Location of the discotic lamellar-nematic tricritical point and isotope effects in the caesium pentadecafluorooctanoate (CsPFO)/water system as established by [133] Cs N.M.R. spectroscopy

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^{133}Cs N.M.R. spectroscopy has been used to locate the discotic lamellar (smectic A)–nematic tricritical point in the CsPFO/H$_2$O and CsPFO/^{2}H$_2$O systems. In both systems this occurs at the same volume fraction of 0·25, but at different temperatures (302·05 and 304·80 K, respectively). The phase diagram for the CsPFO/H$_2$O system has also been studied for the first time and a comparison of the corresponding fixed points shows there to be large isotope effects.

1. Introduction

Until fairly recently it has generally been accepted that surfactants on dissolution in water, would form small discrete micelles in dilute solution [1] and liquid crystals, with extended aggregate structures, in concentrated solution [2]. It is, however, now recognized that small discrete micelles can be stable at high concentrations where they undergo sequences of order–disorder transitions which are quite analogous to those exhibited by thermotropic liquid crystals. The existence of these micellar liquid crystals poses new questions regarding the factors which govern the size and shape of micelles and the nature of the forces between them. They also offer the exciting prospects of being able to investigate hitherto inaccessible phase transition phenomena.

The first micellar mesophases to be identified were the nematics [3, 4]. These have tended to be found over only narrow intervals of concentration in a small number of surfactant/water mixtures containing either a long chain alcohol or an inorganic salt [5–7]. But it is now apparent that nematic phases which are stable over wide concentration intervals in simple binary mixtures can be prepared by designing novel surfactants [8]. Both uniaxial N_C (rod shaped micelles) and N_D (discoid micelles) phases can now be prepared from both ionic [9] and non-ionic [10, 11, 12] amphiphiles without addition of either salt or alcohol. Of these, the caesium pentadecafluorooctanoate (CsPFO)/water system has been by far the most widely studied to date. The heavy water system forms an N_D^+ (diamagnetically positive) phase over a wide range of both concentration (0·225 to 0·632 weight fraction, w, of CsPFO) and temperature (285·3 to 351·2 K) [13]. This phase lies between an isotropic micellar solution phase I to higher temperatures and a lamellar phase to lower temperatures. Significantly, at the transition from N_D^+ to the lamellar phase there is no detectable

change in the size of the discoid micelle [14–17], that is, in the lamellar phase the small discoid micelle is stable with respect to the classical bilayer. This is an unexpected discovery which is not understood at the present time. The demonstration of similar discotic micellar lamellar phases (denoted as L_D) for the tetramethylammonium heptadecafluoronanoate/water [18] and the decylammonium chloride/ammonium chloride/water [19] systems, which also form N_D phases, suggests that such phases may be of wider occurrence.

The I to N_D^+ to L_D sequence of transitions exhibited by the CsPFO/water system is quite analogous to the isotropic liquid to nematic to smectic-A sequence observed for thermotropic mesogens with lath-shaped molecules. There are, however, significant structural differences. First, the packing fraction of the micelles is relatively low: 0·11 (and as low as 0·07 in monotropic phases) to 0·43 along the N_D^+ to I transition line. Secondly, the size of the micelle [17] is a function of concentration and temperature, though there is no simple relationship between the phase behaviour and micelle size. The N_D^+ to I transition has been fairly extensively studied [20–23], but studies of the N_D^+ to L_D transition are only just beginning [15, 24]. The interest in the latter transition stems from the existence [13] of a symmetrical tricritical point T_{cp}, analogous to the $^3He/^4He$ superfluid transition. For experimental studies of the variation of critical exponents on approaching T_{cp}, a first requisite is to locate this point accurately. In a previous study [13] it was fixed at $w = 0.53$ for the CsPFO/^2H_2O system by ^2H N.M.R. spectroscopy. However, because of the intrinsic limitation in the resolution of the signals from the coexisting N_D^+ and L_D phases, it was emphasized that the actual composition could well be less than this value. We have now shown by using ^{133}Cs N.M.R., which has at least an order of magnitude greater resolving power, that this is indeed the case. Moreover, ^{133}Cs N.M.R. can be used to map the phase diagram for the CsPFO/H_2O system. It is important to do this as some workers [20–23] have chosen to study this system rather than the heavy water one. A table of fixed points for the two systems is, therefore, included. Isotope effects are seen to give rise to appreciable shifts in phase transition temperatures.

2.   Experimental results

A partial phase diagram for the CsPFO/^2H_2O system is given in figure 1. It shows the N_D^+ to I and the N_D^+ to L_D transition lines. The coordinates of these lines are mainly as established previously by ^2H N.M.R. spectroscopy of heavy water [13]. The only differences are the positions of T_{cp} and the N_D^+ to L_D transition lines in the vicinity of this point. These improvements have been affected by ^{133}Cs N.M.R. spectroscopy. The advantages of ^{133}Cs as compared to ^2H N.M.R. for this purpose are explained in §2.2.

2.1. *Materials and methods*

CsPFO was prepared by neutralizing an aqueous solution of pentadecafluoro-octanoic acid (Fluorochem. Ltd.) with caesium carbonate (B.D.H. Ltd.). The neutralized solution was evaporated to dryness in an oven and the salt was recrystallized from *n*-butanol. N.M.R. samples were prepared by weighing CsPFO and ^2H_2O/H_2O (deionized, doubly distilled) directly into a 5 mm-o.d. N.M.R. tube which was then flame sealed. ^{133}Cs N.M.R. spectra were measured using a JEOL GX270 spectrometer operating at 35·44 MHz in the pulse Fourier transform mode with a ^{133}Cs pulse width of 10 μs. Typically, the free induction decay signal was sampled using 32 K data points over a 32 kHz spectral width giving a resolution after Fourier
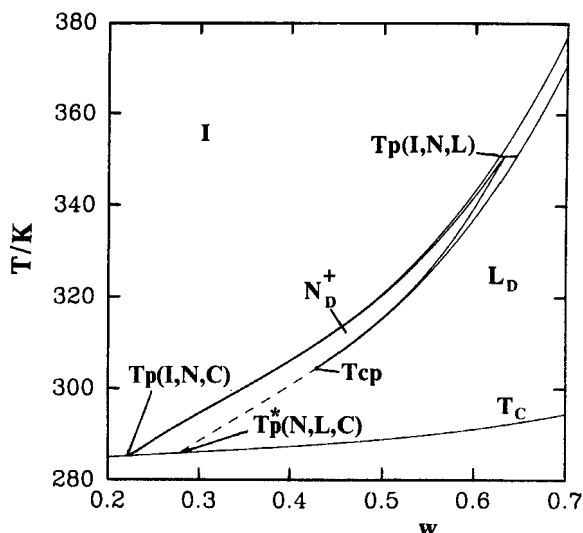
Figure 1. Partial phase diagram of the CsPFO/^{2}H$_2$O system showing the isotropic micellar solution I to nematic N$_D^+$ and the N$_D^+$ to discotic lamellar L$_D$ transition lines, the solubility curve T_C for the crystalline solid C, the N$_D^+$ to L$_D$ tricritical point T_{cp}, the I–N$_D^+$–L$_D$ triple point T_p(I, N, L), the I–N$_D^+$–C triple point T_p(I, N, C) and the N$_D^+$–L$_D$–C pseudo triple point T$_p^*$(N, L, C). The temperatures of the phase boundary curves are estimated to have errors of ± 0.04 K.

transformation of 2 Hz per data point. Temperature control and homogeneity were achieved by mounting the sample tube inside a double water flow cryostat. The lower part of this device was constructed from a standard 10 mm-o.d. N.M.R. tube which enables it to be readily located into the 10 mm multinuclear probe. The temperature was controlled to within ± 5 mK by water pumped from a Colora WK3 cryostat and was measured with the same precision and accuracy by a copper-constantan thermocouple placed as close to the sample as was consistent with good resolution. The thermocouple was calibrated against a quartz oscillator thermometer over the temperature range 0° to 95°C. The experimental protocol used to establish the precise location of phase boundaries is described in detail elsewhere [13, 25].

2.2. *The N.M.R. experiments and results*

The nematic phase of CsPFO/^{2}H$_2$O is diamagnetically positive. Thus, the nematic director **n** undergoes spontaneous alignment along the direction of the spectrometer magnetic field **B** to give a macroscopically aligned sample. For this and, indeed, for any other macroscopically aligned uniaxial mesophase, the first order spectrum for any spin $I > \frac{1}{2}$ will consist of $2I$ equally spaced lines with separation, referred to as the quadrupole splitting, given by [26]

$$\Delta \tilde{\nu}(\phi) \;=\; \frac{3}{2I(2I-1)} \, |\tilde{q}_{zz}|_s SP_2(\cos \phi) \tag{1}$$

where the upper tilde denotes partially averaged quantities. In equation (1), ϕ is the angle between **n** and **B**. S is an orientational order parameter and represents the ensemble average of the orientational fluctuations of the micellar axes $M(\alpha, \beta, \gamma)$ with respect to the direction of **B**. $|\tilde{q}_{zz}|_s$ is the partially averaged component of the nuclear

quadrupole-electric field gradient interaction tensor measured parallel to **n** in a
perfectly ordered mesophase; it is given by

$$\tilde{q}_{zz} = \sum p_n \chi_n \{ S_{cc}^n + \tfrac{1}{3} \eta (S_{aa}^n - S_{bb}^n) \}, \tag{2}$$

where the S_{ij} are the elements of the Saupe ordering matrix for the principal axes
(a, b, c) of the nuclear quadrupole interaction tensor at the nth site which has
statistical weight p_n, $\chi_n = (e^2 qQ/h)_n$ is the corresponding quadrupole coupling con-
stant, and η_n is the asymmetry parameter. The actual values for χ_n and η_n, in addition
to being dependent upon the nucleus being observed, will vary from site to site and
thus will be determined by the detailed structure of the micelle.

The spectrum for a ^{2}H spin $(I = 1)$ in labelled water will be a symmetrical doublet
with separation

$$\Delta \tilde{v}(\phi) = \tfrac{3}{2} |\tilde{q}_{zz}|_s S P_2(\cos \phi), \tag{3}$$

with

$$|\tilde{q}_{zz}|_s = \langle P_2(\cos \alpha) \rangle_s \chi_D (x_A/x_w) n_b S_{OD}. \tag{4}$$

To transform equation (2) into (4) it has been assumed that all of the χ_n are identical
(χ_D) and that for water molecules not bound to the surface $|\tilde{q}_{zz}|_s = 0$. n_b is the number
of water molecules bound per molecule of amphiphile, x_a and x_w are the mole fractions
of amphiphile and water respectively and S_{OD} is an 'order parameter' which represents
the averaging due to the local reorientational motion of bound water molecules. The
quantity,

$$\langle P_2(\cos \alpha) \rangle_s = \langle \tfrac{3}{2} \cos^2 \alpha - \tfrac{1}{2} \rangle_s$$

where α is the angle between the normal to the surface and the symmetry axis of the
micelle and the angular brackets denote an average over the surface, accounts for the
diffusive motion of the molecule over the surface on the micelle. In contrast, the
spectrum for ^{133}Cs $(I = \tfrac{7}{2})$ consists of seven equally spaced lines of relative intensities
$7 : 12 : 15 : 16 : 15 : 12 : 7$ and with separation given by

$$\Delta \tilde{v}(\phi) = \tfrac{1}{14} |q_{zz}|_s S P_2(\cos \phi), \tag{5}$$

with

$$|q_{zz}|_s = \langle P_2(\cos \alpha) \rangle_s \chi_{Cs} \beta_{Cs}, \tag{6}$$

where β_{Cs} is the fraction of ions bound to the micelle. The field gradient at the caesium
nucleus is considered to arise from distortion of the symmetry of the hydration shell
[27], since $110 > (x_w/x_A) > 20$ over the entire nematic range. Furthermore, this
distortion and the surface coverage are assumed to be independent of the angle α.
Thus, a single value for χ_{Cs} obtains. The applicability of this model is established
elsewhere [25].

The ^{133}Cs and ^{2}H spectra observed on cooling a sample with $w = 0.500$ from the
N_D^+ to the L_D phase (figure 1) are shown in figure 2. The $\Delta \tilde{v}$ for ^{133}Cs are seen to be
an order of magnitude greater than those for ^{2}H. This is a consequence of the
difference in the values of the two quantities β_{Cs} (≈ 0.5) and $n_b S_{OD} x_A/x_w$ (≈ 0.004)
which appear in equations (4) and (6), respectively. Thus, ^{133}Cs N.M.R. offers an
improvement of an order of magnitude in the resolution of the spectra from the
coexisting N_D^+ and L_D phases. Moreover, $\Delta \tilde{v}$ for ^{133}Cs at T_{LN} increases on dilution,
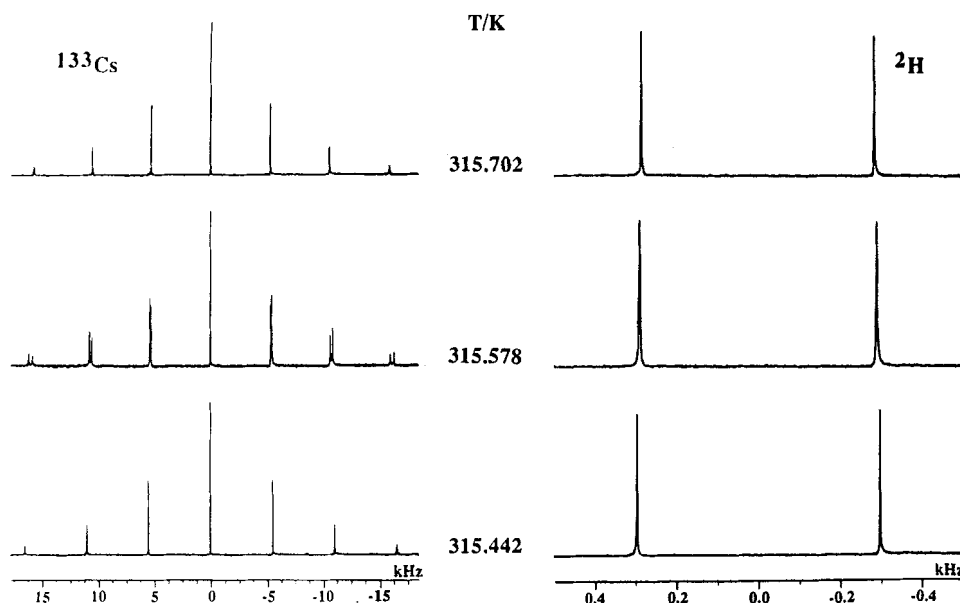
Figure 2. ^{133}Cs and ^{2}H N.M.R. spectra as observed on cooling the sample CsPFO/^{2}H$_2$O ($w = 0.500$) from the N$_D^+$ to the L$_D$ phase. The two distinct multiplets for the ^{133}Cs spectrum at 315·578 K indicate the presence of a mixed nematic/lamellar coexistence regime. In the ^{2}H spectrum a slight broadening of the doublet lines is the only indication of a mixed phase region.

in contrast to that for ^{2}H which decreases. The decrease in the latter is due to its dependence on the factor x_A/x_w, whilst the increase for ^{133}Cs is caused by the increasing value of $\langle P_2(\cos\alpha)\rangle$ [13].

T_{NL} and T_{LN} are obtained from the discontinuities in the temperature dependence of the quadrupole splittings at the nematic to lamellar transition as illustrated in figure 3. At the concentration w of 0·45 the gap $T_{NL}-T_{LN}$ is 20 mK and is at the limit of experimental resolution. At lower concentrations only a single discontinuity in the temperature dependence of the quadrupole splitting was observed. At these concentrations the transition is taken to be second order. The concentration ($w = 0.43$) of the tricritical point was located by plotting $T_{NL}-T_{LN}$ versus w and extrapolating to zero as shown in figure 4. The corresponding temperature (304·80 K) was read from the phase diagram in figure 1. Whilst the value obtained by this procedure may not be exact, it represents, at the very least, a good starting point for experimentalists using more sensitive techniques.

It is instructive to compare the variation with concentration w of the temperature gap for the I to N$_D^+$ transition with that for the N$_D^+$ to L$_D$ transition (figure 5). This is seen to be proportional to w for concentrations between 0·15 and 0·35. This result suggests that the transition is weakening on dilution and is very likely a consequence of the effect of dilution on the intermicellar interactions. On the basis of measurements of the quantity $T_{IN}-T^*$, where T^* is the extrapolated supercooling limit of the isotropic phase, it was at one time considered [20] that, at concentrations w close to 0·30, the transition might be approaching second order behaviour at a Landau point where the nematic phase crosses over from a uniaxial to a biaxial one. Such behaviour would require a transformation from a discotic to a rod shaped micelle. Clearly, this
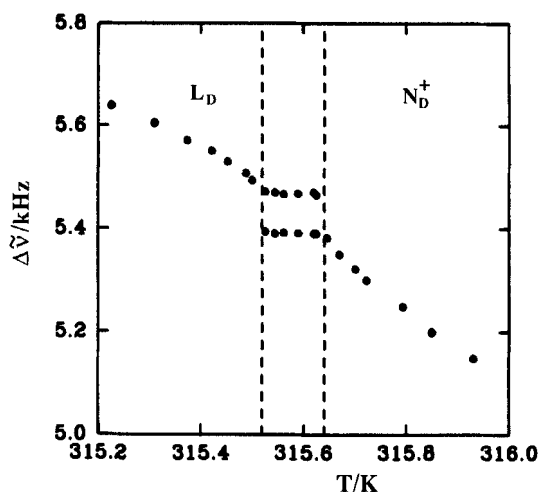
Figure 3.   Partially averaged ^{133}Cs quadrupole splittings $\Delta\tilde{v}$ as observed on cooling the sample CsPFO/^{2}H$_2$O ($w = 0.500$) from the N$_D^+$ to the L$_D$ phase. The temperatures of the upper and lower boundaries to the transition, T_{NL} and T_{LN}, are readily identified from the discontinuities in the $\Delta\tilde{v}$ versus temperature, T, curves.
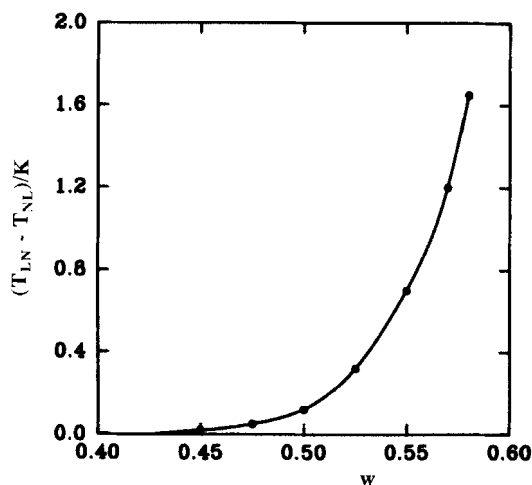

Figure 4.   Plot of the transition gap $T_{NL}-T_{LN}$ as a function of the weight fraction w of CsPFO in the system CsPFO/^{2}H$_2$O. $T_{NL}-T_{LN}$ appears to go to zero in the vicinity of $w = 0.43$ which is taken to be the location of the tricritical point T_{cp}.

does not occur at concentrations w above 0.15. It is, therefore, now of some importance to establish whether or not there is any change in the structure of the micelle at lower concentrations and, provided crystallization can be suppressed, to investigate the manner of the changes in the nature of the isotropic to nematic transition on dilution.

2.3. *The phase diagram of the CsPFO/H$_2$O system*

The phase diagram for this system has been established by ^{133}Cs N.M.R. The full details of this study are to be presented elsewhere. Qualitatively, the diagram is the
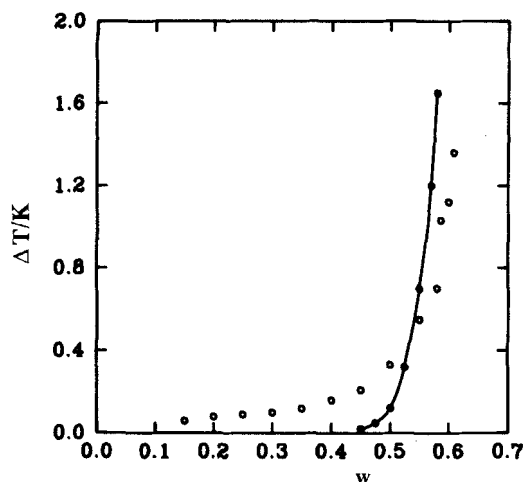
Figure 5. Comparison of the transition gaps $T_{NL}-T_{LN}$ (closed circles) and $T_{IN}-T_{NI}$ (open circles) as a function of the weight fraction w of CsPFO in the system CsPFO/^{2}H$_2$O.

Fixed points at standard pressure in the phase diagrams of the CsPFO/H$_2$O and CsPFO/^{2}H$_2$O systems

CsPFO/^{2}H$_2$O	T/K	w	ϕ	c/mol dm^{-3}	x
T_p(I, N, L)	351·23				
Isotropic		0·626	0·419	1·946	0·0578
Nematic		0·632	0·426	1·975	0·0592
Lamellar		0·648	0·443	2·054	0·0632
T_p(I, N, C)	285·29				
Isotropic		0·221	0·111	0·510	0·0103
Nematic		0·225	0·114	0·520	0·0105
T_p(HI, I, C)	275·8				
Isotropic		0·011	0·0049	0·0224	0·00041
T_p^*(N, L, C)	285·72				
Nematic = lamellar		0·287	0·151	0·691	0·0145
K_p	278·5	0·014	0·0062	0·029	0·00052
T_f (heavy ice)	276·95				
T_{cp}	304·80	0·43	0·25	1·14	0·027
CsPFO/H$_2$O					
T_p(I, N, L)	342·72				
Isotropic		0·628	0·398	1·821	0·0527
Nematic		0·632	0·402	1·840	0·0536
Lamellar		0·644	0·414	1·897	0·0563
T_p(I, N, C)	281·31				
Isotropic		0·233	0·108	0·496	0·00992
Nematic		0·235	0·109	0·501	0·0100
T_p(Ice, I, C)	272·0				
Isotropic		0·009	0·0036	0·016	0·0003
T_p^*(N, L, C)	281·7				
Nematic = lamellar		0·302	0·148	0·675	0·0141
K_p	274·0	0·013	0·0052	0·024	0·00043
T_f (heavy ice)	273·15				
T_{cp}	302·05	0·46	0·25	1·16	0·027

same as that for the $CsPFO/^2H_2O$ system. The quantitative differences can be seen by comparing the values of the fixed points as summarised in the table. The main effect of changing from H_2O to ^2H_2O is to raise the temperature of the L_D to N_D^+ and the N_D^+ to I transitions by approximately 3 K at the volume fraction $\phi = 0\cdot1$ and by 1 K at $\phi = 0\cdot4$. For both systems the tricritical point occurs at $\phi = 0\cdot25$; the temperature of this point is $2\cdot75$ K higher for the ^2H_2O system.

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