all these) interactions arise at $\sim 115\text{ cm}^{-1}$ and $\sim 160\text{ cm}^{-1}$ and that one species (at $\sim 115\text{ cm}^{-1}$) gradually tends to predominate at highest surfactants concentrations. It is well-known [69] that tetra alkyl ammonium chlorides have interionic ($R_4N^+ \text{-----} X^-$) bands in this region so the bands at 115 cm^{-1} is possibly partly due to this type of mode (at very low water concentrations). Nevertheless, it is clear that the far-infrared spectra confirm the existence of at least two forms of interaction-

Table 2. Assignment of far-infrared spectra of water in C_{12} TACl.

Band	Proposed assignment
200 cm^{-1} (± 10)	ν_T (bulk water)
$\sim 160\text{ cm}^{-1}$ (± 10)	Bound water, ν_T (O—H-----Cl ⁻ ?)
$\sim 115\text{ cm}^{-1}$ (± 10)	Bound water/interionic mode?
$\sim 85\text{ cm}^{-1}$	Interionic mode?
$\sim 65\text{ cm}^{-1}$	Bending mode of bound water(?)

N.b. the solid shows bands at 85 cm^{-1} and 130 cm^{-1} .

perturbed water molecules. Our assignments are shown in table 2. Both sets of spectra would seem to indicate that differently perturbed (or bound) water molecules are in equilibrium with each other. The frequency shifts and band-width changes clearly point to *gradual* changes in the proportions of water molecules interacting in a particular way with the micellar surfaces without any need to invoke the concept of different distinct layers of water. Indeed, it is obvious that long-range interactions due to differences in mesophase structure [24] do not give rise to observable spectral changes. In this sense, at least, our results fit very nicely with the ideas presented recently by Tiddy *et al.* for non-ionic surfactant-containing mesophases [56, 57]. Quantitative intensity data, very difficult to obtain for these materials, would help to confirm or refute this interpretation since measurements of water activity at different total concentrations could then be obtained. However, higher signal-to-noise ratios would be required in the far-infrared and band deconvolution would be required to separate the different overlapping water bands.

4. Summary and conclusions

The water molecules in these lyotropic liquid-crystalline phases are rather strongly perturbed compared with bulk water. This might have some relevance to the currently popular theories of hydration forces [1–12]. Certainly, in the lamellar phase, with only 1–2 water molecules per surfactant head group, the molecules are electronically very different from those in the bulk. Although we have some definite evidence of two types of perturbed water molecules, it is clear that the *two* species are present *together* over the whole concentration range studied. It is possible that these two species are cation and anion bound water molecules. There is no direct evidence of different layers of water molecules, nor of any discontinuous changes when a phase boundary is crossed (where distinct changes in separation of surfactant/water interfaces do occur). Thus, only differences in short-range interactions are probed; the differences in curvature and surface/volume ratio between the organizes in different mesophases are not reflected in the water spectra. Our data are therefore in support of an equilibrium binding model for water in lyotropic phases [56, 57]. This seems to us to be the most sensible approach anyway, given the high rates of H_2O translational diffusion [24, 65] in liquid-crystalline phases (although reduced, of course, from the value in bulk water). However, it is also clear that the water molecules trapped or bound between the polar organic interfaces are dynamically confined in the sense that their vibrational relaxation rates are much slower (i.e. band-widths much lower) and they are subjected to a narrower distribution of interaction induced environments. This means, in effect, that the bound water at the polar interface has a narrower range of states than in bulk water—an observation which tend to mediate against models involving *different* polarized layers at the organic interface.

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References

- [1] RAND, R. P., 1981, *A. Rev. biophys. Bioengng*, **10**, 272.
- [2] NINHAM, B. W., 1981, *Pure appl. Chem.*, **52**, 2135.
- [3] PROUTY, M. S., SHECHTER, A. N., and PARSESIAN, V. A., 1984, *J. molec. Biol.*, **184**, 517.
- [4] PARSESIAN, V. A., FULLER, N., and RAND, R. P., 1979, *Proc. natn. Acad. Sci. U.S.A.*, **76**, 2750.
- [5] WHITE, S. H., and KING, G. I., 1985, *Proc. natn. Acad. Sci. U.S.A.*, **82**, 6532.
- [6] PARSESIAN, V. A., 1982, *Adv. Colloid Interface Sci.*, **16**, 49.
- [7] MARVA, J., and ISRAELACHVILI, J., 1985, *Biochemistry*, **24**, 4608.
- [8] ISRAELACHVILI, J., 1985, *Intermolecular and Surface Forces* (Academic Press).
- [9] PASHLEY, R. M., MCGUIGGAN, P. M., NINHAM, B. W., and EVANS, D. F., 1985, *Science N.Y.*, **229**, 1088.
- [10] LE NEVEU, D. M., RAND, R. P., PARSESIAN, V. A., and GINGELL, D., 1977, *Biophys. J.*, **18**, 209; LIS, C. L. J., MCALISTER, M., FULLER, N., RAND, R. P., and PARSESIAN, V. A., 1982, *Biophys. J.*, **37**, 657.
- [11] MARCELJA, S., and RADIC, N., 1976, *Chem. Phys. Lett.*, **42**, 129.
- [12] RENDELL, K., and TIDY, G. J. T., 1984, *J. chem. Soc. Faraday Trans. I*, **80**, 3339.
- [13] TIDY, G. J. T., 1977, *J. chem. Soc. Faraday Trans. I*, **73**, 1731.
- [14] LEIGH, I. D., McDONALD, M. P., WOOD, R. M., TIDY, G. J. T., and TREVETHAN, M. A., 1981, *J. chem. Soc. Faraday Trans. I*, **77**, 2867.
- [15] CHACHATY, C., and QUAEGBEUR, J. P., 1983, *J. phys. Chem.*, **87**, 4341.
- [16] NIEDERBERGER, W., and TRICOT, Y., 1977, *J. magn. Reson.*, **28**, 213; 1979, *Biophys. Chem.*, **9**, 195.
- [17] GOLDFARB, D., LABES, M. H., LUZ, Z., and POUPKO, R., 1982, *Molec. Crystals liq. Crystals*, **87**, 259.
- [18] HALLE, B., and WENNERSTRÖM, H., 1981, *J. chem. Phys.*, **75**, 1928.
- [19] BROWN, M. F., SEELIG, J., and HÄBERLEN, U., 1979, *J. chem. Phys.*, **70**, 5045.
- [20] LINDMAN, B., and PERSSON, N. O., 1975, *J. phys. Chem.*, **79**, 1410.
- [21] HALLE, B., and CARLSTÖM, G., 1981, *J. phys. Chem.*, **85**, 2142.
- [22] PERSSON, N. O., and JOHNSON, A., 1971, *Acta chem. scand.*, **25**, 2118.
- [23] WALTER, W. V., and HAYES, R. G., 1971, *Biochem. biophys. Acta*, **249**, 528.
- [24] TIDY, G. J. T., 1979, *Nucl. magn. Reson.*, **8**, 174; 1980, *Phys. Rep.*, **57**, 1.
- [25] WONG, M., THOMAS, J. K., and NOWAK, T., 1977, *J. Am. chem. Soc.*, **99**, 4730.
- [26] BOCIAN, D. F., and CHAN, S. I., 1978, *A. Rev. phys. Chem.*, **29**, 307.
- [27] CHACHATY, C., and QUAEGBEUR, J., 1984, *Molec. Phys.*, **52**, 1081.
- [28] ROBIN-LHERBIER, B., CAMET, D., MARCHAL, J. P., and BRONDEAU, J., 1984, *Surfactants in Solution*, edited by K. Mittal (Plenum).
- [29] PETHIG, R., 1979, *Dielectric and Electronic Properties of Biological Material* (Wiley).
- [30] HAYTER, J. B., HECHT, A. M., WHITE, J. W., and TIDY, G. J. T., 1974, *Faraday Discuss. chem. Soc.*, **57**, 130.
- [31] BONE, S. C., GASCOYNE, P. R. C., EDEN, J., and PETHIG, R., 1977, *J. chem. Soc. Faraday Trans. I*, **73**, 1605.
- [32] GASCOGNE, P., and PETHIG, R., 1977, *J. chem. Soc. Faraday Trans. I*, **73**, 171; 1981, *Ibid.*, **77**, 1733.
- [33] EDEN, J., GASCOYNE, P. R. C., and PETHIG, R., 1980, *J. chem. Soc. Faraday Trans. I*, **76**, 426.
- [34] HARVEY, S. C., and HOEKSTRA, P., 1972, *J. phys. Chem.*, **76**, 2987.
- [35] KENT, M., and MEYER, W., 1983, *J. Phys. D*, **16**, 915; 1984, *Ibid.*, **17**, 1687.
- [36] GOLTON, I., 1980, Ph.D. Thesis, University of London.
- [37] GENZEL, L., POGLOTSCH, A., and KREMER, K., 1984, *J. molec. Biol.*, **173**, 137.
- [38] BIRCH, J. R., and BENNOUNA, M., 1981, *Infrared Phys.*, **21**, 229.
- [39] UMEMURA, J., CAMERON, D. G., and MANTSCH, H. H., 1980, *J. phys. Chem.*, **84**, 2272.
- [40] FALK, M., POOLE, A. G., and GOYMOUR, C. G., 1970, *Can. J. Chem.*, **48**, 1536.
- [41] CARERI, G., GRATTON, E., YANG, P.-H., and RUPLEY, J. A., 1980, *Nature, Lond.*, **284**, 572.

- [42] BUONTEMPO, U., and CARERI, G., 1972, *Biopolymer*, **11**, 579.
- [43] KISE, H., IWAMOTO, K., and SENO, M., 1982, *Bull. chem. Soc. Japan*, **55**, 3856.
- [44] SENO, M., ARAKI, K., and SHIRAIISHI, S., 1976, *Bull. chem. Soc. Japan*, **49**, 899; 1980, *J. Colloid Interface Sci.*, **78**, 57.
- [45] SUNAMOTO, J., HAMADA, T., SETO, T., and YAMAMOTO, S., 1980, *Bull. chem. Soc. Japan*, **53**, 583.
- [46] SENO, M., SAWADA, K., ARAKI, K., IWAMOTO, K., and KISE, H., 1980, *J. Colloid Interface Sci.*, **78**, 57.
- [47] KIMURA, N., UMEMURA, J., HAYASHI, S., and TAKENAKA, T., 1984, *J. molec. Struct.*, **116**, 153.
- [48] MCNEIL, R., and THOMAS, J. K., 1981, *J. Colloid Interface Sci.*, **83**, 57.
- [49] FRANCOISE, P. J., 1973, *Kolloid-Z Z-Polymere*, **251**, 594.
- [50] KAWAI, T., UMEMURA, J., TAKENAKA, T., and KODAMA, M., and SEKI, S., 1985, *J. Colloid Interface Sci.*, **103**, 56.
- [51] McDONALD, M. P., and WILFORD, L. D. R., 1974, *Liquid Crystals and Ordered Fluids*, edited by J. J. Johnson and R. S. Porter (Plenum), p. 225.
- [52] WELLS, M. A., 1974, *Biochemistry*, **13**, 4937.
- [53] LUCAS, M., DE TROBRIAND, A., and CECCALDI, M., 1975, *J. phys. Chem.*, **79**, 913.
- [54] BIOCCELLI, C. A., GIOMINI, M., and GIULIANI, A. M., 1984, *Appl. Spectrosc.*, **38**, 537.
- [55] MALLAMACE, F., MIGLIARDO, P., VASI, C., and WANDERLINGH, F., 1981, *Phys. Chem. Liq.*, **11**, 47.
- [56] LYLE, I., and TIDY, G. J. T., 1986, *Chem. Phys. Lett.*, **124**, 423.
- [57] CARRELL, M., HALL, D. G., LYLE, J. G., and TIDY, G. J. T., 1986, *Faraday Discuss. chem. Soc.*, **81** (in the press).
- [58] BALMBRA, R. R., CLUNIE, J. S., and GOODMAN, J. F., 1969, *Nature, Lond.*, **222**, 1159.
- [59] RENDELL, K., TIDY, G. J. T., and TREVETHAN, M. A., 1983, *J. chem. Soc. Faraday Trans. I*, **79**, 637.
- [60] EIZENBERG, D., and KAUZMANN, W., 1969, *The Structure and Properties of Water* (Oxford University Press).
- [61] LUTZ, H. D., POBITSCHKA, W., FRISCHEMEIMER, B., and BECKER, R. A., 1978, *Appl. Spectrosc.*, **32**, 541.
- [62] BACELON, P., CORSET, J., and DE LOZE, C., 1975, *Chem. Phys. Lett.*, **32**, 458.
- [63] HARTMAN, J., 1966, *J. phys. Chem.*, **70**, 270.
- [64] WALRAFEN, G. E., 1972, *Water—A Comprehensive Treatise*, edited by F. Franks, (a) Vol. 1, Chap. 5; (b) VERRALL, R. F., Vol. 3, Chap. 5 (Plenum).
- [65] OXTOBY, D. W., 1981, *Adv. chem. Phys.*, **47**, 487.
- [66] ROTHSCHILD, W. G., 1984, *Dynamics of Molecular Liquids* (Wiley).
- [67] TIDY, G. J. T., and BLACKMORE, E., (unpublished results).
- [68] VINCENT, J. M., and SKOULIOS, A., 1966, *Acta crystallogr.*, **20**, 441.
- [69] YARWOOD, J., JAMES, P. L., and BARKER, C., 1978, *Protons and Ions Involved in Fast Dynamic Phenomena*, edited by P. Lazlo (Elsevier), p. 63.