

(4.2),³⁹ cyclopropane (6.0),⁴⁵ and benzene (10.4).⁴⁴

When one examines the Topsom parameter correlations, similar effects are seen, as expected, in the variation in m_F (Table VIII) as compared to m_1 . However, m_X also becomes more negative upon going from methyl to ethyl stabilization, and this is more difficult to understand.

In any case, it is quite clear that the magnitude of nonresonance stabilization (destabilization) effects is strongly dependent upon the identity of the acyclic model.

Conclusions

Stabilization energies (4-31G) of monosubstituted ethylenes, ethynes, cyclopropanes, and benzenes successfully reproduce the corresponding values based upon experimental $\Delta H_f^\circ(g)$. The values can be employed in linear free energy relationships since the entropy changes of isodesmic equations are negligible. Correlations using the Taft dual substituent parameter (DSP) approach as well as Topsom's three parameter approach yield similar conclusions: (a) correlations involving π -donor substituents are superior to those including π -acceptor substituents; (b) stabilization energies of substituted ethylenes, benzenes, and cyclopropanes are more sensitive to resonance rather than inductive interaction with the substituents, in contrast to ethynes where the reverse is true; (c) the sensitivities of the four series of molecules to resonance stabilization involving π -acceptor substituents correlates well with the adiabatic ionization potentials of the parent hydrocarbons,

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and this suggests that cyclopropyl is a stronger π -donor than vinyl which contrasts with the more conventional view based upon UV and IR spectral and molecular geometry studies; (d) cyclopropane has the least electron affinity of the four parent hydrocarbons and, thus, it is logical that cyclopropane shows the lowest sensitivity to π -donor substituents and is therefore a very weak π -acceptor, however, no obvious order is apparent for the other three parent hydrocarbons; (e) values of m_R show little variation with the model employed while m_1 varies significantly, reflecting the polarizabilities of the model hydrocarbons. Cyclopropane's high π -donor/low π -acceptor ability may combine to make it a poor transmitter of resonance effects.⁴⁶

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Supplementary Material Available: Listing of total energies, level of geometry optimization, and gas-phase enthalpies of formation for substituted methanes, ethanes, 2-propanes, acetylenes, ethylenes, cyclopropanes, and benzenes (12 pages). Ordering information is given on any current masthead page.

(45) This value is the average of calculations according to ref 39 based upon alkyl and vinyl carbons.

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Lyomesophases of the Diethylammonium Flufenamate-Water System Studied by Deuterium NMR Spectroscopy

I. Kustanovich,[†] R. Poupko,^{*‡} H. Zimmermann,^{†‡} Z. Luz,[†] and M. M. Labes[§]

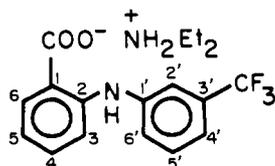
Contribution from The Weizmann Institute of Science, Rehovot 76100, Israel, and the Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122.

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Abstract: It was confirmed by using ^2H NMR spectroscopy that mixtures of water and diethylammonium flufenamate (DEAF) form lyomesophases in the concentration range 2.5-60 wt % DEAF. Depending on the concentration of the DEAF, two phases are formed with different structural characteristics. In solutions containing below 20 wt % DEAF, the mesophase consists of micellar structures of various shapes that are not well aligned by the magnetic field. Deuterium NMR of deuterated DEAF molecules in this phase exhibit powderlike spectra. At high concentration of DEAF (>20 wt %), monodomain samples are formed which are well aligned by the magnetic field. Deuterium NMR spectra in this phase consist of sharp doublets for each of the various deuterons. The results are consistent with the bilamellar structure for the mesophases as suggested by Eckert and Fischer. The DEAF molecules are highly ordered in the layers and appear to orient with the aromatic rings parallel to the director. In the high concentration range, the order parameter for the DEAF molecules exceeds 0.4.

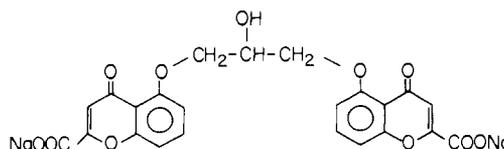
I. Introduction

In 1981 Eckert and Fischer¹ (EF) have shown that mixtures of diethylammonium flufenamate (DEAF) and water form lyomesophases over a wide range of DEAF concentrations (2.5 to ~60 wt %) and temperatures (up to ~60 °C). The phe-



nomenon is quite unusual since most amphiphiles that are known to form lyomesophases consist of rod-like (or double rodlike)

molecules with well-defined polar heads to which one or two long hydrophobic chains are bonded, e.g., alkali-metal soaps, phospholipids, and other detergents.² The structure of the DEAF molecule differs from these amphiphiles in that it consists of two aromatic rings bonded via a polar bridge and substituted on both rings with polar groups. A similar nonconventional amphiphile is the disodium cromoglycate salt which in aqueous solutions also forms lyomesophases.³ Both of these compounds are remarkable



[†] Minerva Fellow 1983/1984. Permanent address: Max-Planck-Institut für medizinische Forschung, D-6900 Heidelberg, Germany.

[‡] The Weizmann Institute of Science.

[§] Temple University.

(1) Eckert, T.; Fischer, W. *Colloid Polym. Sci.* **1981**, *259*, 553.

(2) Wilson, P. A. In "Liquid Crystals and Plastic Crystals"; Gray, G. A., Wilson, P. A., Eds.; Wiley: New York, 1974; Vol 1, pp 60, 199.

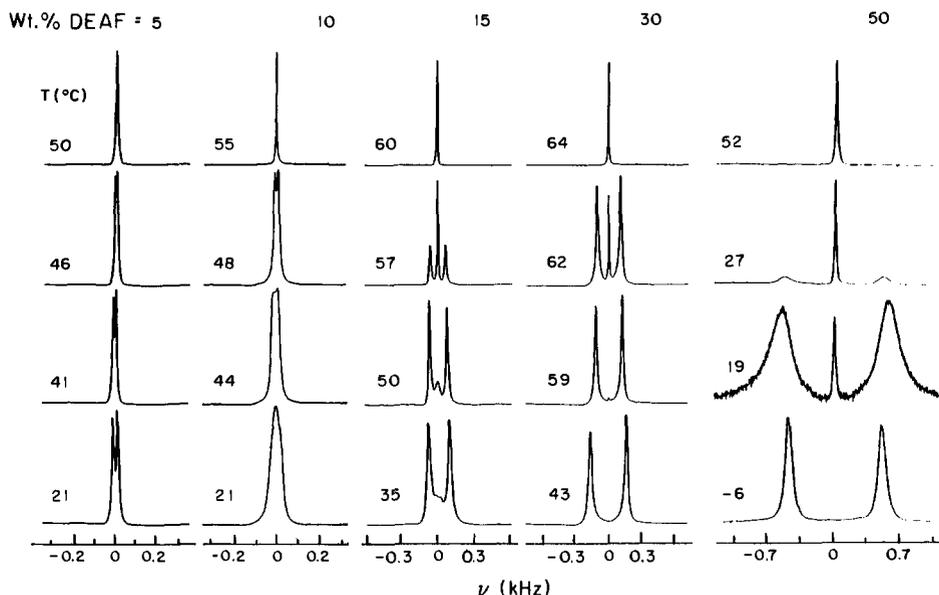


Figure 1. ^2H NMR spectra in solutions containing various concentration of (normal) DEAF in D_2O at different temperatures, as indicated in the figure. The spectra were obtained after allowing the liquid solution to cool in the magnetic field of the CXP300 spectrometer to the desired temperature.

in that they can form mesophases at concentrations as low as 4 wt % and even lower.

The investigation of EF was mainly based on electron microscopy of freeze-etched samples¹ as well as other physicochemical methods including differential scanning calorimetry, optical microscopy, specific conductance, light scattering, rheology, and ^{19}F NMR.⁴ They identified two types of morphological units; spherical micelles which dominate at low DEAF concentrations (<20 wt %) and planar structures which dominate at higher concentrations. They suggested that both forms have a bilamellar structure. It is interesting to note that flufenamic acid and its salts serve as antiinflammatory agents.⁵ It is not clear, however, whether their pharmacological activity is related to their ability to form lyomesophases.

In the present paper we extend the study of the DEAF-water system by the deuterium NMR technique, using D_2O and specifically deuterated DEAF species. The NMR results confirm the conclusions of EF and in addition provide information on the symmetry of the mesophase, its magnetic anisotropy, and the degree of ordering of its constituents. The measurements of the water ordering were done in D_2O solutions, and the results are described in section III. This study provided a phase diagram for the system as well as information on the water ordering and its dependence on the DEAF concentration and temperature. The measurements on the deuterated DEAF species are described in section IV. They provided information on the ordering of the DEAF molecules and on the structures of the two mesophases.

The preparation of specifically deuterated DEAF species required special synthetic procedures. These are described in the Experimental Section (II) which also includes details on the NMR measurements.

The ^2H NMR of a deuterated species in a single domain of a mesophase sample consists of a doublet whose overall splitting, ν_Q , reflects the degree of ordering of the particular deuterated species.⁶ In general five motional constants C_i are required to describe the ordering of a molecule in a mesophase. When the director is parallel to the magnetic field direction, ν_Q is given by

$$\nu_Q = \frac{3}{2} \left(\frac{e^2 q Q}{h} \right) \sum_{i=-2}^2 f_i(\alpha\beta\gamma) C_i \quad (1)$$

where $(e^2 q Q)/h$ is the major principal component of the deuteron quadrupole coupling tensor, $f_i(\alpha\beta\gamma)$ are factors depending on the molecular geometry and the asymmetry parameter η^p of the deuteron quadrupole tensor

$$f_i = D_{0i}^2(\alpha\beta\gamma) + \frac{\eta^p}{(6)^{1/2}} [D_{2i}^2(\alpha\beta\gamma) + D_{-2i}^2(\alpha\beta\gamma)] \quad (2)$$

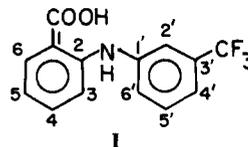
The $D_{1m}^2(\Omega)$ are elements of the Wigner rotation matrices, and α, β, γ , are the Euler angles that describe the principal coordinate system of the quadrupole tensor in the molecular frame.

In certain cases of symmetric molecules the number of independent C_i 's required to describe the molecular orientation can be reduced by choosing a molecular frame according to its principal symmetry axes. However, the DEAF molecule has no element of symmetry, and no simplification of eq 1 is a priori possible for the exact analysis of its ν_Q 's. The situation is further complicated by the fact that DEAF can in principle be at different conformations, each contributing to the average measured ν_Q . The water molecule has C_{2v} symmetry and thus requires only two motional constants to describe its orientation in the mesophase. However, for this case we only have one observable, i.e., ν_Q , of the OD deuterons (in fact only $|\nu_Q|$ is measured), and thus no quantitative analysis of the water ordering can be made.

Nevertheless the dependence of the deuterium spectral behavior on the composition of the phase and on the temperature may provide interesting qualitative information on the ordering of the various species in the mesophase and on the phase transformations and phase diagram of the system under investigation. Also when the sample does not fully align by the magnetic field, the resulting spectra will reflect the distribution of the domain in the mesophase and may provide information on the shape of its structural units. In the following, we report ^2H NMR measurements of deuterated species in the DEAF-water system and analyze the results in terms of possible structures of its lyomesophases.

II. Experimental Section

A. Material. Diethylammonium flufenamate was prepared by neutralization of flufenamic acid (2-[[3-(trifluoromethyl)phenyl]amino]benzoic acid) (I) with diethylamine in ether solutions.¹ The salt was



(3) Goldfarb, D.; Labes, M. M.; Luz, Z.; Poupko, R. *Mol. Cryst. Liq. Cryst.* **1982**, *87*, 259.

(4) Fischer, W.; Eckert, T., *Colloid Polym. Sci.* **1982**, *260*, 880.

(5) Lambardino, J. G.; Otterness, I. G.; Wiseman, E. M. *Arzneim.-Forsch.* **1975**, *25*, 1629.

(6) Goldfarb, D.; Poupko, R.; Luz, Z. *J. Chem. Phys.* **1983**, *79*, 4035.

precipitated by addition of *n*-hexane and purified by repeatedly dissolving

Chart I

compound	1	2	3	4	5	6	7	8
position(s) labeled	5,6- d_2	5- d_1	4- d_1	3,5- d_2	3,4,5,6- d_4	2',4',6'- d_3	5',6'- d_2	5'- d_1

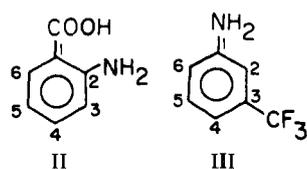
Chart II

compound	9(III)	10(III)	11(III)	12(II)	13(II)	14(II)	15(II)
position labeled in compds II or III	2,4,6- d_3	5,6- d_2	5- d_1	4- d_1	5- d_1	3,5- d_2	3,4,5,6- d_4

in ether and precipitation with hexane.

For the normal undeuterated compound, commercial flufenamic acid (Aldrich) and diethylamine (BDH) were used. One set of experiments was also done on DEAF perdeuterated in the ethyl groups of the diethylammonium ion. This species was prepared by using commercial perdeuterated diethylamine (Merck, Sharp & Dohm).

Most of the ^2H NMR measurements were performed on DEAF species specifically deuterated in the flufenamate anion, which were prepared from the corresponding specifically deuterated acid. The various isotopic species of flufenamic acids used are tabulated in Chart I. These compounds were prepared from the corresponding deuterated precursors by two methods: For isotopic species labeled in the benzoic acid ring, specifically deuterated anthranilic acid (II) was reacted with



(isotopically normal) *m*-(trifluoromethyl)bromobenzene; for isotopic species labeled in the trifluoromethylphenyl ring, specifically labeled *m*-(trifluoromethyl)aniline (III) was reacted with normal *o*-iodobenzoic acid.⁷ Both condensation reactions were carried out by using copper powder in DMF or isoamyl alcohol as solvents. The resulting deuterated flufenamic acid species were repeatedly recrystallized from 1:1 ethanol/water and finally bulb-to-bulb distilled under high vacuum.

The deuterated precursors used are indicated in Chart II. These precursors were prepared by the following procedures: trifluoromethylaniline-2,4,6- d_3 , 9(III), by exchange of the hydrochloric salt in $\text{D}_2\text{O}/\text{DCl}$ under reflux; trifluoromethylaniline-5,6- d_2 , 10(III), by exchange of III with reduced Adam's catalyst using D_2O at 130 °C (this resulted in ~80% deuteration of positions 5,6 and about 10% deuteration at positions 2,4); trifluoromethylaniline-5- d_1 , 11(III), was prepared by partially back-exchanging trifluoromethylaniline-5,6- d_2 in $\text{H}_2\text{O}/\text{HCl}$ under reflux.

Anthranilic-4- d_1 and -5- d_1 acids, 12(II) and 13(II), were prepared by dehalogenation of the corresponding 4- and 5-bromoanthranilic acids with sodium amalgam (5%) in $\text{D}_2\text{O}/p$ -dioxane, followed by isolation and purification via the corresponding copper complexes. Anthranilic-3,5- d_2 acid, 14(II), was prepared from *o*-toluidine by the following sequences of steps: exchange of the ortho and para sites of *o*-toluidine with $\text{D}_2\text{O}/\text{DCl}$ under reflux, acetylation to acetanilide, followed by oxidation with KMnO_4 to 3,5- d_2 -acetylated anthranilic acid, and finally deacetylation and purification by copper complexation. Anthranilic-3,4,5,6- d_4 acid, 15(II), was prepared by exchange with D_2O by using Pt on carbon (5%) as catalyst at 130 °C.

Compound 1 (flufenamic-5,6- d_2 acid) was prepared from normal flufenamic acid by direct exchange using rhodium(III) chloride as catalyst in a *p*-dioxane/ D_2O mixture.⁸

All deuterated compounds (i.e., the precursors and the resulting flufenamic acid) were checked by mass spectrometry and by ^1H and ^{13}C NMR in order to verify the position and to determine the degree of deuteration. The results were then used for assigning the deuteron peaks in the mesophase spectrum (see section IV).

Solutions for the NMR measurements were made gravimetrically by weighing DEAF crystals into a known amount of water (H_2O or D_2O as the case may be). Their concentrations are reported at wt. % = $100 \times$ (weight of DEAF)/(weight of solvent water + weight of DEAF).

B. NMR Measurements. Most NMR measurements were made on a Bruker CXP300 superconducting spectrometer operating at a deuterium frequency of 46.07 MHz. Some measurements were also made on a Bruker WH-90, employing a resistive electromagnet and operating at a deuterium frequency of 13.8 MHz. The spectra were obtained by averaging a series of FID signals resulting from single $\pi/2$ pulses followed by Fourier transformation. In both spectrometers, a B-VT 1000 unit was used to control the temperature. Its absolute value was cali-

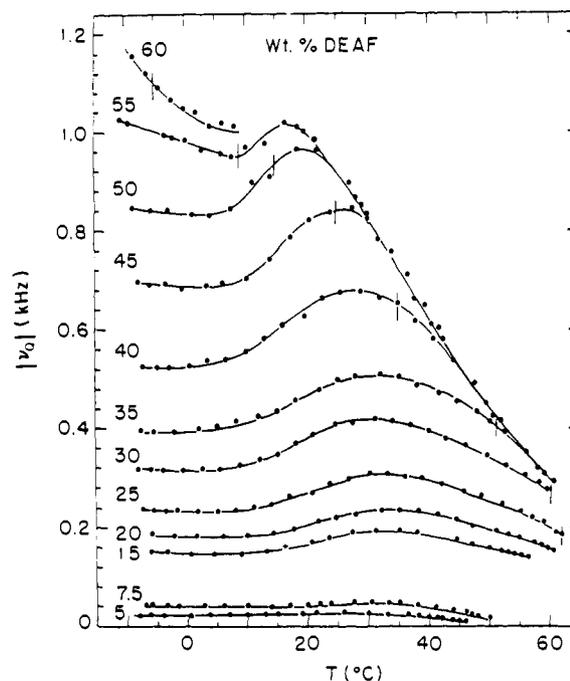


Figure 2. Plots of the observed magnitude of the quadrupole splitting ν_Q of the D_2O deuterons, as function of temperature in the DEAF-water mesophase, containing various concentration of DEAF, as indicated in the figure. The vertical bars indicate for each series of experiments the boundary between the neat mesophase and the biphasic (mesophase plus isotropic solution) regions.

brated by using a Fluke 2190A digital thermometer. Except when otherwise stated, the mesophase spectra were obtained by first heating the solution to the isotropic phase and then allowing it to cool within the magnetic field to the desired temperature. In this way, well-aligned samples were obtained which kept their alignment throughout the measurements of the mesophase.

III. Deuterium NMR of the Solvent D_2O

In this section we describe ^2H NMR measurements of the solvent D_2O in DEAF- D_2O mixtures containing different concentrations of isotopically normal DEAF within the mesophase region. Examples of spectra taken with the CXP300 spectrometer are shown in Figure 1. In each series of experiments, we first observed a single resonance in the isotropic phase until a biphasic region was reached at which both a singlet due to the isotropic phase and a doublet due to the mesophase were observed. The relative intensity of the doublet signal gradually increased with decreasing temperature until the signal from the isotropic phase completely disappeared. The mesophase was then stable down to about -10 °C. At this point, the sample solidified and the mesophase signal vanished. The doublet splittings, ν_Q , as a function of temperature for solutions containing between 5 and 60 wt % DEAF are shown in Figure 2. Solutions containing below 2.5 or above 60 wt % DEAF remain isotropic and do not give a mesophase on cooling. Within the mesophase region, in each temperature run, the ν_Q curves pass through a maximum at around 20-30 °C, while at a given temperature the splittings increase monotonically, with the DEAF concentration. This is shown for three different temperatures in Figure 3.

The boundary between the single and biphasic (mesophase plus isotropic solution) regions is indicated in Figure 2 for the more concentrated solutions by short vertical bars. According to the phase rule, the composition of the mesophase in the biphasic region

(7) Wilkinson, J. H.; Finar, I. L. *J. Chem. Soc.* **1948**, 32.

(8) Lockley, W. J. S. *Tetrahedron Lett.* **1982**, 23, 3819.

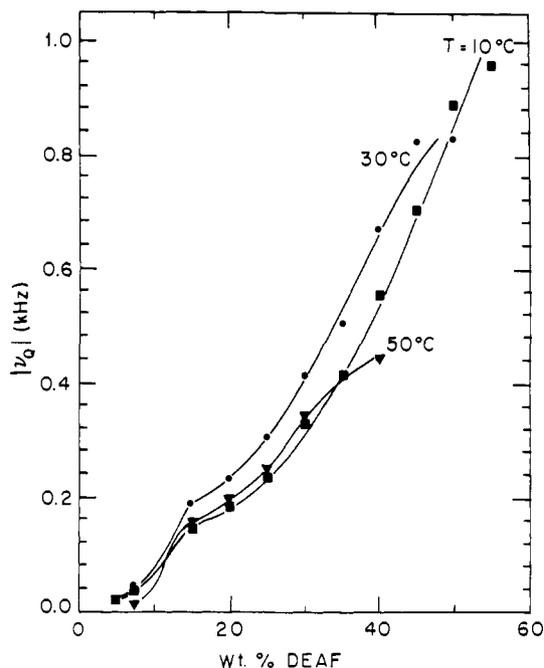


Figure 3. Plots of the observed quadrupole splittings at three fixed temperatures as indicated in the figure as a function of the DEAF concentration in the mesophase region. The ν_Q values are from Figure 2.

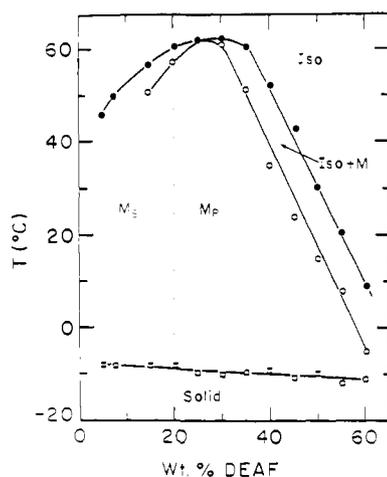


Figure 4. Phase diagram of the DEAF-water system based on results from ^2H NMR of solvent D_2O . The dashed vertical line represents the boundary between the spherical and lamellar phases according to Eckert and Fischer.

(three phases at equilibrium, including the vapor phase) is determined by a single variable, i.e., the temperature. Indeed, the splittings of all solutions in the biphasic region lie on a common continuous line, since the ν_Q 's are continuous functions of the solution composition and temperature. In the low concentration range (<20 wt %), such a common line is not obtained, but as explained below, in this region the samples consist of a mixture of two types of structures and the above rule does not apply. Some deviation from the common line may also be noted in the solutions with the higher DEAF concentration. This may perhaps be due to incomplete equilibration between the two phases. Depending on the concentration of the solution, the phase transformation from the isotropic phase to mesophase may take from less than 1 min up to several tens of minutes.

Based on the ν_Q measurements of the solvent D_2O deuterons, a phase diagram as shown in Figure 4 was constructed. In its main features, it is essentially the same as that obtained by EF, although there are certain differences in the exact boundaries of the mesophase region in the two diagrams. In both diagrams the maximum stability range of the mesophase (over more than 70 °C) is at around 30 wt % DEAF. As expected from thermody-

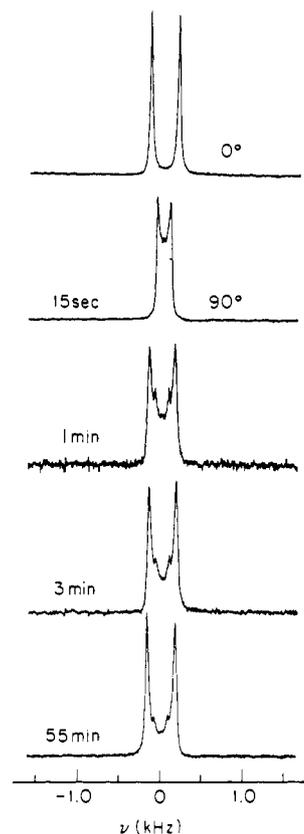


Figure 5. Determination of the sign of the anisotropic magnetic susceptibility, $\Delta\chi$, of the DEAF-water system: The upper trace corresponds to the ^2H NMR of D_2O obtained after cooling a sample containing 30 wt % DEAF in D_2O to the mesophase region (47 °C) within the probe head of a WH90 spectrometer. The sample was then rotated by 90° about an axis perpendicular to the magnetic field direction followed by recording the spectrum at different time intervals as indicated in the figure.

namics, at this point the biphasic region disappears, but it exists on both sides of it. The ^2H NMR results of the D_2O solvent do not indicate a boundary line between a low and high concentration phase as found by EF (see dashed line in Figure 4). However, as will be seen below, such a boundary line is suggested by the ^2H NMR of deuterated DEAF.

The magnitude of the ^2H quadrupole splitting is of the same order as observed for D_2O in the disodium cromoglycate-water system;³ however, the temperature dependence in the DEAF-water mesophase is somewhat unusual. In particular we note that at each series of experiments there is a range at which the splitting increases with temperature. This may reflect the presence of several solvation sites for the water molecules with different ordering parameters. Thus, the observed splitting is a function of the population of the various sites as well as their specific ordering, both of which are temperature-dependent. It is, however, not possible to quantify this model since only one splitting (whose sign is not known) is measured, while a large number of parameters are required to describe the system (the population distribution between the sites and two motional constants for each site).

The fact that relatively sharp doublets are observed for the deuterium spectra of the D_2O solutions indicates that the mesophase is aligned by the magnetic field. From the spectra of the type shown in Figure 1 alone, it is not possible, however, to tell whether the mesophase aligns with the director parallel to the magnetic field or perpendicular to it, corresponding respectively to $\Delta\chi$ positive or negative.⁹ In fact these spectra do not even indicate whether the mesophase is uniaxial or biaxial. To check on these points, the following experiment was done: A 30 wt % DEAF solution in D_2O was allowed to cool from the liquid phase to the

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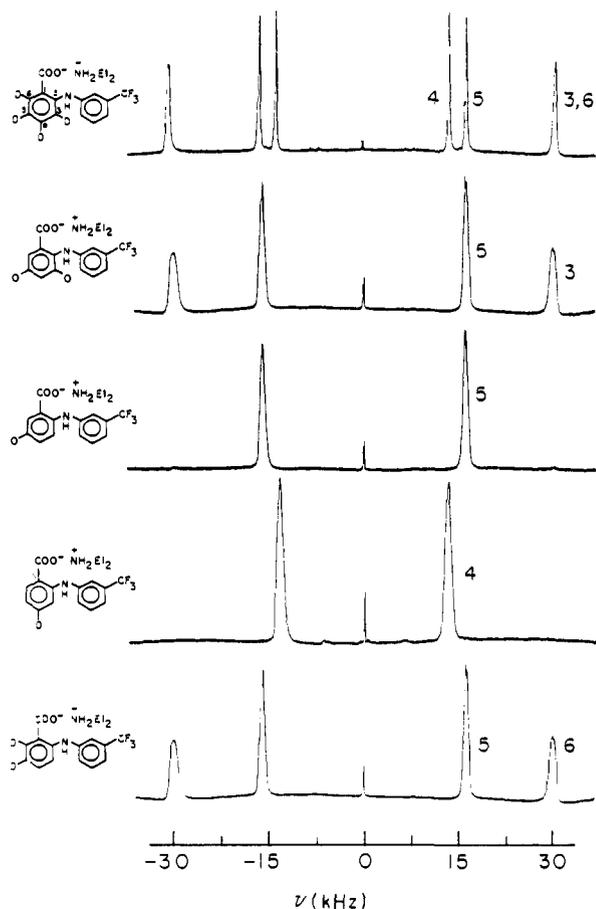


Figure 6. ^2H NMR spectra of specifically labelled DEAF in the DEAF-water mesophase. All solutions contained 30 wt.% DEAF and were recorded at 50 °C. The isotopic species were labelled in the benzoic acid ring and are indicated next to each spectrum. The weak central band (doublet) corresponds to the ^2H signal from solvent water (natural abundance).

mesophase at 47 °C within the probe of a WH90 electromagnet spectrometer. The ^2H NMR spectrum obtained after equilibration is shown in the upper trace of Figure 5. The sample tube was then rotated by 90° about its long axis, i.e., about an axis perpendicular to the field direction, and the spectrum repeatedly recorded at different time intervals. The results of several such spectra are shown in the other traces of Figure 5. It may be seen that immediately after the sample rotation (second trace in the figure), a relatively sharp doublet is obtained with half the original splitting. This indicates that the original sample consisted of a single uniaxial domain with its director parallel to the field direction. After rotation, the single domain is aligned perpendicular to the field direction, exhibiting perpendicular features with a splitting $\nu_Q^\perp = 1/2(3 \cos^2(\pi/2) - 1)\nu_Q = -1/2\nu_Q$. With time, however, the sample reorients back to the parallel orientation, as may be seen in Figure 5 by the reappearance and growth of the parallel features at the expense of the perpendicular ones. Under the condition of this particular experiment, a steady-state spectrum is obtained after about 5 to 10 min. As may be seen, it still exhibits weak perpendicular features apparently due to anchoring effects on the sample tube surface.

Finally a comment is in order about the low concentration solutions (<15 wt %). Here ν_Q has reduced very considerably, and it is not possible to discern a weak central peak due to the isotropic phase between the doublet components. Also when an aligned dilute solution is rotated in the magnetic field, a broad structureless peak of overall width similar to the original splitting is obtained, and no realignment of the sample is subsequently observed even after long periods of time. This change in behavior of the D_2O signal may be related to the phase transformation from a planar to a spherical micellar structure which was suggested by EF to occur when the DEAF concentration is reduced to below

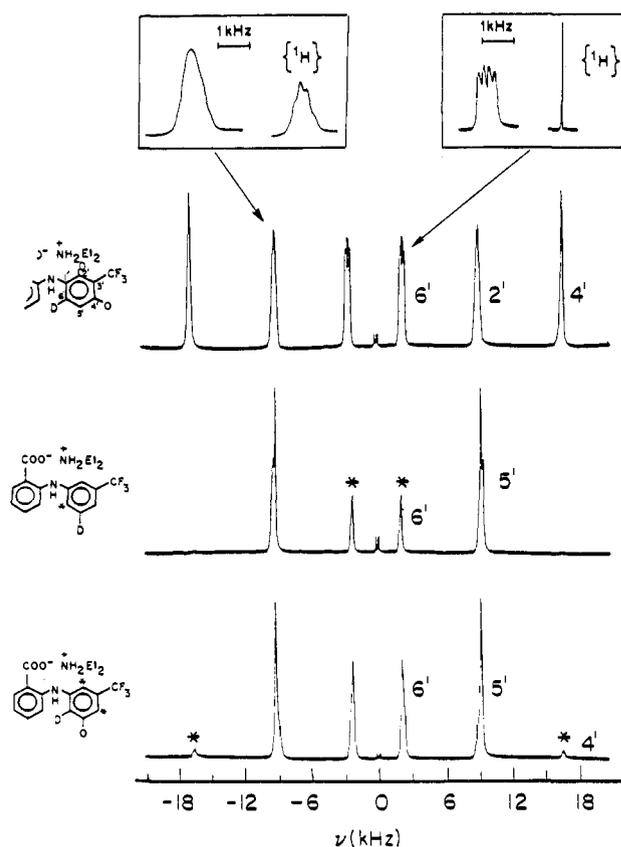


Figure 7. As in Figure 6 but for isotopic species labeled in the trifluoromethylphenyl ring. (A starred position in the formulas indicates a weakly deuterated site). The inserts show the spectrum of the particular peaks under conditions of proton decoupling.

20 wt %. We show below that ^2H NMR of deuterated DEAF support this suggestion.

IV. Deuterium NMR of Deuterated DEAF Species

In addition to measuring the ^2H signal from solvent D_2O we have also studied the ^2H NMR of several specifically deuterated species of DEAF in the mesophase region of the DEAF-water system. In the present section we describe these results in some detail.

A. Peak Assignment. In Figure 6 and 7 are shown ^2H NMR spectra of aqueous DEAF solutions in the mesophase region containing specifically deuterated species, in both the benzoic acid and trifluoromethylphenyl rings. All spectra are for a 30 wt % solution and were recorded at the same temperature of 50 °C. The assignment of the various peaks can be made in a straightforward manner from comparison of the spectra of the various isotopic species. They are indicated in the figures according to the numbering system in the formula given in the Introduction section.

Several features in the DEAF spectra may be pointed out. We note first that peaks of deuterons that are in the para position to each other give, within the experimental line width, identical splittings. Compare, e.g., peaks 3,6 in the benzoic acid ring (Figure 6) and peaks 2',5' in the trifluoromethylphenyl ring (Figure 7). This is of course as expected for nuclei with colinear axially symmetric tensors. In the latter ring, two of the deuterons also exhibit splittings due to dipolar interaction with neighboring magnetic nuclei (see inserts in Figure 7). Each of the components of the 6' quadrupole doublet appear as a doublet of doublets apparently due to dipolar interaction with the proton in the 5' position and proton 3 in the benzoic acid ring. Proton decoupling causes this splitting to collapse. The other case is that of the 2' deuteron. In the DEAF-2',4',6'- d_3 solution, it gives a relatively broad peak. However, on proton decoupling a quartet structure is obtained apparently due to coupling with the trifluoromethyl nuclei.

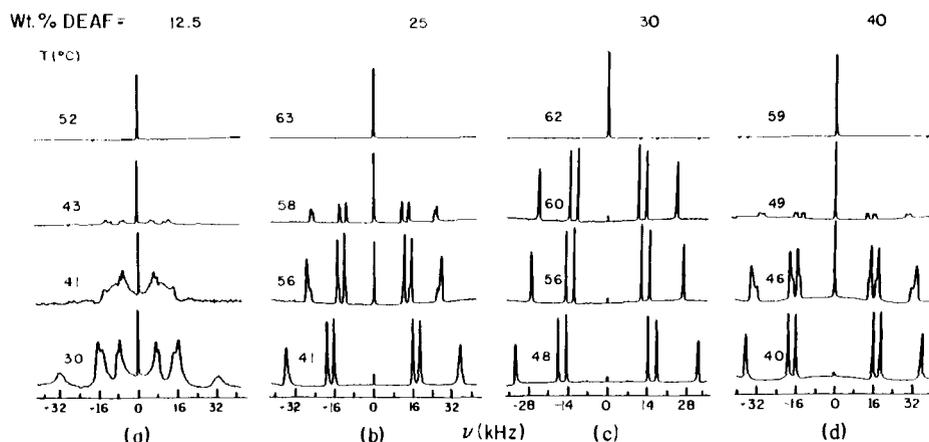


Figure 8. ^2H NMR spectra of H_2O solutions containing various concentrations of DEAF-3,4,5,6- d_4 at different temperatures. The concentrations and temperatures are indicated in the figure.

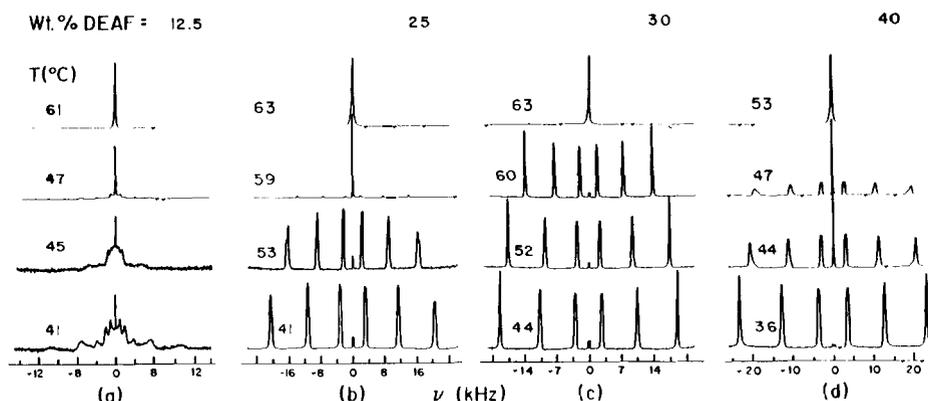


Figure 9. Same as Figure 8 for DEAF-2',4',6'- d_3 solutions.

B. Deuterium NMR in the High Concentration Solutions. To study the temperature and concentration dependence of the quadrupole splitting of the various deuterons, two sets of solutions were first used; one consisting of DEAF-3,4,5,6- d_4 and the other of DEAF-2',4',6'- d_3 . Together they provided quadrupole splittings of all discernible aromatic deuterons. Examples of spectra from both ring deuterons at different temperatures and different DEAF concentrations are shown in Figure 8 and 9. In the 30 wt % solution, there is essentially no biphasic region; a single peak is observed in the isotropic liquid and a set of three symmetrical doublets in the mesophase region. The weak central peak in the latter region comes from the water deuterons (natural abundance). On an expanded scale, and absence of broadening by apodization, this peak appears as a doublet as discussed in the previous section. At higher and lower concentrations of DEAF, there is a biphasic region in which signals from both the mesophase as well as from DEAF in the isotropic phase are observed. The phase diagram obtained from these spectra is similar to that obtained from the D_2O measurements (see Figure 4); however, it is less accurate because of the lower sensitivity of the DEAF signals. The DEAF spectra exhibit, however, an additional boundary line in the phase diagram at around 20 wt % DEAF. Spectra taken from more dilute solutions were more complicated and appeared as mixtures of phases exhibiting powder patterns (cf. spectra in columns a of Figures 8 and 9) while solutions containing above 20 wt % DEAF gave simple spectra as discussed in the previous section. Recalling that EF found two different morphological structures for solutions containing above and below 20 wt % DEAF, we shall discuss the two concentration regions separately. We start with the high-concentration phase.

In the biphasic region of the more concentrated solutions, there is often a weak accompanying peak next to the major DEAF signals (cf. traces of the biphasic region in columns d of Figures 8 and 9). As the temperature is lowered within the biphasic region, the weak component decreases in intensity, and, eventually, when the neat mesophase region is reached, only the major components

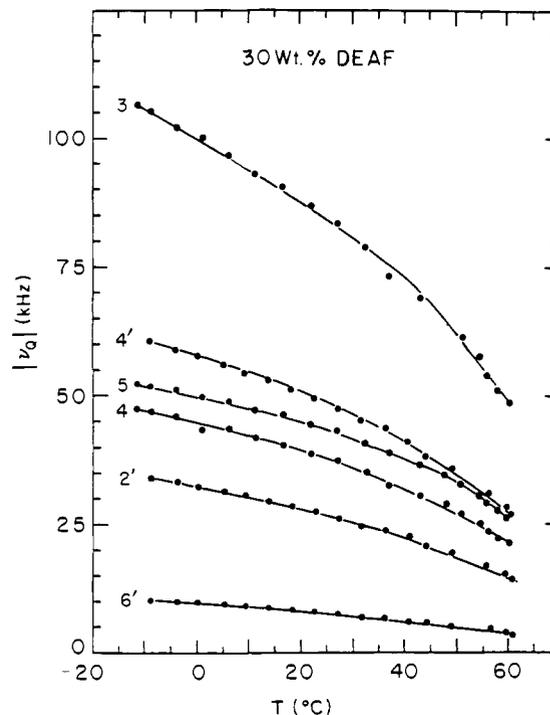


Figure 10. Plots of the observed quadrupole splittings, ν_Q of the various flufenamate deuterons in the DEAF-water mesophase region as a function of temperature for a solution containing 30 wt % DEAF.

remain. We have subsequently found that if excess base (diethylamine) is added to the neutralized solution, this "doubling" of the spectrum does not occur; however, the transition temperature of the isotropic phase is reduced. This effect may reflect the presence of two different mesophases over a very narrow tem-

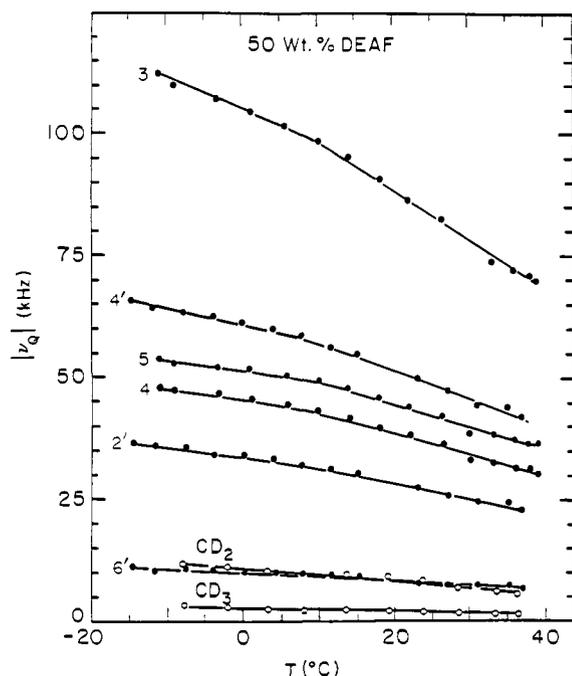


Figure 11. Same as Figure 10 for a solution containing 50 wt % DEAF. Note that for this solution, results are also given for the deuterons of the diethylammonium ion.

perature range, consisting perhaps of different flufenamate species or different types of aggregates (*vide infra*).

The observed quadrupole splittings for two different DEAF concentrations (30 and 50 wt %) are plotted as a function of temperature in Figure 10 and 11. It may be seen that there is a continuous decrease in the ν_Q 's with increasing temperature; however, the relative splittings of the various sites remain almost constant over the whole temperature range. This suggests that the molecular ordering can approximately be described by a single motional constant associated with an effective principal symmetry axis of the molecule. If there were additional contributions to ν_Q from other independent motional constants, they would in general have different temperature dependencies and consequently the ν_Q 's of different sites would depend differently on the temperature. The same observation applies to the deuteron signals in solutions containing perdeuterated diethylammonium ions. These solutions exhibited two pairs of doublets due to the methylene and methyl deuterons, which could readily be assigned on the basis of their relative intensities. The results for these deuterons in the 50 wt % solution are included in Figure 11. The splittings are somewhat lower than those for most of the flufenamate deuterons; however, the relative splittings compared with the latter are fairly constant, supporting the "one motional constant" model discussed above.

Finally we note that for the high-concentration solutions, at constant temperature, the quadrupole splittings of the various deuterons are almost independent of concentration in the range 17–50 wt % DEAF.

C. Deuterium NMR in the Low-Concentration Solutions. We now turn to the spectra of the low-concentration region (<20 wt %) of the DEAF–water system (columns a in Figures 8 and 9). In this region, the spectra exhibit a multitude of features including powder patterns that are difficult to interpret in particular for the three and four deuteron species, DEAF-2',4',6'- d_3 and -3,4,5,6- d_4 . We have therefore repeated the measurement in this region by using a single deuteron species *i.e.*, DEAF-5- d_1 . In Figure 12 are shown ^2H NMR spectra of this species in the mesophase region containing between 7.5 and 30 wt % DEAF. All spectra correspond to the same temperature of 30 °C. Similar sets of spectra are obtained for other temperatures within the mesophase region. In the 30 wt % solution, the spectrum consists of a single sharp doublet. This spectrum corresponds to the same species observed in the high concentration range discussed above

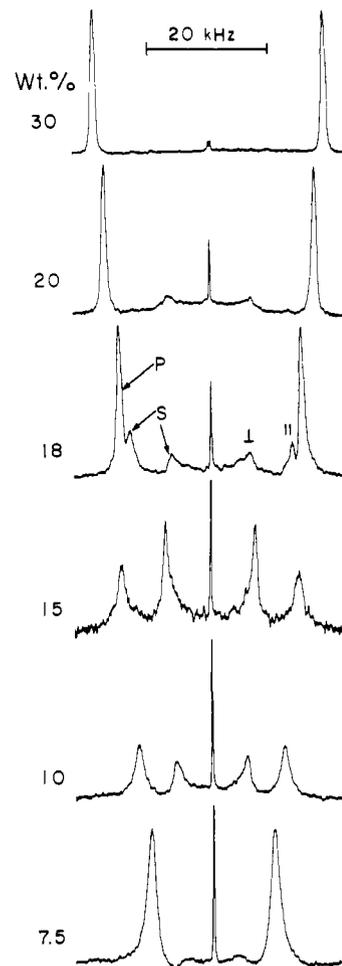


Figure 12. ^2H NMR spectra of DEAF-5- d_1 solutions in the low-concentration region as indicated in the figure. All spectra were taken at 30 °C. p and s label the signals obtained from the planar lamellar and spherical lamellar phases, respectively.

and is marked by "p". In the 20 wt % solution, it may be seen that in addition to the p spectrum, weak peaks appear due to another species which we label "s". The s spectrum consists of two broad features whose relative splittings are at a ratio 2:1. We therefore interpret these signals as the parallel and perpendicular features of a uniaxial powder spectrum of the s species. As the concentration of DEAF is decreased, the intensity of the s-species spectrum increases at the expense of the p spectrum, until at 15 wt % the latter disappears and the spectrum is solely due to the s species. On further decreasing the concentration of DEAF, the spectrum of the s species develops stronger parallel features, while the perpendicular features gradually lose intensity.

This behavior of the spectrum indicates that the DEAF mesophase exhibits two structural forms, one which is stable at low concentrations (<20 wt %) and which gives rise to the powderlike s spectrum and one that is stable at high concentrations (>20 wt %) of DEAF, and which gives the sharp doublet p spectrum. The boundary line between the two mesophases corresponds to the same concentration region at which EF found a dividing line between a phase, giving rise to spherical lamellar micelles and a phase of planar lamellae (*cf.* Figure 4). Hence we associate the s and p spectrum with, respectively, the spherical and planar lamellar phases of EF.

At a given concentration of DEAF, the pattern of the s-species spectrum does not change as a function of temperature, except that there is a decrease in the overall splitting with increasing temperature. This is shown for both the parallel and perpendicular features in Figure 13. Note the inverted cusp in the plots at around 40 °C which corresponds to the transition from neat mesophase to mesophase plus isotropic solution. The cusp for the primed and unprimed deuterons does not fall at exactly the same

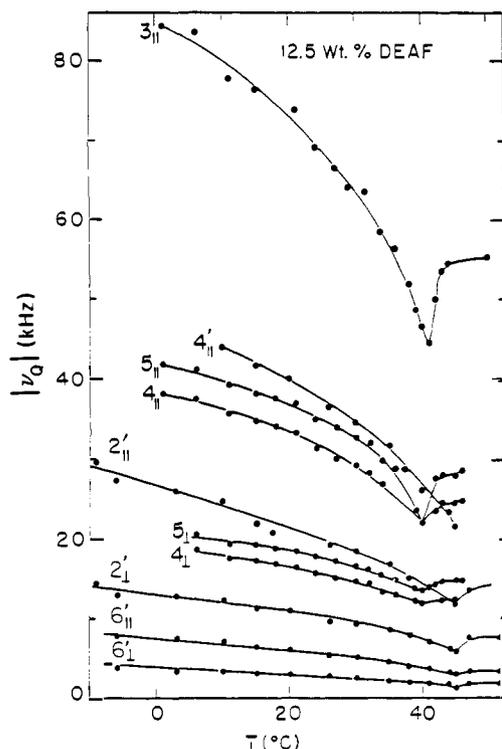


Figure 13. Plots of the splittings of the parallel (||) and perpendicular (⊥) features of the various DEAF deuterons as function of temperature in the mesophase region of solutions containing 12.5 wt % DEAF.

temperature because the measurements of the two types of deuterons were done on two different solutions which apparently had slightly different concentrations.

V. Discussion

The main result of the previous section indicates that depending on the composition, the DEAF-water system exhibits two types of lyomesophases which exhibit different NMR spectra. In the high-concentration range (>20 wt %), the spectrum of each deuteron consists of a sharp doublet which is shown to correspond to uniaxial domains whose directors are aligned parallel to the magnetic field. The phase in this region was suggested by EF to consist of a planar bilayer structure in which the DEAF molecules are held together by dipolar forces involving hydrated trifluoromethyl groups, while the diethylammonium carboxylate ion pair serves as the boundary region with the interlamellar water.

The NMR results are consistent with this picture and indicate that in a magnetic field, the layered structures form monodomains whose layers are perpendicular to the field direction. Moreover, from the fact that $\Delta\chi$ is positive, it follows that molecular ordering within the layers must be such that the aromatic planes prefer to lie parallel to the director rather than perpendicular to it. In principle one could determine the ordering parameters of the molecules within the bilayers from the deuterium quadrupole splittings using formulas given in the Introduction section.

However, even if we assume the molecules to be rigid, axially symmetric objects, we would still require to fit five parameters to the experimental data (two angles describing the orientation of the "symmetry axis" in the molecule, two dihedral angles, and a motional constant C_{00}). Actually more geometrical parameters may be required since it is not clear whether the solid-state results^{10,11} apply to the mesophase. It is also likely that the DEAF molecules exist in the mesophase in several conformations at equilibrium. Considering the fact that we have only six independent experimental parameters (whose relative signs are not known), we deemed it not very useful to perform a complete analysis of the molecular ordering. A lower limit of 0.4 for a single-order parameter can, however, be estimated from the largest observed splitting, i.e., of the 3 and 6 deuterons in the benzoic acid ring.

When the concentration of the DEAF is reduced to below 20 wt %, the spectrum changes quite abruptly (over a concentration range of 4–5%) into a new type of spectrum which is characteristic of an unoriented sample. This result is consistent with the suggestion of EF that the low-concentration phase consists of spherical lamellar micelles. If these structural units are sufficiently large so that their tumbling rate and the rate of molecular diffusion on the micellar surface are too slow on the NMR time scale to effectively reorient the molecules relative to the director, such samples would result in powderlike spectra. The exact line shape of these spectra, in particular the relative intensities of their parallel to perpendicular features, depends on the shape of the micelles and their orientational distribution relative to the director.

The results in Figure 12 suggest that apparently the shape of the micelles depends on the concentration of the solution. Thus, at around 20 wt % DEAF where the planar lamellar and spherical lamellar structures coexist, the micelles are indeed spherical as suggested by the random powderlike spectra of the s species in this concentration range. At around 15 wt % DEAF, the micellar spectrum appears as a two-dimensional distribution of directors. Such a spectrum would, e.g., be expected from cylindrical micelles oriented perpendicular to the magnetic field. Finally, at lower concentrations (<10 wt %), the intensity of the parallel features in the spectra became much more intense than the perpendicular ones. Such spectra are expected from disklike micelles lying perpendicular to the field direction. It should be noted, however, that this qualitative interpretation of the spectra in terms of micellar shapes is not unique, and other shapes or distributions may also be consistent with the observed line shapes. It is, however, quite evident that the micellar shapes depend on the concentration of the DEAF in the s phase.

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Registry No. DEAF, 64196-61-8.

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