Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Water ordering in a MTAB/decanol/water lyotropic system

G. Arabia[a]; G. Chidichimo[a]; A. Golemme[a]; P. Ukleja[b]
[a] Dipartimento di Chimica, Universitá della Calabria, Italy [b] Department of Physics, Southeastern Massachussets University, North Dartmouth, Massachusetts, U.S.A.

To cite this Article Arabia, G. , Chidichimo, G. , Golemme, A. and Ukleja, P.(1991) 'Water ordering in a MTAB/decanol/water lyotropic system', Liquid Crystals, 10: 3, 311 — 323

To link to this Article: DOI: 10.1080/02678299108026278

URL: http://dx.doi.org/10.1080/02678299108026278

Liquid Crystals, 1991, Vol. 10, No. 3, 311–323

Water ordering in a MTAB/decanol/water lyotropic system

by G. ARABIA, G. CHIDICHIMO*, A. GOLEMME and P. UKLEJA†
Dipartimento di Chimica, Universitá della Calabria, 87036 Rende, Italy
† Department of Physics, Southeastern Massachussets University,
North Dartmouth, Massachusetts 02747, U.S.A.

(Received 30 July 1990; accepted 7 March 1991)

Lyotropic mesophases consisting of myristyltrimethylammonium bromide and water or MTAB, water and decanol have been investigated. ^{2}H NMR studies from both the binary and the ternary systems are reported in which the quadrupolar splittings from D_2O and decanol (α-deuteriated) have been analysed. ^{17}O NMR, ^{81}Br NMR and optical microscopy have also been used. In the concentration and temperature ranges studied, the binary system exhibits a cylindrical phase, while for the ternary system a discotic phase is found. An anomalous behaviour of the quadrupolar splitting of water is observed: it vanishes at a particular temperature, where optical microscopy does not show any phase transition and the quadrupolar splitting of deuteriated decanol does not exhibit any discontinuity. We found that the change in the order of water does not depend on a variation of micellar structure. We have interpreted this behaviour in terms of the existence of two different sites occupied by water molecules at the interface, with their molecular axes oriented in different ways. From the ^{17}O and ^{2}H NMR data, a calculation of the water order parameters is possible.

1. Introduction

Myristyltrimethylammonium bromide (MTAB) is used in pharmacology because of its antimicrobial and bactericidal properties [1], its haemolitic activity [2] and its ability to solubilize androgens and estrogens [3]. In spite of its widespread use, relatively little research has been carried out on the self-association behaviour of MTAB. It is known that in aqueous solutions the salt forms a lyotropic liquid-crystalline mesophase [4] with aggregates that are cylindrical in shape. Addition of small amounts of decanol to this system yields a phase with disc-shaped micelles [4].

In particular, little is known about the dynamics of water molecules on the surface of MTAB aggregates. In general, the study of the dynamics and of the orientational properties of water in lyotropic systems is a problem of great interest. Some studies have been conducted to obtain the value of the molecular order parameter [5] and information on the overall phase ordering [6]. In this work we have investigated the ordering of water in two nematic liquid-crystalline systems consisting of MTAB/water and MTAB/water/decanol. Both NMR spectroscopy and optical microscopy have been used for phase identification at various concentrations of the components and at different temperatures. Although the different phases exhibited by the MTAB/decanol/water system have been identified previously [4], such work was necessary to confirm the correctness of our procedure. Ordering of water has been monitored by ^{2}H and ^{17}O NMR. In some of the mixtures studied the order of the α-deuteriated methylene of decanol has also been investigated. The aim of our work was

* Author for correspondence.

to clarify the connection between the surface structure of the lyotropic aggregates and the ordering and dynamics of water. NMR constitutes a very good experimental technique in this case, since it is extremely sensitive to molecular motions. In particular, in liquid crystals the anisotropy of molecular motion is directly reflected in spectral lineshapes.

The structure of this paper is as follows. The experimental details are given in § 2, while § 3 deals with phase identification. The problem of mesophase identification needs to be addressed before starting the interpretation of NMR data. The NMR experimental results, together with their analysis, are the subject of § 4. In § 5 a brief summary of the conclusions is given.

2. Experimental

Some of the components used for the preparation of the samples were of commercial origin: MTAB and D_2O were purchased from Aldrich (Milano, Italy), decanol from Merck (Darmstadt, Germany). They were used without further purification. ^{17}O enriched D_2O and decanol-αd_2 were generous gifts from Professors Z. Luz and P. W. Westerman, respectively. Samples were prepared by weighing the appropriate quantities of the components in glass tubes, which were then sealed, heated and centrifuged to obtain a homogeneous system. Polarizing glasses were used to control the homogeneity of the samples and to distinguish between isotropic and anisotropic systems.

NMR experiments were performed on two different spectrometers, a Bruker MSL 300 and a Varian XL 100. The former spectrometer was equipped with a 10 mm broadband probe, tuned for deuterium at 46·07 MHz, and a B-VT 1000 temperature control unit, with an accuracy of $\pm 1°C$. The Varian XL 100 spectrometer operated at 15·35 MHz for deuterium and it allowed a rotation of the sample around an axis normal to the static field. On both spectrometers, temperature scans were performed starting from the lower end, to avoid supercooling effects. Usually 16 scans were enough to ensure a good signal-to-noise ratio for D_2O spectra while 500 scans were necessary in the case of decanol-αd_2. ^{81}Br spectra were obtained using a 7·5 mm high power probe at 81·056 MHz on the MSL 300. In this case the $\pi/2$ pulse was 2·0 μs and the relaxation delay 100 ms. About 100 000 scans per spectrum were accumulated.

Optical observations were carried out on a Leitz Laborlux 12 POL polarizing microscope, equipped with a Linkam TH 600 heating stage. The same samples used to collect NMR data were also used for microscope observations. The glass tubes were opened and part of the content was rapidly introduced in to flat capillaries 0·2 mm thick, which were then cooled with liquid nitrogen and sealed.

3. Phase identification

A series of samples with different concentrations of the components was made. The table shows the exact composition of each sample, also with respect to isotopic enrichment. Both ^2H NMR and optical microscopy were used for phase identification purposes. Let us first discuss the optical observations.

In the binary MTAB/water sample 16 of the table, textures typical of a nematic lyotropic system with rod-shaped micelles, the N_c phase, were observed [7] at temperatures between 20°C and ~32°C. This confirms previous literature data [4]. All ternary samples at low MTAB concentration ($< \sim 40$ wt%), when observed between crossed polarizers, showed the typical focal conic textures [7] of nematic lyotropic phases with disc-like micelles, the N_d phase. To confirm such observations, the flat capillaries containing the mixtures were kept for several hours in a 2·5 T magnetic field oriented normally with respect to the direction of optical observation. After this period all samples were black when observed between crossed polarizers and no texture appeared on rotating them around the observation axis. These results are in agreement with the existence of disc-shaped aggregates with negative diamagnetic anisotropy, as in most N_d phases. In fact, in this case the director is expected to orient normal to the field but, out of all the degenerate orientations, the director prefers to orient normal to the surface of the capillary. This is the so-called homeotropic alignment, due to the preferred interaction of the glass surface with the polar heads of the molecules at the micelle surface. At higher temperatures all of those samples exhibiting a N_d phase undergo a transition into an optically isotropic phase. Samples where MTAB > 40 per cent show typical mosaic textures of lamellar phases [8] over a very broad temperature range above room temperature. In most cases we did not investigate the temperature range below room temperature.

^{2}H NMR results confirm and extend microscopy observations. For a nucleus of spin $I \geqslant 1$ the NMR spectrum is dominated, in anisotropic phases, by the quadrupolar interaction with electric field gradients [9]. In this case, to first order and for a uniaxial phase, $2I$ lines are obtained, separated by [9]:

$$\Delta = \frac{3}{2}\,\frac{\nu_Q}{I(2I-1)}\left(\frac{3\cos^2\theta-1}{2}\right)\left\{S_{zz}\left(\left\langle\frac{3\cos^2\beta-1}{2}\right\rangle+\tfrac{1}{2}\eta\langle\sin^2\beta\cos2\alpha\rangle\right)\right.$$

$$+\tfrac{1}{2}(S_{xx}-S_{yy})(\langle\sin^2\beta\cos2\alpha\rangle+\tfrac{1}{3}\eta\langle(1+\cos^2\beta)\cos2\alpha\cos2\gamma$$

$$\left.-2\cos\beta\sin2\alpha\sin2\gamma\rangle)\right\}, \tag{1}$$

Sample compositions. The binary sample exhibits a N_c phase while the ternary ones have N_d phases for MTAB < 40 per cent and lamellar phases for MTAB > 40 per cent.

	Decanol		MTAB		Water		
Sample	wt%	mole%	wt%	mole%	wt%	mole%	Enriched species
1	4·01	0·78	33·62	3·08	62·36	96·14	D_2O
2	4·80	0·92	31·70	2·87	63·40	96·21	D_2O
3	5·21	0·91	32·15	2·65	62·64	96·44	D_2O decanol-αd_2
4	5·20	1·01	32·36	2·96	62·44	96·03	D_2O decanol-αd_2
5	5·60	1·08	31·30	2·83	63·10	96·09	D_2O ^{17}O
6	5·30	1·16	39·50	4·05	55·10	94·79	D_2O
7	5·74	1·19	36·50	3·58	57·76	95·22	D_2O
8	6·03	1·42	43·96	4·90	50·00	93·67	D_2O
9	6·14	1·55	47·82	5·72	46·04	92·73	D_2O
10	6·00	2·63	70·00	14·46	24·00	82·00	D_2O
11	8·67	2·26	46·73	5·76	44·60	91·98	D_2O
12	7·08	1·67	42·83	4·76	50·09	93·57	D_2O
13	5·20	1·01	32·40	2·96	62·40	96·02	D_2O
14	4·40	0·87	33·70	3·12	61·90	96·01	D_2O
15	6·81	1·37	33·03	3·11	60·16	95·52	D_2O
16	—	—	36·00	3·25	64·00	96·75	D_2O

where θ is the angle between the nematic director and the magnetic field and α, β and γ are the Euler angles relating the principal molecular frame with the principal frame of the electric field gradient tensor. The S_{ii}s are the elements of the molecular ordering matrix, ν_Q is the quadrupole coupling constant and η the asymmetry parameter in the principal frame of the interaction for the nucleus considered and the $\langle\ \rangle$ brackets stand for a thermal average. The angles α, β and γ are related to conformational motions in the molecules and in the case of water they can be considered as fixed. The S_{ii}s contain information on all water motions in the sample, including for example exchanges between bound and unbound sites as well as averaging due to diffusion over the surface of the micelles.

For the binary MTAB/D_2O system a doublet is observed between 20 and ~32°C. The doublet splitting is ~70 Hz and it is not dependent upon temperature. *Immediately after a $\pi/2$ rotation of the sample around an axis normal to the external* field direction the width of the doublet is reduced by half, as shown in figure 1. This corresponds to a change from $\theta=0$ to $\theta=\pi/2$ in equation (1) and it confirms that the binary phase has positive diamagnetic anisotropy, typical of N_c phases. For the MTAB/decanol/D_2O system we obtain the lineshapes shown in figure 2. Here we again

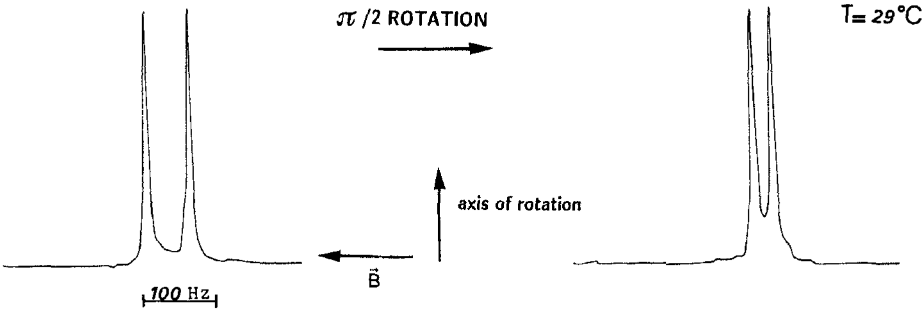


Figure 1. ^2H NMR spectra of D_2O from binary mixture MTAB/water, sample 16 in the table. The reduction of the splitting by a factor of a 1/2 after a $\pi/2$ rotation around an axis normal to B indicates the existence of a N_c phase.

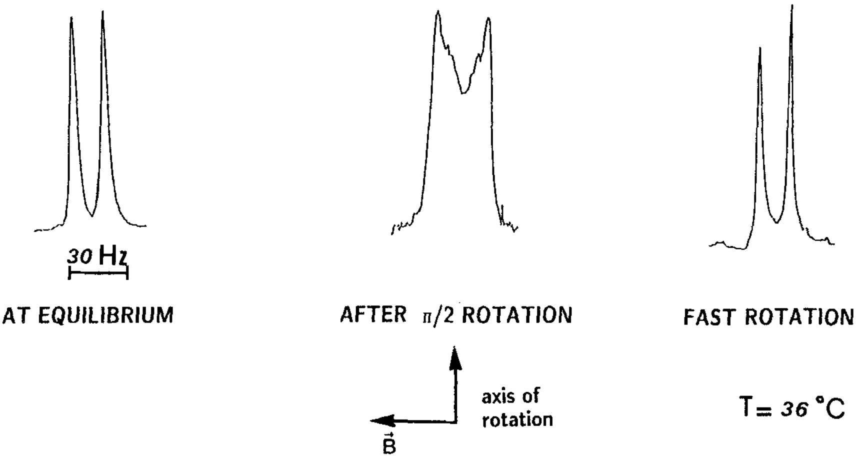


Figure 2. ^2H NMR spectra of D_2O from sample 3 in the table. The lineshapes obtained by sample rotation indicate the existence of a N_d phase.

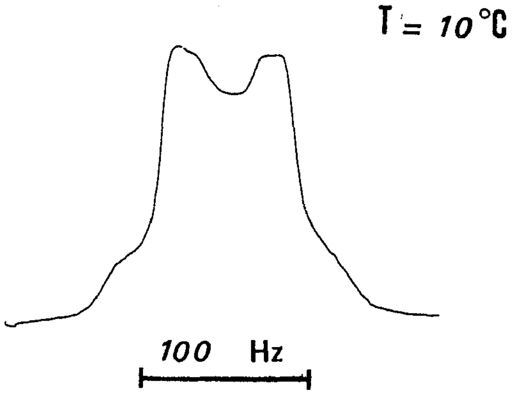


Figure 3. ^{2}H NMR spectrum of D_2O from sample 12 in the table. The spectrum is unchanged after sample rotation.

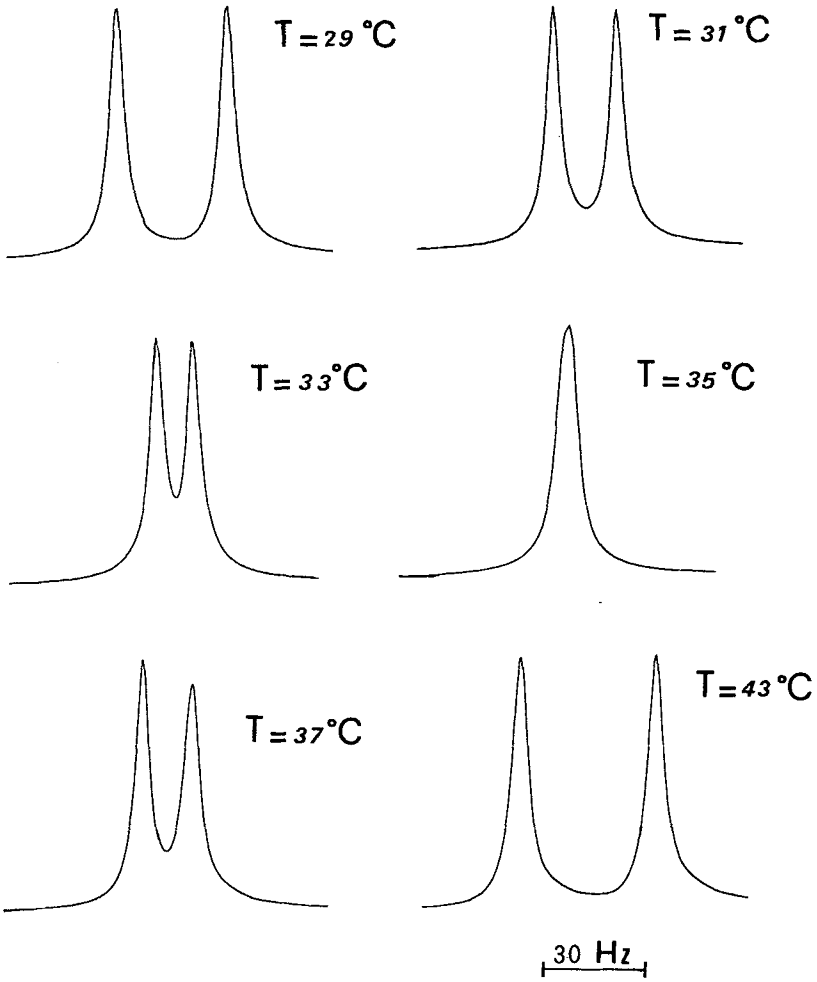


Figure 4. Temperature dependence of the D_2O ^{2}H NMR spectral profiles from sample 13 in the table.

start with a doublet and after a $\pi/2$ rotation a lineshape corresponding to a cylindrical distribution of directors around the magnetic field direction is observed. If we acquire the spectrum while rotating the sample around the same axis we obtain the same lineshape as in the static case. This confirms the existence of a phase with negative diamagnetic anisotropy for the ternary system, typical of N_d phases. The behaviour described in figure 2 is typical of those ternary systems where MTAB < 40 per cent, at temperatures below the N–I transition.

For MTAB > 40 per cent the typical spectra shown in figure 3 were obtained. In this case we recognize a powder pattern, which is not affected by any rotation of the sample. These samples are also much more viscous than those containing less MTAB. It should be noted that these spectra are usually about twice as wide as the corresponding ones with less MTAB. All of this evidence supports the existence of lamellar phases for MTAB concentrations larger than 40 wt%.

4. Results and discussion

Typical D_2O spectral profiles from a ternary mixture of MTAB/decanol/water at different temperatures are shown in figure 4. The temperature dependence of the quadrupolar splitting is very unusual: starting from lower temperatures it decreases, vanishes and then increases. Optical microscopy observations of the same samples do not show any phase transition in this temperature range, where our mixtures exist in the N_d phase. In this case we would expect the quadrupolar splitting to follow the typical temperature dependence of a nematic order parameter [10], which decreases with increasing temperature. The temperature dependence of the splitting shown in

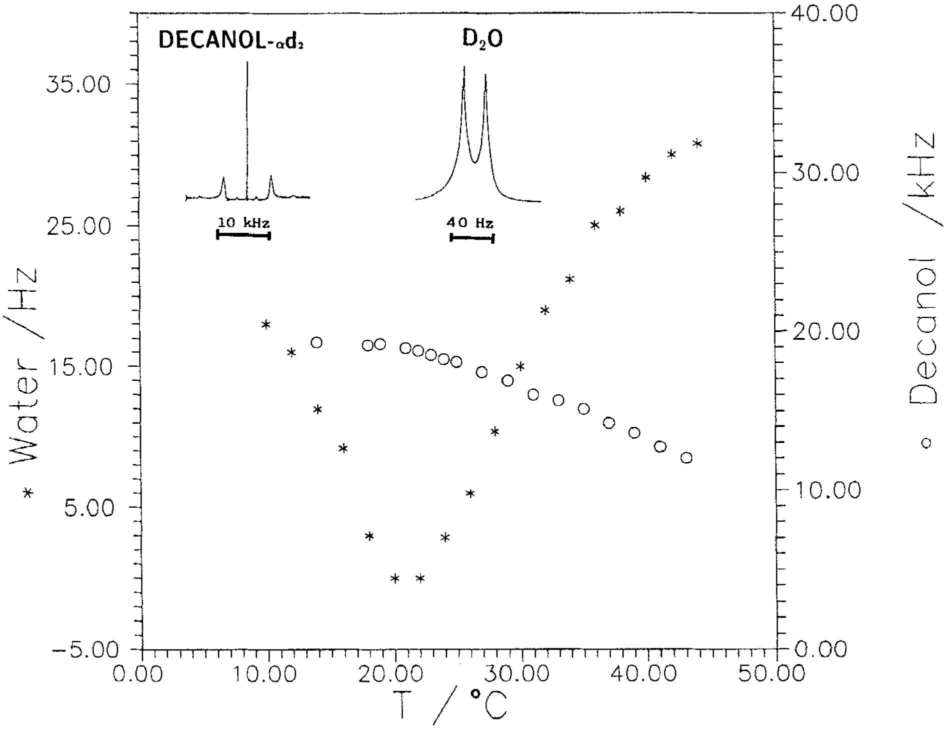


Figure 5. Temperature dependence of the D_2O and decanolα-d_2 ^2H NMR quadrupolar splittings from sample 3 in the table. Typical lineshapes are shown in the inset.

figure 4 is common to all ternary samples when MTAB <40 wt%, the only difference between samples being the temperature at which the splitting vanishes.

In order to better understand this behaviour we decided to prepare samples using both D_2O and *n*-decanol-αd_2. In the nematic phase the signal from the deuterium atoms of decanol is also a doublet but the quadrupolar splitting is much larger than in water. The temperature dependence of both splittings for sample 5 of the table is shown in figure 5. The decanol data confirm the optical observations that there is no phase transition at the temperature where the water splitting vanishes. In addition we can now see that the decanol splitting has the expected temperature dependence. This is a good indication that there is no major change either in the micellar structure or in the phase behaviour throughout the N_d temperature range.

It seems reasonable to associate the anomalous behaviour of the quadrupolar splitting with a change in its sign, as already observed in other cases [11, 12]. This could derive in our case from the existence of different possible orientations for the water molecules, each associated with a different sign of the quadrupolar splitting. The observed splitting is, in this hypothesis, the weighted average of the splitting associated with each orientation. This is also suggested from the unusually small value of the splitting, about one order of magnitude smaller than in most other N_d phases [13]. In our system the different water orientations could be associated with the interaction of water with different regions of the disc-shaped aggregate. If the shape of the aggregate was temperature dependent then a change of the sign of the total quadrupolar splitting could result. Such a hypothesis can be ruled out by considering the NMR results for samples where MTAB >40 wt%. A typical temperature dependence of the D_2O spectral profile from one of these samples is shown in figure 6. As mentioned previously such spectra are powder patterns obtained from a lamellar phase. We note that their width is much larger than the quadrupolar splitting obtained from the N_d phase of samples with less MTAB. The important feature of these samples is that the same temperature dependence of the quadrupolar splitting is observed as in the case of the N_d phase, i.e. the splitting changes sign. This rules out the previously stated hypothesis since in this case there are no micelles.

The change in the sign of the quadrupolar splitting is then to be attributed to some peculiar molecular motion of water. Water molecules could in principle undergo very complicated motions. Nevertheless our data can be explained by assuming that on the aggregates' surfaces there are only two sites of interaction with water, each one associated with a different H_2O orientation and a quadrupolar splitting of opposite sign. In this case the total quadrupolar splitting Δ can be considered as the sum of the two splittings of opposite sign, each one weighted with the relative population of the site:

$$\begin{aligned}\Delta &= P^-\Delta^- + (1-P^-)\Delta^+ \\ &= \Delta^+ - P^-(\Delta^+ - \Delta^-),\end{aligned} \tag{2}$$

where $\Delta^+ > 0$ and $\Delta^- < 0$. We assume, in a first approximation, that Δ^+ and Δ^- are temperature independent while the observed variation in the splitting is a consequence of the change of the populations of the two sites. At the temperature where $\Delta = 0$ we must have

$$\frac{\Delta^+}{\Delta^+ - \Delta^-} = P^-. \tag{3}$$

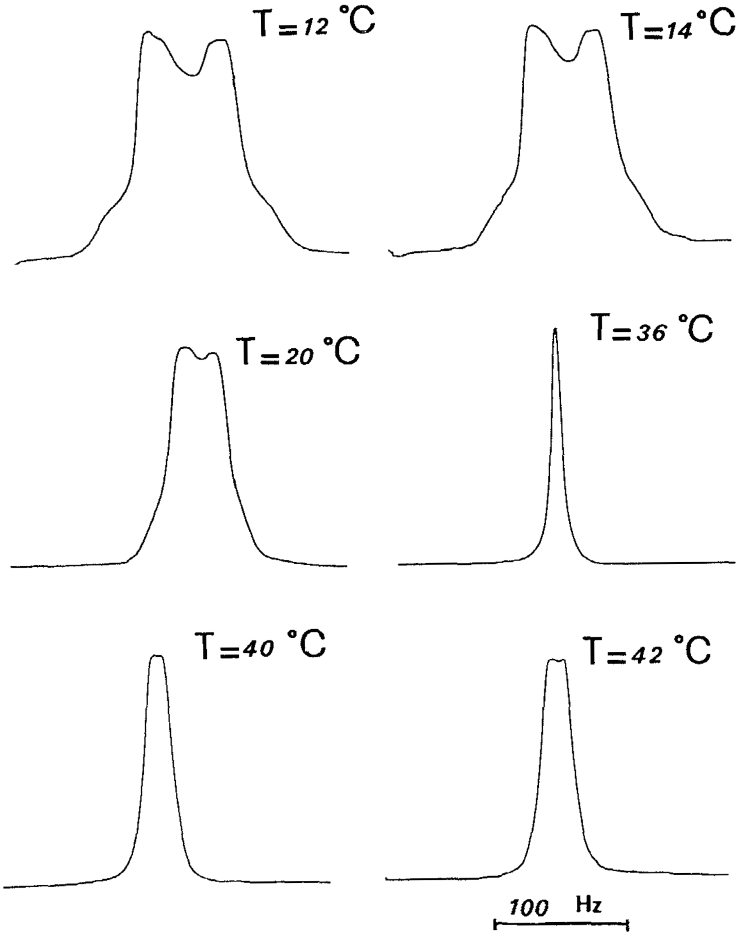


Figure 6. Temperature dependence of the D_2O ^2H NMR quadrupole splitting from sample 12 in the table. In this case a lamellar phase exists.

The left hand side of this equation is, in our model, temperature independent while the populations are not. In the simplest approach we can associate each site with either the decanol or the MTAB polar head. We can define the probabilities for water to interact with a polar head of a particular kind as

$$P_D = \frac{x_D A_D}{x_D A_D + x_M A_M} = \frac{x_D}{x_D + x_M(A_M/A_D)} = \frac{1}{1+(n_M/n_D)R} \tag{4a}$$

and

$$P_M = \frac{x_M A_M}{x_D A_D + x_M A_M} = \frac{x_M}{x_M + x_D(A_D/A_M)} = \frac{1}{1+(n_D/n_M)R}, \tag{4b}$$

where x_D and x_M are the relative mole fractions of decanol and MTAB, respectively and n_D/n_M is the decanol/MTAB molar ratio. The factor $R = A_M/A_D$ expresses the relative tendency of MTAB and decanol to interact with water. It needs to be introduced since the existence of an equal number of the two kinds of sites for water interaction does not necessarily mean that $P_D = P_M$. In fact, one kind of site may be more effective than the other in binding water. The factor R can be related to a variety of physical factors, but we shall not investigate this here. We do not have an *a priori* knowledge of which site is associated with the positive or the negative splitting. Nevertheless it is instructive to consider how the temperature at which $\Delta = 0$ changes with the sample composition. In figure 7 we plot $T(\Delta = 0)$ as a function of the decanol/MTAB molar ratio. In order to avoid problems connected with having different isotopic species, only data from samples with the same isotopic composition have been considered. In addition, data from samples in which NMR showed the existence of more than one phase are not included in figure 7. It is clear how the temperature of zero splitting increases with increasing decanol content. This means that, although we do not know whether $P^- = P_D$ or $P^- = P_M$, in any case, considering equations (4), R must increase with increasing temperature. In fact, if P_D or P_M in equations (4) have to be kept constant, then R must increase when n_D/n_M increases. We can give further insight to this point by considering that in most of our samples at high temperature the D_2O splitting in the N_d phase tends to be half the value obtained from the binary N_c phase (see figure 5). This factor of $\frac{1}{2}$ can be explained by considering equation (1), since in the N_d phase the director is oriented normal to the external field while in the N_c phase it is directed along B. Such behaviour of the ^2H splitting of water is well-known in samples which exhibit both an N_d and an N_c phase at different temperatures [14]. This means that, in the high temperature range of the N_d phase of the ternary mixtures, the ordering of water is the same as in the binary N_c phase, i.e. decanol does not contribute to the ordering of water.

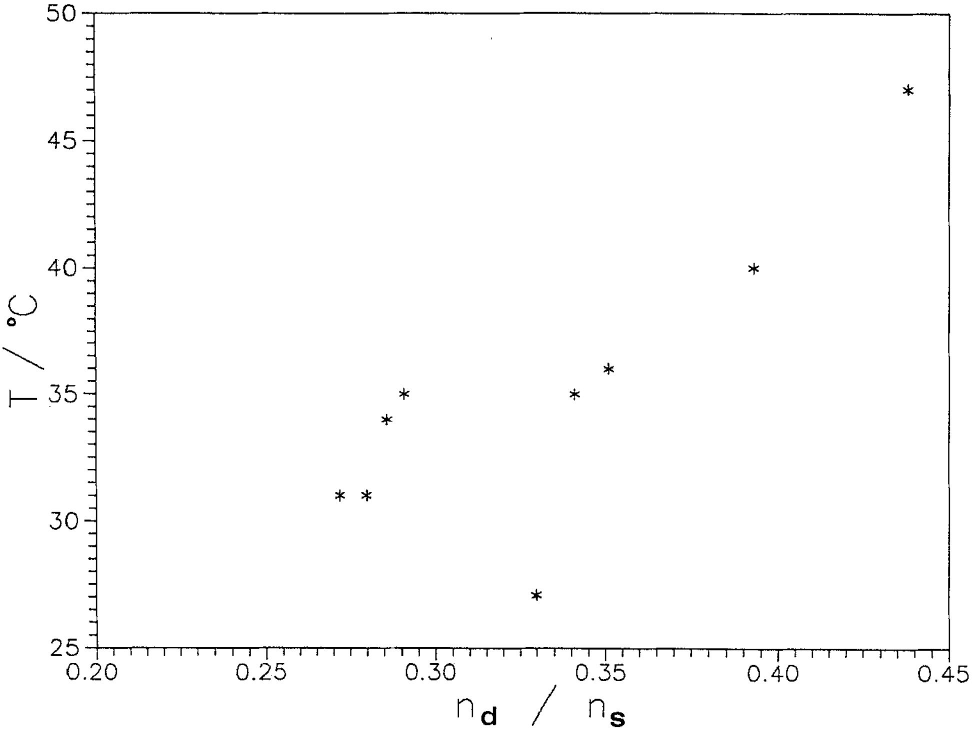


Figure 7. Dependence of the temperature of vanishing splitting, $T(\Delta = 0)$, on the decanol/MTAB molar ratio.

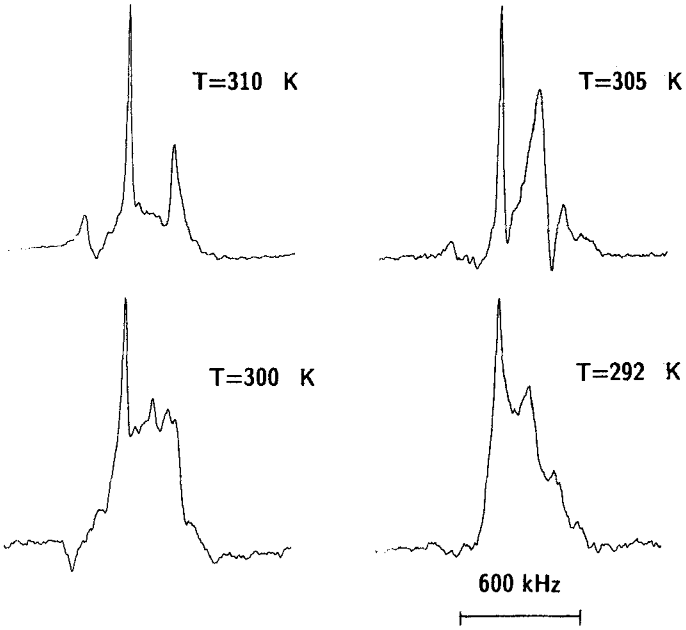


Figure 8. ^{81}Br NMR spectra of sample 7 in the table at different temperatures.

In our model this means that the factor R becomes very large. Since our N_d phase is stabilized by decanol, it makes sense that the effectiveness of the role of decanol decreases near the N_d–I transition, i.e. where the N_d phase becomes less stable.

In some samples we have investigated the possibility of a temperature dependent bromine ion binding and its influence on our measurements. We recorded ^{81}Br NMR spectra in the same temperature range over which the deuterium doublet changes sign. Typical spectra obtained in this case are shown in figure 8. ^{81}Br spectra are rather wide, about 300/400 kHz, and show a temperature dependence which is in no way comparable to the evolution of the ^{2}H lineshape. For the sample whose spectra are shown in figure 8 the ^{2}H splitting vanishes at 300 K while the bromine spectra are almost unchanged between 290 and more than 300 K. Although, given their width, the quality of the spectra is not excellent, we note that the bromine spectra seem to derive from the superposition of two components. One of them, consisting of sharp lines, as expected for a spin 3/2 nucleus in an ordered and oriented sample, is dominant at high temperatures and the other one, much less well defined, is present at lower temperatures. Since optical microscopy, ^{2}H and ^{17}O NMR confirm the existence of a single phase in these samples, the only explanation for the two different signals in the bromine spectra could be the existence of two different binding sites. The quality of the spectra does not allow us to extract further information but this can be taken as an indication that different binding sites indeed exist.

In an attempt to obtain more quantitative information on the water orientation we prepared sample 5 of the table using water enriched both in ^{17}O and in ^{2}H. ^{17}O is a nucleus with spin 5/2 and, as seen from equation (1), we expect to see five peaks for an oriented nematic phase. The values of the ^{2}H and ^{17}O quadrupolar splittings and typical lineshapes obtained from sample 5 are shown in figure 9. For the ^{17}O spectra, line broadening prevents a direct observation of the splitting, which can anyway be calculated from the total linewidth assuming $\Delta=0$ for the narrowest peak. It is important to note how for both nuclei the splitting vanishes at the same temperature. This confirms that this behaviour is associated with a property of the molecule as a whole. We can use equation (1) to calculate the orientational properties of the water molecules. Since we can measure in the same sample both Δ_D and Δ_O, i.e. the splittings from the deuterium and the oxygen, respectively, we can, using equation (1), calculate the two unknowns S_{zz} and $S_{xx}-S_{yy}$. From NMR experiments we actually measure $|\Delta|$ and we ignore its sign. We can then have four sets of equations, corresponding to the four combinations of $\Delta_O \lessgtr 0$ and $\Delta_D \lessgtr 0$. Two of these sets give, for the water order parameter, values equal in modulus but opposite in sign. To use equation (1) we need to

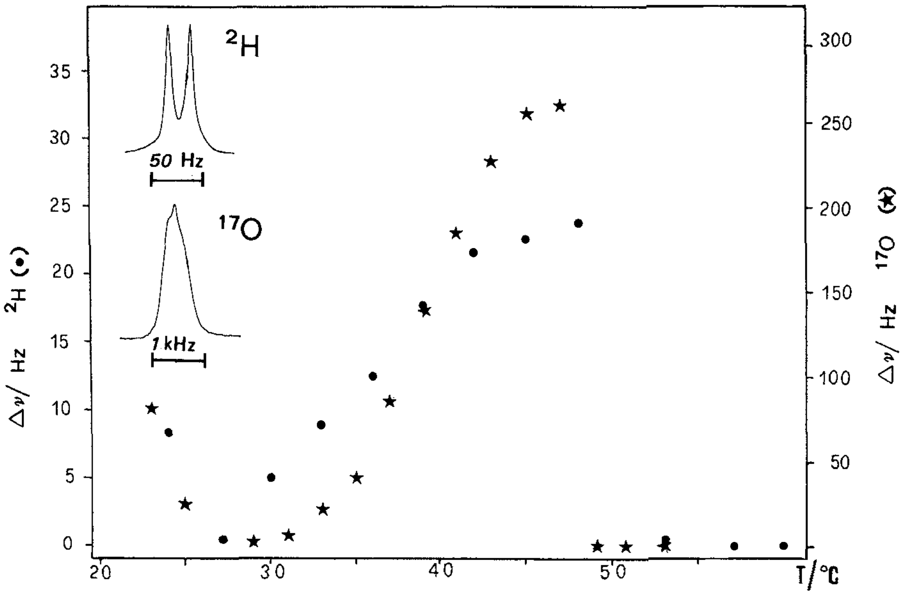


Figure 9. Temperature dependence of the ^{2}H and ^{17}O water quadrupolar splittings of sample 5 in the table. Typical lineshapes are shown in the inset.

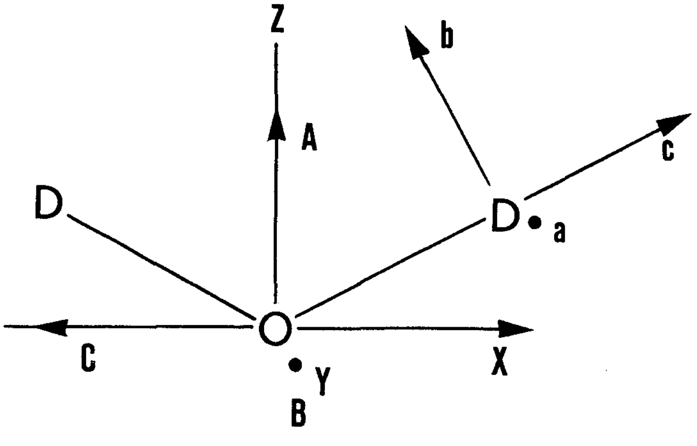
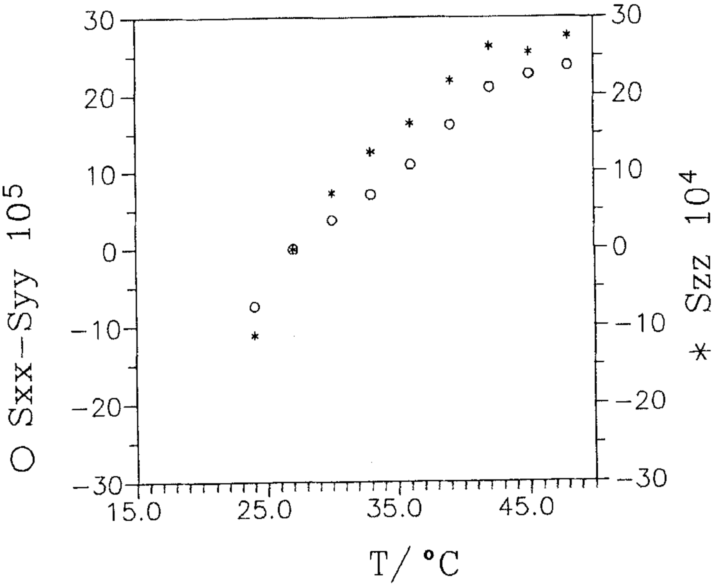


Figure 10. Orientation of the molecular coordinate system (XYZ) and of the deuterium (abc) and oxygen (ABC) principal axes frames of the electric field gradient tensors.



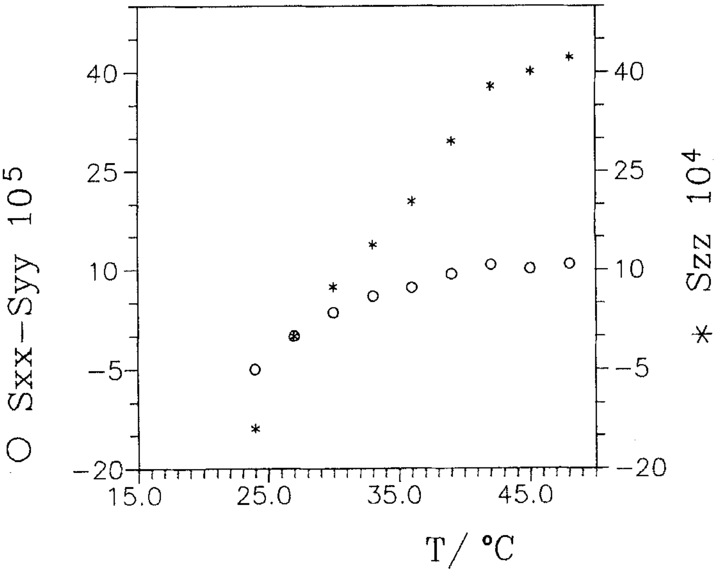


Figure 11. Water order parameters calculated using equation (1) from the ^{2}H and ^{17}O splittings obtained for sample 5 in the table and shown in figure 8. Only two of the four possible sets of values are shown. The other two can be obtained by changing the sign of the vertical axes.

consider the orientation of the principal frame of the electric field gradient tensor at the nuclei with respect to the molecular frame, shown in figure 10. The values of the quadrupolar coupling constant and of the asymmetry parameter used are [15, 16]

$$^{2}\mathrm{H} \quad \nu_Q = 213\,\mathrm{kHz}, \qquad \eta = 0{\cdot}1,$$

and

$$^{17}\mathrm{O} \quad \nu_Q = 6{\cdot}66\,\mathrm{MHz}, \qquad \eta = 0{\cdot}935.$$

In figure 11 the calculated values for the water order parameters in two of the four cases are shown. The order parameters in the other two cases can be obtained by changing the sign of the scale of the vertical axis. In both solutions the order parameters are of the same order of magnitude and rather small if compared to the values observed in similar phases [13].

5. Conclusions

We presented experimental evidence that in mixtures of MTAB, decanol and water the H_2O order parameter has an anomalous temperature dependence. We have shown that such behaviour is not associated with any phase transition or modification. In fact, both ^{2}H NMR of decanol-αd_2 and optical microscopy do not detect any phase modification. We have also shown that the water order is not determined or associated with the variation in micellar shape or size since non-nematic phases obtained at higher MTAB content show similar effects. We have developed a model in which two sites for water interaction at the aggregate interface can exist, each one associated with a splitting of different sign. The change in the water splitting is then determined by the relative populations at the sites. Using this model we have established that the ability of decanol to interact with water decreases with temperature. Finally, in a sample where the water was enriched both in ^{2}H and ^{17}O, water order parameters S_{zz} and $S_{xx} - S_{yy}$ were calculated at different temperatures in the N_d phase.

The authors would like to thank Professor Z. Luz for suggesting the ^{17}O NMR experiment and for a generous gift of ^{17}O enriched water and Professor P. W. Westerman for providing the decanol-αd_2.

References

[1] Gilbert, P., and Al-Taae, A., 1985, *Lett. Appl. Microbiol.*, **1**, 101.

[2] Klein, R. A., and Ellory, J. C., 1980, *J. Memb. Biol.*, **55**, 123.

[3] Lovgren, T., Heikius, B., Lundberg, B., and Sjoblom, L., 1978, *J. Pharm. Sci.*, **67**, 1419.

[4] Boden, M., Radley, K., and Holmes, M. C., 1981, *Molec. Phys.*, **42**, 493.

[5] Niederberger, W., and Tricot, Y., 1977, *J. Magn. Reson.*, **28**, 313.

[6] Goldfarb, D., Labes, M. M., Luz, Z., and Poupko, R., 1982, *Molec. Crystals liq. Crystals*, **77**, 259.

[7] Yu, L. J., and Saupe, A., 1980, *J. Am. chem. Soc.*, **102**, 4879.

[8] Rosevear, F. B., 1954, *J. Am. Oil chem. Soc.*, **31**, 628.

[9] Doane, J. W., 1979, *Magnetic Resonance of Phase Transitions*, edited by F. J. Owens, C. P. Poole and H. Farach (Academic Press).

[10] de Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon).

[11] Goldfarb, D., Luz, Z., and Zimmermann, H., 1982, *J. Phys., Paris*, **43**, 421.

[12] Goldfarb, D., Luz, Z., and Zimmermann, H., 1982, *J. Phys., Paris*, **43**, 1255.

[13] Hertel, G., and Hoffmann, H., 1988, *Prog. Colloid Polym. Sci.*, **76**, 123.

[14] Yu, L. J., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.

[15] Waldstein, P., Rabideau, S. W., and Jackson, J. A., 1964, *J. chem. Phys.*, **41**, 3407.

[16] Spiess, H. W., Garret, B. B., Sheline, R. K., and Rabideau, S. W., 1969, *J. chem. Phys.*, **51**, 1201.