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Deuterium NMR of perdeuteriated di and monoacids dissolved in the lyomesophases of dipotassium hexadecanedioate

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The behaviour of α,ω-diacid and α-monoacid guest molecules (with carbon atoms ranging between 6 to 22) in the lamellar and hexagonal mesophases of dipotassium thapsate ($KOOC(CH_2)_{14}COOK$)-water mixtures have been investigated, using deuterium NMR spectroscopy. Addition of short diacids to either the lamellar or hexagonal phases results in phase separation and essentially no incorporation into the mesophase structure. The deuterium spectra of the guest molecules exhibit characteristic patterns which are qualitatively interpreted in terms of their ordering properties. In no case were separate signals observed due to folded diacid guest molecules which have their carboxyl groups on the same side of the interface.

1. Introduction

We have recently investigated the binary phase diagram of mixtures of the disoap dipotassium hexadecanedioate (dipotassium thapsate-$KOOC(CH_2)_{14}COOK$) with water [1, 2], using optical microscopy, X-ray and NMR spectroscopy. Depending on the concentration and temperature two mesophases were identified, an hexagonal phase (LTP) which is formed in solutions containing more than about 40 wt. % disoap and is only stable below about 120°C, and a uniaxial lamellar phase (HTP) which appears in solutions containing above 55 wt. % disoap and is stable above 120°C. The structure of these mesophases (see figure 1) resembles very closely the corresponding phases of monosoaps [3–5]. The lamellar phase consists of stacks of disoap monolayers, interleaved by water sheets, while the hexagonal phase consists of a two dimensional array of disoap rods embedded in a water surrounding. The disoap molecules traverse the rods or lamellae and the carboxyl groups form the interfaces with the water.

A problem frequently addressed by researchers of lyomesophases concerns the ordering and the conformational equilibra of alkyl chains dissolved in mesophases [6–12]. One of the main methods to study this problem has been to use the quadrupole interactions, ν_Q, observed in the deuterium NMR of deuteriated amphiphiles [13, 14] or guest molecules [15–17]. Here we apply this approach to deuteriated α,ω-diacids and α-monoacids dissolved in the lamellar and hexogonal phases of the dipotassium

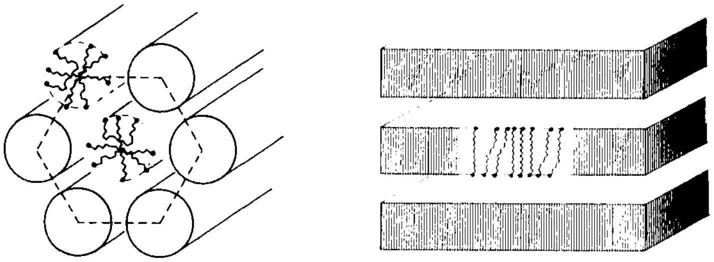

Figure 1. Schematic representations of the lamellar and hexagonal lyomesophases in the dipotassium thapsate–water system.

thapsate–water system. The diacid guest molecules, if long enough, are expected to anchor with their carboxyl groups on opposite sides of the lamellae or rods and consequently the ordering of the methylene segments should depend on the ratio of their length to the widths of the lamellae or rods in the respective mesophases. Clearly, if the diacid molecules are short they must stretch to the all-trans state in order to fit into the host disoap structures, while if they are very long they will probably be in a highly folded and disordered state.

The guest diacid molecules can also fold back on themselves, confining both carboxyl groups to the same side of the lamellae interface. Such conformations are expected to occur particularly in short-chain diacid guests which cannot extend the width of the lamellae (or the diameter of the rods). This has been observed in ESR and NMR studies of dicarboxylic spin probes [18] and deuteriated diacids [19] in lamellar phases of monosoaps, in both cases exhibiting distinct signals due to folded molecules. The method was in fact used to estimate the difference in energy of the trans and gauche configurations, as well as the effective width of the lamellae.

For convenience we use a shorthand notation and refer to the α,ω-diacid $HOOC(CD_2)_{n-2}COOH$ as C_nH_2 and to the α-monoacid $CD_3(CD_2)_{n-2}COOH$ as C_nH_1. In analogy the dipotassium thapsate salt $KOOC(CH_2)_{14}COOK$ is referred to as $C_{16}K_2$.

2. Experimental

Material and sample preparation. Isotopically normal monoacids and α,ω-diacids were obtained commercially from Fluka (Switzerland), Larodan (Sweden), Pfaltz and Bauer (U.S.A.), Aldrich (U.S.A.) and Merck (F.R. Germany). Perdeuteriated monoacids and diacids were prepared from corresponding normal acids by exchange with D_2O in a basic solution using a platinum on carbon catalyst at 180–220°C in a high pressure stainless steel vessel. The details of the procedure including the purification and isolation of the products are described in [20]. The level of perdeuteriation usually ranged between 90 and 98 at. %. Two diacids ($n = 12$ and 16) were also specifically α-deuteriated by exchange with D_2O but without the platinum on carbon catalyst [21].

The samples were prepared by mixing weighed amounts of dipotassium thapsate, water and the desired guest in 5 mm glass tubes, flame sealed and allowed to equilibrate at about 140–160°C for several days. The NMR measurements were recorded by the quadrupole echo method [22], normally 5000 to 10 000 scans were accumulated with a repetition time of 0·2 s before Fourier transformation.

3. Results

The deuterium NMR of the di and monoacid guests were measured in two regions of the dipotassium thapsate–water phase diagram [1, 2]. The first region, corresponds to high dipotassium thapsate concentrations (> 55 wt. %) in which the phase sequence is (see figure 1 of [2]):

$$\text{solid} \rightarrow \text{hexagonal} \rightarrow \text{liquid} \rightarrow \text{lamellar} \rightarrow \text{liquid}.$$

The intermediate liquid in this sequence is a reentrant isotropic liquid usually observed only on slow heating. This region of the phase diagram was used to study the spectra of the guests in the lamellar phase, but it was not suitable for the hexagonal phase since it was considerably destabilized by the diacid guests. The second region, where the deuterium spectra of the guest molecules in the hexagonal phase were measured, corresponds to a lower dipotassium thapsate concentration (< 55 wt. %), in which the phase sequence is

$$\text{solid} \rightarrow \text{hexagonal} \rightarrow \text{liquid}.$$

3.1. *Diacids* (C_nH_2) *in the lamellar phase*

The compositions of the mixtures used to measure the deuterium NMR of the various diacid guests in the lamellar phase are given in table 1 (*a*). The number of carbon atoms, *n*, of the diacid guests ranged from 10 to 22 and the mole ratios, $[C_nH_2]/[C_{16}K_2]$ were generally 0·1 or less. An attempt to dissolve the shorter diacid C_6H_2 was unsuccessful and resulted in separation of the sample into two phases. The addition of the diacids did not lower the clearing temperature of the lamellar phase significantly but narrowed drastically the stability range of the hexagonal phase (sometimes eliminating it completely) by suppressing the transition temperature between the lamellar and the hexagonal phases from 115°C in the guest-free system to about 80°C in the doped samples. The lamellar phase readily aligned in the

Table 1. Composition of the mixtures used to study the deuterium spectra of diacids dissolved in the lamellar (*a*) and hexagonal (*b*) phases.

n	$C_{16}K_2$/wt. %	H_2O/wt. %	C_nH_2/wt. %	$\frac{[H_2O]}{[C_{16}K_2]}$	$\frac{[C_nH_2]}{[C_{16}K_2]}$
			(*a*)		
10	58·3	38·1	3·6	13·1	0·101
11	57·5	37·0	5·5	12·9	0·149
12	58·3	38·4	3·3	13·2	0·075
13	57·8	37·3	4·9	13·0	0·115
14	57·6	37·1	5·3	13·0	0·076
15	55·6	41·1	3·3	13·0	0·065
16	57·9	37·4	3·1	13·0	0·092
17	59·5	37·4	3·1	12·6	0·057
22	58·0	37·4	4·6	13·0	0·070
			(*b*)		
14	48·9	48·1	2·9	19·8	0·077
15	48·3	47·6	4·1	19·8	0·103
16	46·8	49·7	3·5	21·3	0·086
17	46·8	49·6	3·5	21·3	0·082
22	48·2	48·4	3·4	20·2	0·061

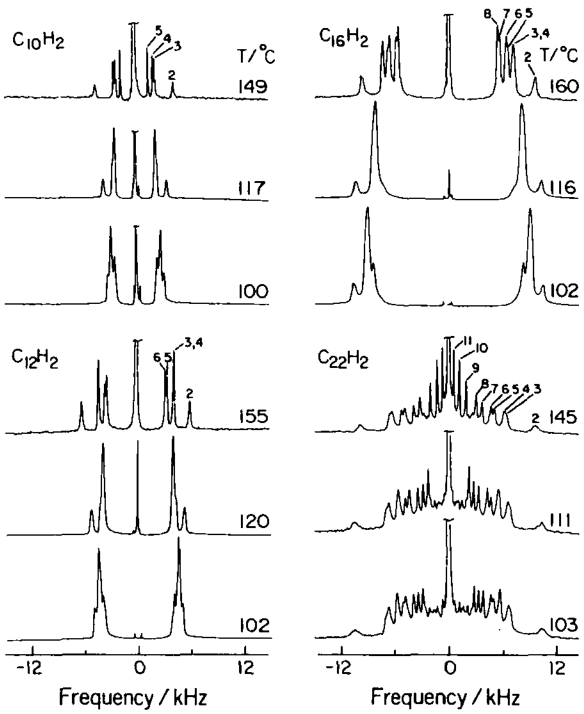

Figure 2. Deuterium NMR spectra of deuteriated diacid guest molecules, C_nH_2 dissolved in the lamellar phase of $C_{16}K_2$–H_2O at the temperatures indicated. The composition of the solutions are given in table 1 (*a*) and the peak assignment is as explained in the text.

magnetic field, with the director perpendicular to the magnetic field direction ($\Delta\chi < 0$) and produced relatively well resolved spectra for the diacid guest molecules. Examples of the spectra for four such guests at several temperatures are shown in figure 2. It may be seen that for each sample quadrupole doublets are observed whose splittings depend on the temperature. In all cases, at sufficiently high temperatures, almost complete spectral resolution was obtained with at most one pair of doublets remaining degenerate as demonstrated by the relative intensities and number of peaks in the spectrum. Since the alignment of the lamellar phase is perpendicular to the field direction we identify the spacing between the doublet components, ν^i_Q, with the average quadrupole interaction parameter of the *i*th deuteron. Usually a very weak and sharp doublet, due to HDO molecules in the solvent water, and sometimes also a central peak due to an isotropic component in the sample were observed. No additional peaks which might be associated to other conformations of the diacids were observed. In two cases ($n = 12$ and 16) the signals due to the α-deuterons (carbon number 2) were identified by comparing the spectra of the perdeuteriated species with the corresponding spectra of the α-deuteriated diacids. As expected from observation in similar systems [23] these peaks correspond to the doublets with the largest splitting and we have accordingly assigned the outermost pairs of peaks which were usually well separated from the rest of the signals in all other spectra to the α-deuterons. No similar assignment, i.e. by specific deuteriation of other sites in the aliphatic chain, was made. For the later discussion we have, therefore, labelled these peaks sequentially according to decreasing splittings in the high temperature spectra

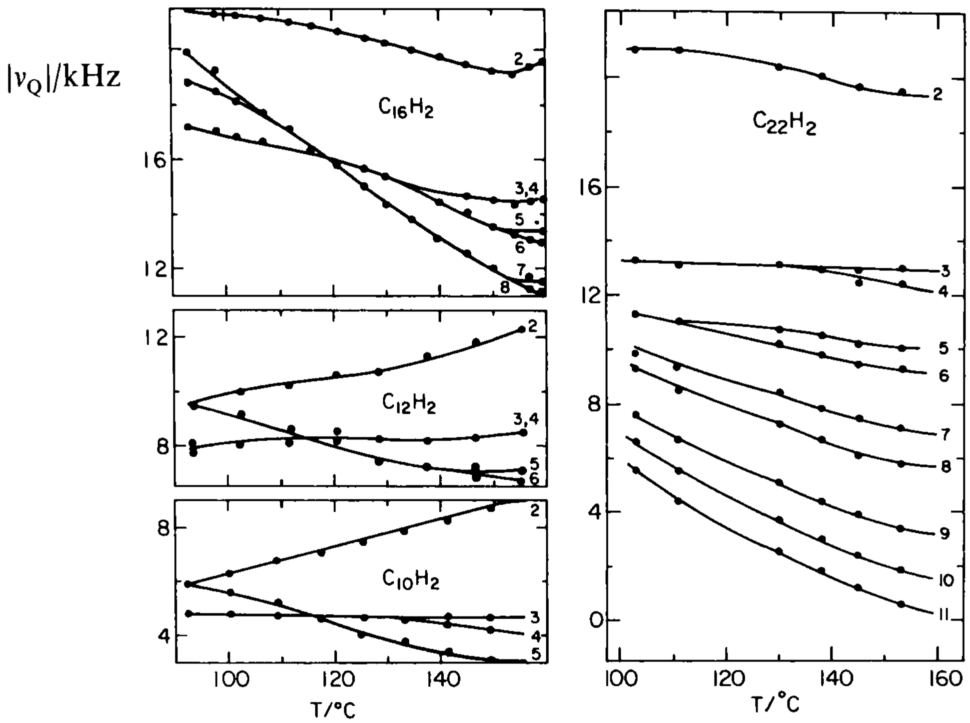

Figure 3. The average (absolute values) quadrupole interaction parameters, ν_Q, of the various deuterons in the diacid guest molecules, shown in figure 2, as function of temperature in the lamellar phase.

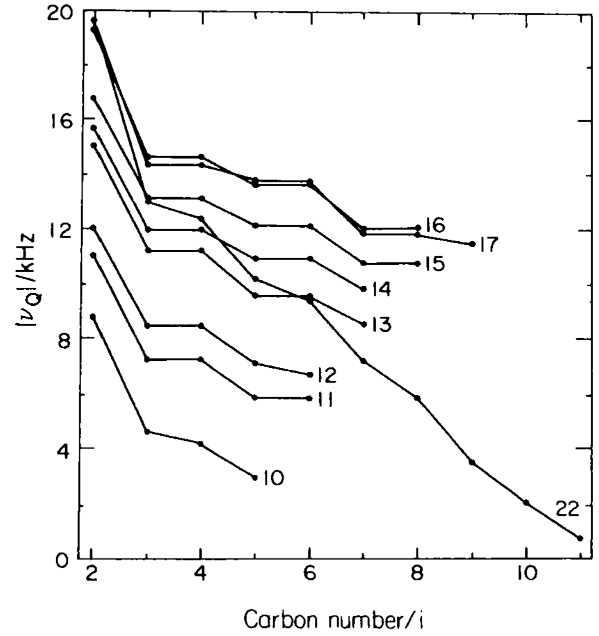

Figure 4. The average (absolute values) quadrupole interaction parameters, ν_Q, for the diacid studied in the lamellar phase (see table 1 (*a*)), versus the labelling index, *i*, identified with the carbon number in the chain. The results are interpolated to 150°C.

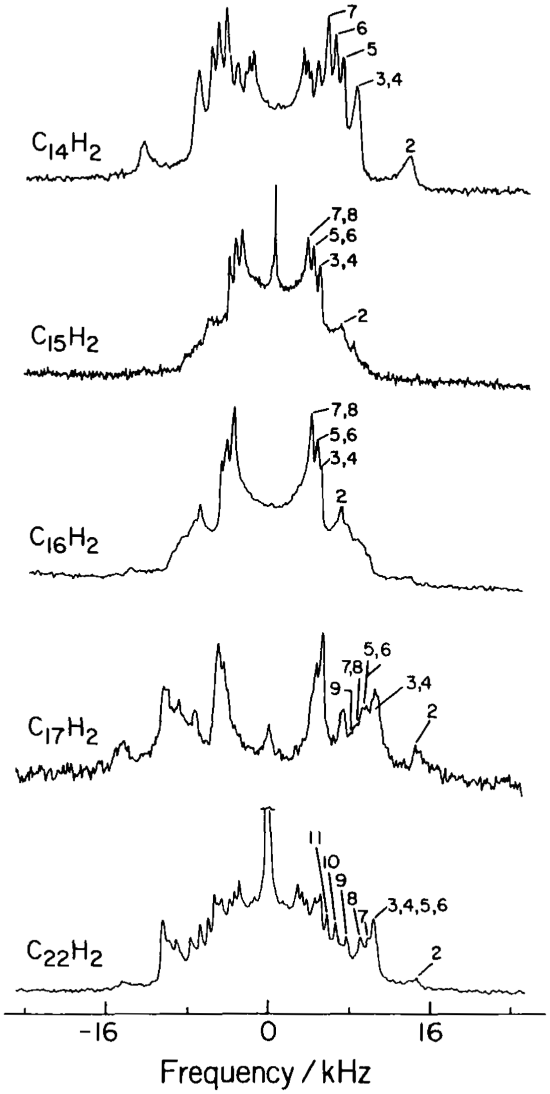

Figure 5. Deuterium NMR spectra of deuteriated diacid guest molecules, C_nH_2, dissolved in the hexagonal phase of $C_{16}K_2$–H_2O at 78–80°C. The composition of the solutions are given in table 1 (*b*) and the peak assignment is of the perpendicular features of the powder patterns for $C_{15}H_2$ and $C_{16}H_2$ and of the parallel features of the alignmed domains for the other diacid guests.

(see figure 2). In the later discussion we identify these numbers with the sequence of methylenes in the diacid chains starting from carbon 2 to the chain centre. The temperature dependence of the absolute values of the various quadrupole interaction parameters in the same guest diacids shown in figure 2, is shown in figure 3. As we see upon cooling there is peak merging and sometimes even crossing over. In figure 4 plots of $|\nu_Q^i|$ interpolated to a common temperature of 150°C, for the whole set of diacid guests studied are shown as a function of the methylene position. In the discussion section we attempt to interpret these patterns in terms of the chain conformations of the guest diacids.

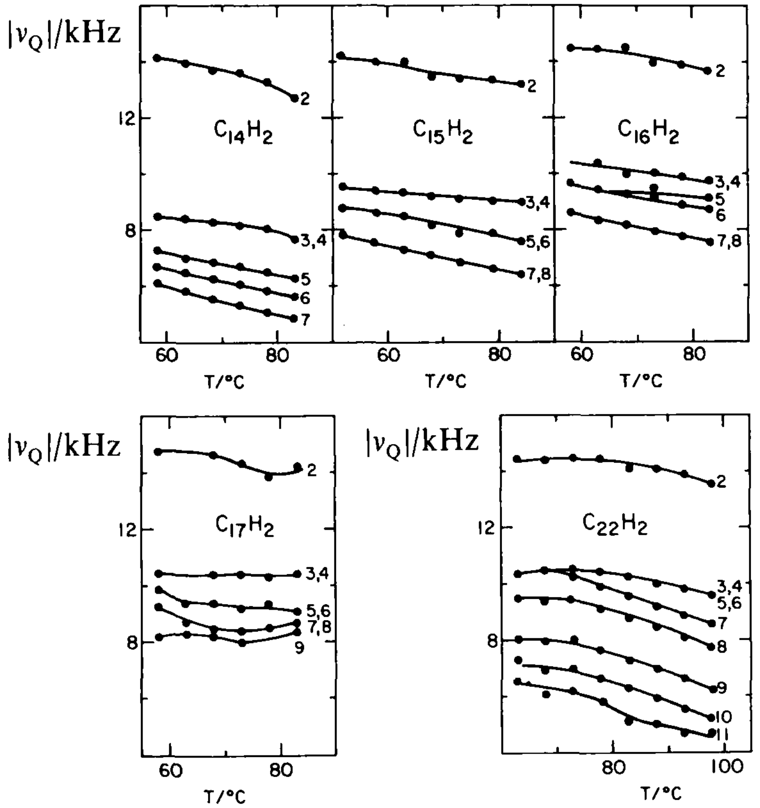

Figure 6. The average (absolute values) quadrupole interaction parameter, ν_Q, of the deuterons in the diacid guest molecules, shown in figure 5, as function of temperature in the hexagonal phase.

3.2. *Diacids* (C_nH_2) *in the hexagonal phase*

The composition of the solutions used in the measurements of the diacid spectra in the hexagonal phase are summarized in table 1 (*b*). Only diacids containing fourteen or more carbons are included. Attempts to dissolve shorter diacid molecules ($n \leqslant 13$) at similar concentrations ($[C_nH_2]/[C_{16}K_2] \sim 0{\cdot}1$) failed, as indicated by phase separation of the samples with the diacids dissolved in the isotropic liquid. The diacid guests reduced the stability range of the hexagonal mesophase by lowering its clearing temperature by about 30°C. The hexagonal phase is not aligned as well as the lamellar phase by the magnetic field and consequently powder spectra or a superposition of powder patterns and spectra due to aligned domains (parallel to the field direction since for this phase $\Delta\chi > 0$) are observed. Examples of spectra assigned as in the lamellar phase are shown in figure 5. Note that in these spectra both parallel features due to aligned domains as well as perpendicular features of the powder patterns are observed. Examples of spectra assigned as in the lamellar phase are shown in figure 5. Note that in these spectra both parallel features due to aligned domains as well as perpendicular features of the powder pattern are observed. In $C_{14}H_2$, $C_{17}H_2$ and $C_{22}H_2$ the parallel features are assigned, while for $C_{15}H_2$ and $C_{16}H_2$ the perpendicular features. The temperature dependence of the various $|\nu_Q'|$ is given in figure 6 and the splitting patterns of all diacids interpolated to 80°C are shown in figure 7.

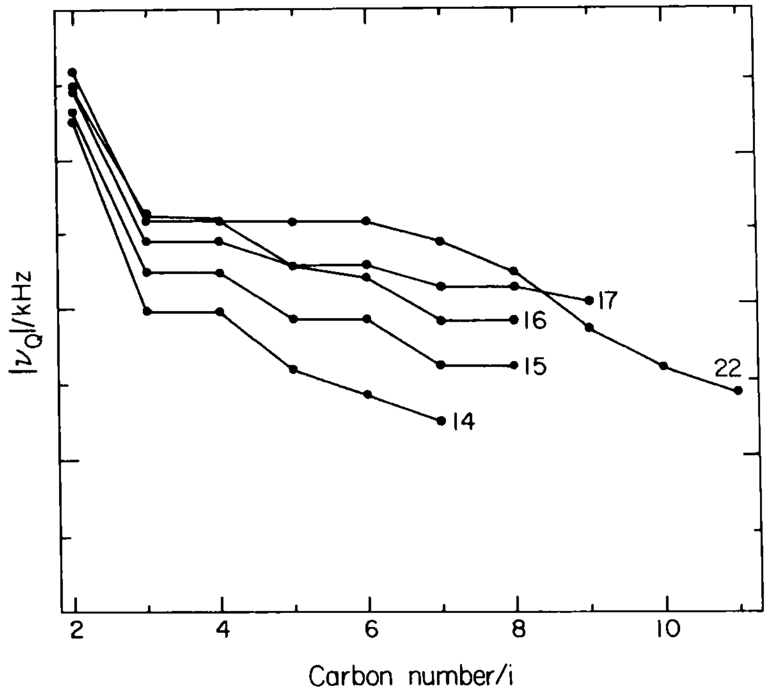

Figure 7. The average (absolute values) quadrupole interaction parameters, ν_Q, for the diacid guest molecules studied in the hexagonal phase (see table 1 (*b*)), versus the labelling index, *i*, identified with the carbon number in the chain. The results are interpolated to 80°C.

3.3. *Monoacid guests* (C_nH_l) *in the lamellar and the hexagonal phases*

As for the diacids, the spectra, of the monoacid guests in the lamellar phase were studied in samples with higher $C_{16}K_2$ concentrations, while the spectra in the hexagonal phase were measured in solutions with lower $C_{16}K_2$ concentrations. The compositions of the various solutions used to study the spectra of the monoacids are summarized in tables 2 (*a*) and (*b*). Addition of the monoacids to the dipotassium thapsate–water mixtures had less effect on the stability range of the mesophases than had the incorporation of the diacids (at comparable concentrations). Thus, although some reduction (10–20°C) in the transition temperature from the lamellar phase to the hexagonal phase was observed in the high concentration samples both phases in these mixtures remained stable over similar temperature ranges as in the guest-free samples. In fact it was possible to dissolve quite large amounts of low molecular weight monoacids (e.g. $n = 6$ see table 2 (*a*)) in the $C_{16}K_2$ mesophases without affecting phase separation.

In figures 8 and 9 we show examples of monoacid spectra, recorded in the lamellar and hexagonal phases, respectively. In the lamellar phase the spectra correspond to well aligned (perpendicular to the magnetic field) samples, while those in the hexagonal phase are sometimes aligned (parallel to the field) and in other cases exhibit powder pattern. As for the diacid guests the best spectral resolution was observed at the higher end of the temperature range, but even then sometimes pairs of peaks remained unresolved. The largest splittings were assigned to the α-deuterons, while the end methyl groups were identified on the basis of their relative intensities. Their signals were usually narrower and they always showed much smaller splittings compared to

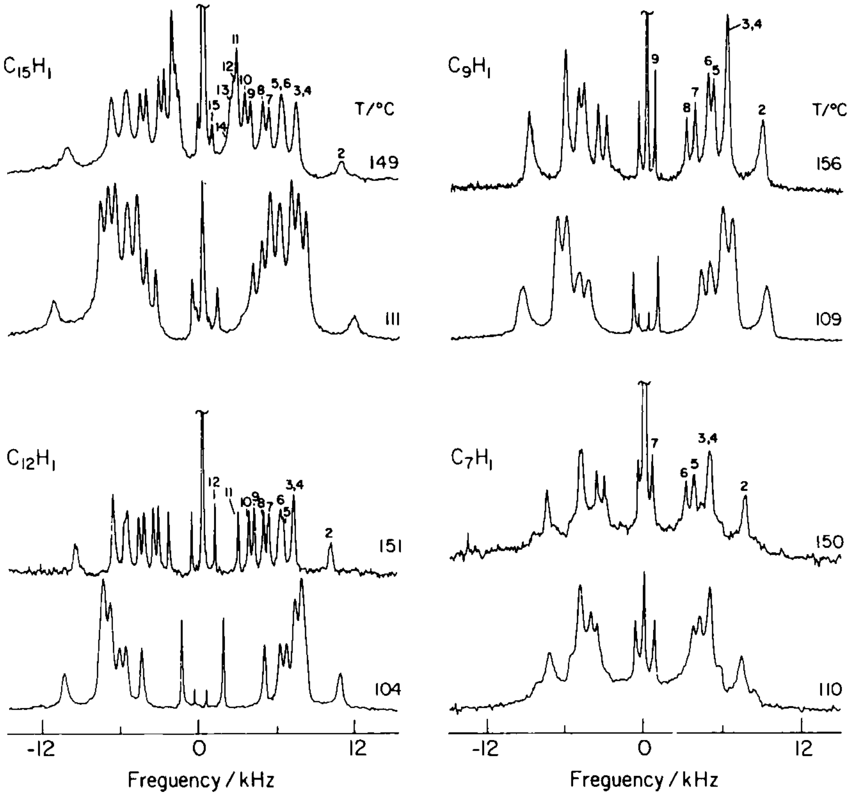

Figure 8. Deuterium NMR spectra of deuteriated monoacid guest molecules, C_nH_1, dissolved in the lamellar phase of $C_{16}K_2$–H_2O at the indicated temperatures. The composition of the solutions are given in table 2(*a*) and the peak assignment is as explained in the text.

Table 2. Composition of the mixtures used to study the deuterium spectra of monoacids dissolved in the lamellar (*a*) and the hexagonal (*b*) phases.

n	$C_{16}K_2$/wt. %	H_2O/wt. %	C_nH_1/wt. %	$\frac{[H_2O]}{[C_{16}K_2]}$	$\frac{[C_nH_1]}{[C_{16}K_2]}$
			(*a*)		
6	53·7	35·1	11·1	13·1	0·619
7	58·4	36·8	4·8	12·7	0·207
8	60·4	36·6	2·9	12·2	0·111
9	57·3	37·0	5·7	13·0	0·207
10	58·7	37·7	3·6	12·9	0·116
12	57·8	38·7	3·4	13·5	0·096
14	59·0	38·4	2·6	13·1	0·063
15	59·1	37·6	3·3	12·8	0·074
16	59·0	38·0	3·0	12·9	0·064
			(*b*)		
6	49·8	48·0	2·2	19·4	0·128
8	46·6	47·6	5·8	20·6	0·284
10	46·2	48·3	5·5	21·1	0·224
14	48·5	49·6	1·9	20·6	0·054
15	48·5	49·5	2·0	20·5	0·054

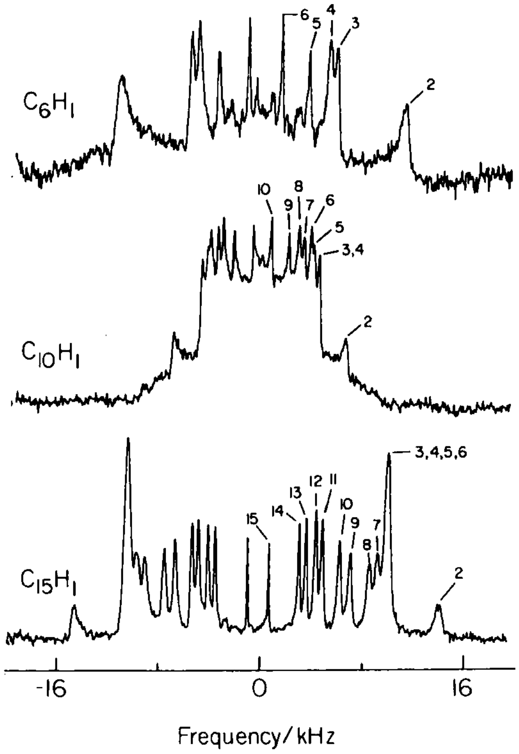

Figure 9. Deuterium NMR spectra of deuteriated monoacids guest molecules, C_nH_1, dissolved in the hexagonal phase of $C_{16}K_2$–H_2O at approximately 80°C. The composition of the solutions are given in table 2(*b*).

the rest of the methylene deuterons. As for the diacids we have assigned the peaks sequentially, starting with the α-deuterons, according to the decrease of the quadrupole splittings and taking into account possible degeneracies, as exhibited by the peak intensities. In all cases we were able to assign all peaks according to the number of inequivalent deuterons in the monoacid chains.

The temperature dependence of the quadrupole interaction parameters for a number of monoacid guests in the lamellar and hexagonal phases are given in figures 10 and 11, and the splitting patterns as function of the carbon number along the chain, interpolated to 80°C, are shown in figures 12 and 13.

4. Discussion

In this discussion we assume that the carboxyl groups of the guest (mono- or diacid) molecules are anchored at the disoap–water interfaces and that the counter cations (i.e. H^+ and K^+) are distributed statistically among the COO^- groups. It appears from the experimental results that partial substitution of K^+ by H^+ does not affect the phase structure although, depending on the guest, their stability range may be more or less affected.

4.1. *Solubility of the mono- and diacids in the lamellar and hexagonal phases*

The results show that there is a significant difference in the solubility of the diacids compared to those of the monoacids. Monoacids readily dissolve in the $C_{16}K_2$

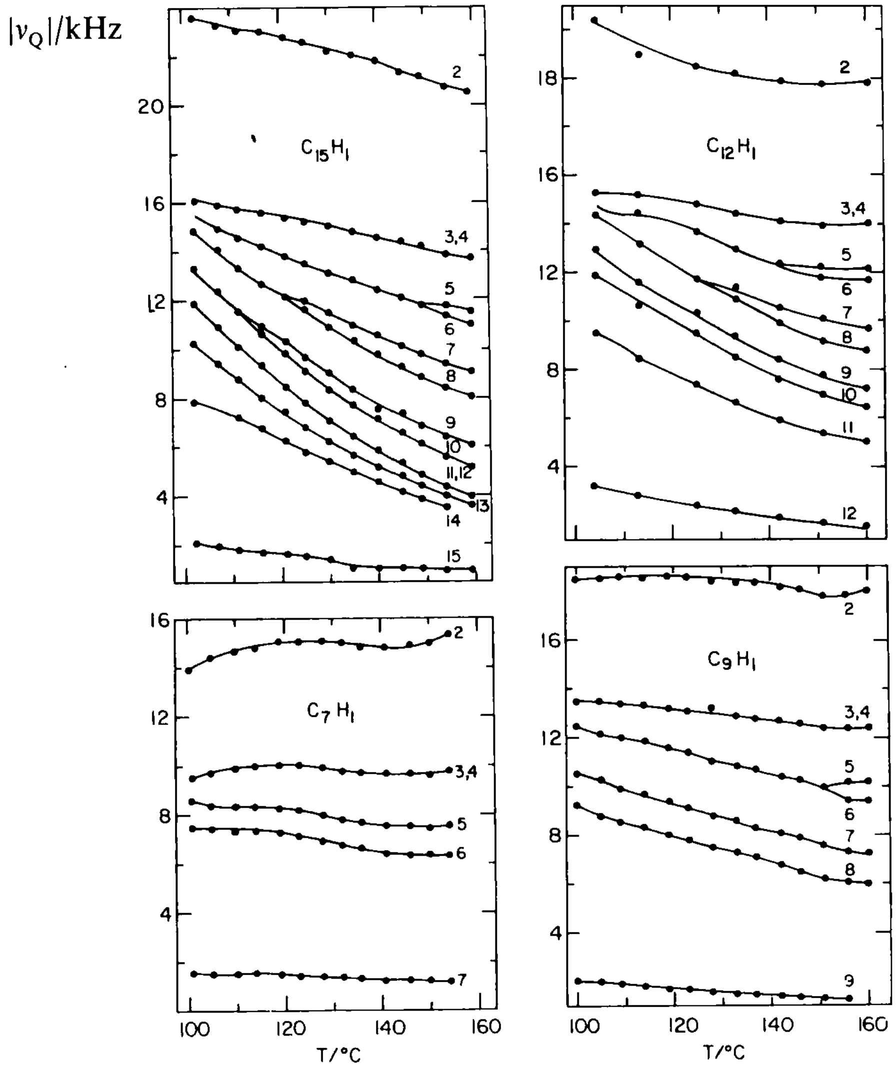

Figure 10. The average (absolute values) quadrupole interaction parameters, ν_Q, as a function of temperature, of the various deuterons in the monoacid guests dissolved in the lamellar phase.

mesophases even for short alkyl chains ($n = 6$), while diacids with chains shorter than $n = 10$ will not dissolve in the lamellar phase, and to dissolve in the hexagonal phase n must be larger than 13. Most likely this reflects the constraint imposed on the guest molecules, requiring the carboxyl groups to anchor at the interface and for the methylenes to be accommodated in the hydrophobic regions of the lamellae or rods. Monoacids can readily fulfil these requirements by simply anchoring their carboxyl groups at the interface and allowing the alkyl chains to mix with the aliphatic chains of the $C_{16}K_2$ host. For diacids with alkyl chains too short to stretch across the lamellae or rods this is not possible and the molecules will have to bend back, or else one of their carboxyl groups will be forced into the hydrophobic region of the host. The absence of NMR signals attributable to bent diacid species indicates that such

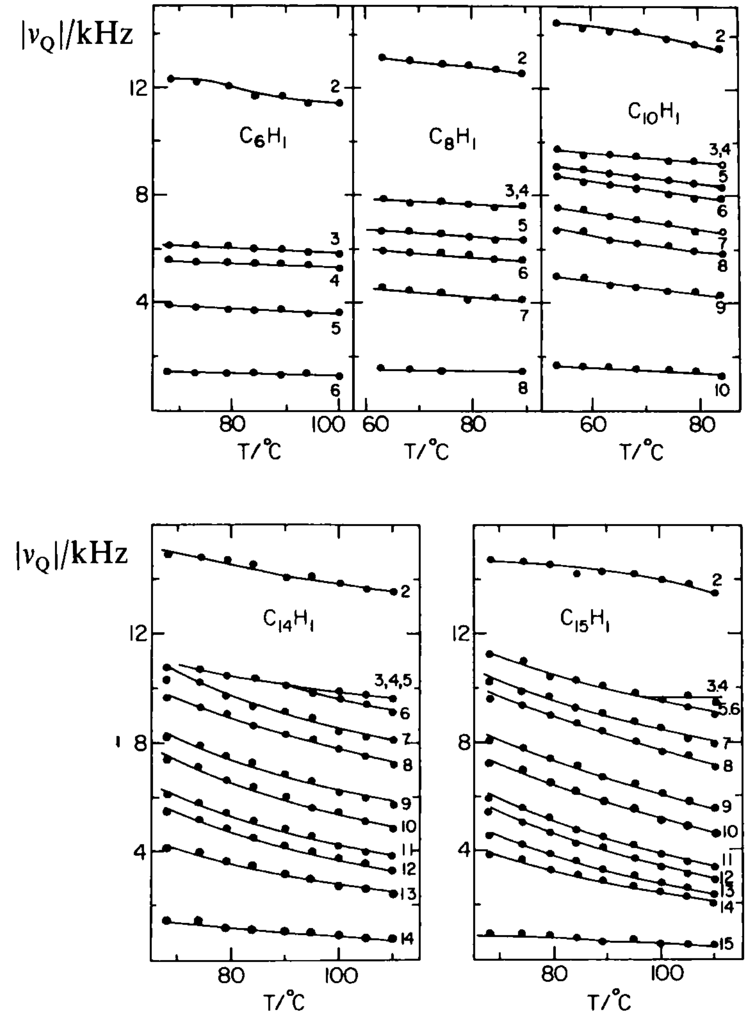

Figure 11. The average (absolute values) quadrupole interaction parameters, ν_Q, as a function of temperature, of the various deuterons in the monoacid guests dissolved in the hexagonal phase.

conformations are highly unfavourable. The possibility that such bent conformations do exist, but are in fast equilibrium with the rest of the species and therefore not observed in the NMR spectra seems unlikely in view of the results obtained for diacids in monosoap lamellar systems [19]. Also having the free carboxyl group floating in the hydrophobic region is energetically unfavourable and consequently short diacids are rejected from the lyomesophases of the $C_{16}K_2$–water system.

The widths of the disoap layers and rods in the lamellar and hexagonal phases were estimated to be 11·6 Å and 19 Å respectively [2]. Assuming a specific length of 1·25 Å per CD_2 fragment (in an all-trans configuration) shows that the shortest chains which can be accommodated conveniently in these phases is $n = 9$ for the lamellar phase and $n = 15$ for the hexagonal phase. These values are very close to those of the shortest diacids found to be soluble in the lamellar and hexagonal phases, i.e. $n = 10$ and 14, respectively.

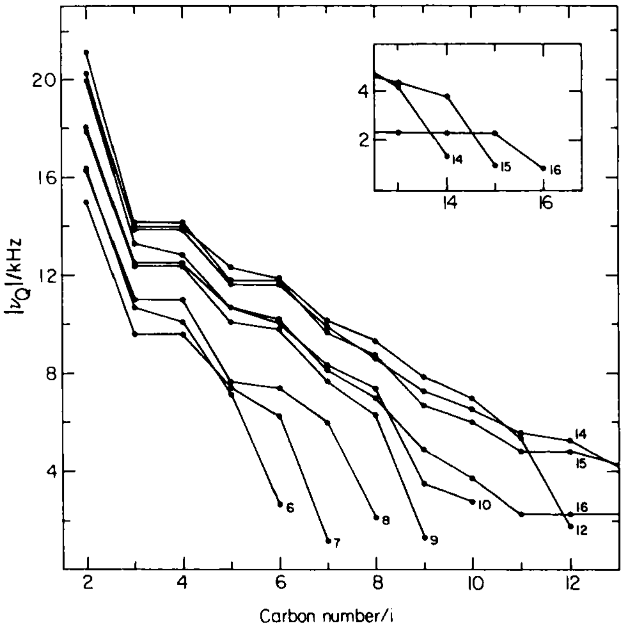

Figure 12. The average (absolute values) quadrupole interaction parameters, ν_Q, versus the carbon labelling index, i, for the monoacid guest molecules in the lamellar phase interpolated to 150°C.

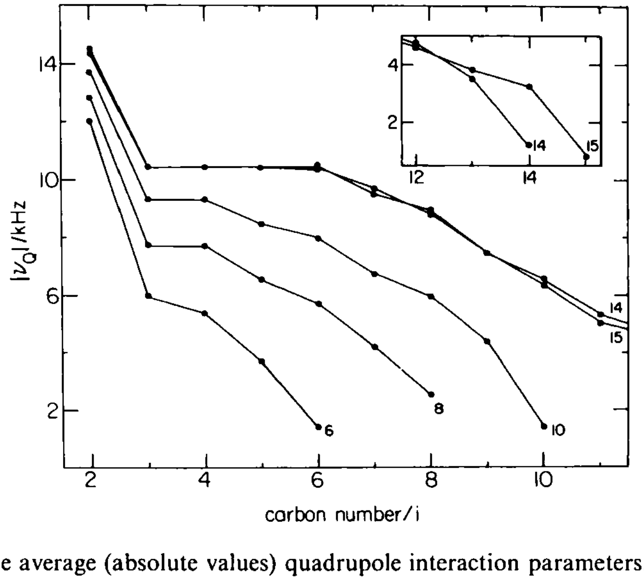

Figure 13. The average (absolute values) quadrupole interaction parameters, ν_Q, versus the carbon labelling index, i, for the monoacid guest molecules in the hexagonal phase interpolated to 80°C.

4.2. *The average quadrupole interaction parameter, ν_Q^{α}, of the α-deuterons*

Referring to the splitting patterns in the various systems (see figure 4, 7, 12 and 13) we recall, as already noted previously, that in all cases the α-deuterons exhibit the largest splittings and usually by a significant amount compared to the rest of the CD_2-deuterons. This probably reflects the anchoring of the carboxyl group at the interface rendering the chain head less mobile compared to the rest of the methylenes. However within the homologous series of diacids in the lamellar phase there is a gradual increase in ν_Q^α with increasing the chain length until $n \approx 16$, beyond which the splitting remains constant. This may be understood in terms of the torque inflicted on the carboxyl head group by the stretched chains of the diacids with shorter chains than in the host disoap, causing a tilt of the α-methylenes and consequently a reduction in their quadrupole splitting. Once the length of the guest has reached that of the host, the strain on the carboxyl group is relieved and the ν_Q^αs remain constant, independent of *n*. In contrast to the behaviour of the diacids in the lamellar phase, the ν_Q^αs of the monoacids in the lamellar (as well as in the hexagonal) phase are much less dependent on the lengths of the chains. Thus, on going from C_7H_1 to $C_{16}H_1$ in the lamellar phase results in an increase of ν_Q^α by a factor of 1·4, compared to a factor larger than 2 on going from the diacid $C_{10}H_2$ to $C_{16}H_2$ in the same phase.

This dependence of ν_Q^α on the chain length could also be attributed to the formation of patches in the lamellae (or rods) in which the diacid guest molecules form isolated islands rather than being randomly distributed. Such structures have been observed in the lamellar phase of sodium decyl sulphate–decanol–water by neutron scattering [24]. In the present case, their formation can be ruled out from the observation that the splitting profile of the guest molecules when measured at different $[C_nH_2]/[C_{16}K_2]$ ratios appeared to be independent of the diacid concentrations.

4.3. *The even–odd pattern of the* ν_Q^i*s*

Finally we discuss the overall splitting patterns of the mono and diacid guests in the dipotassium thapsate–water mesophases. In lyomesophases of monosoaps a characteristic plateau in the deuterium splitting pattern of host or guest alkyl chains is often observed [23, 25] in which (except for the α-carbon) the splitting of the first few methylenes is fairly constant, while towards the chain end there is a sharp decrease in ν_Q^i with increasing carbon number. In alkoxy end chains of thermotropic liquid crystals typical even–odd effects [7, 9, 26] are usually found in which the splitting of an even numbered methylene (i) and the successive odd methylene ($i + 1$) have a similar splitting, while on going from an odd methylene ($i + 1$) to the next even ($i + 2$) there is a relatively large drop in the splitting. In other cases [9, 27–29] zig-zag patterns are observed with alternating small and large splittings (sometimes with alternating signs) along the chain. Our results for the diacids in the lamellar phase and to some extent also in the hexagonal phase exhibit even–odd effects similar to those described for end chains in thermotropic liquid crystals and is given by $\nu_Q^2 \gg \nu_Q^3 \approx \nu_Q^4 > \nu_Q^5 \approx \nu_Q^6 > \nu_Q^7 \cdots$. Such splitting patterns have been thoroughly investigated in terms of the conformational equilibria due to the internal and external potential energies which act on the chain fragments [9]. A detailed quantitative analysis of these patterns requires extensive computations which we have not carried out so far. We are currently studying ^{13}C NMR spectra on the $C_{16}K_2$ system and hope to combine these results with the present ones in order to perform a more complete analysis of the ordering characteristics of this system.

We have, however, performed calculations using a very simple minded model in which it is assumed that the only conformations adopted by the alkyl chains include besides the all-trans only the so-called kink conformation [7, 30]. A good fit with the experimental results was obtained for the diacids in the lamellar phase and somewhat less satisfactory in the hexagonal phase. The fit failed in both phases for monoacid probes. It is possible that the better fit obtained for the diacids reflects the fact that these molecules must stretch from one interface to the other, so that kinks appear to be natural defects, while this is not necessarily the case for monosoaps which anchor only to one interface. Whether this is indeed so can only be determined by using more advanced theories and more realistic models for the probe molecules which consider all possible chain configurations.

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