Nuclear Magnetic Resonance of Aqueous Solutions of Alkylpolyoxyethylene Glycol Monoethers

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Increasing the concentration of alkylpolyoxyethylene glycol monoethers in water results in an upfield shift of the water proton signal and a decrease in the longitudinal relaxation time. These effects have been discussed in terms of perturbation of the hydrogen-bonded solvent structure. Variable temperature experiments have revealed no discontinuities in the temperature coefficient of either the water chemical shift or the relaxation time in passing from the mesomorphic phase state to isotropic solution. The change in the chemical shift at phase boundaries has been shown to be associated with long-range order in the mesomorphic phases. It is concluded that in these systems the extent of motion and hydrogen bonding of the water molecules is independent of the nature of the phase, and determined only by the temperature and composition of the system.

Although other physical methods have been extensively applied to the investigation of surface-active agents in water, there have been relatively few studies using nuclear magnetic resonance (n.m.r.) techniques. The behaviour of the water resonance in dilute solutions of ionic surface-active agents has been investigated by Clifford and Pethica,[1,2] and the effect of micellization on the solute signals in aromatic [3,4] and partially fluorinated [5] materials has also been described. A study of the lyotropic mesophases given by surface-active agents with water and D_2O has been made by Flautt and Lawson.[6] The present study is concerned with the behaviour of the n.m.r. signals in aqueous systems of some non-ionic surface-active agents, the n-alkylpolyoxyethylene glycol monoethers (C_xE_y), in both the isotropic micellar solution and mesomorphic phase states.

EXPERIMENTAL

MATERIALS

The n-alkylpolyoxyethylene glycol monoethers C_xE_y were prepared and purified by the methods previously described.[7] The terminally methylated compounds $C_xE_yC_1$ were prepared by reaction of the appropriate monoether with thionyl chloride followed by condensation with sodium methoxide in methanol solution. These materials were purified by chromatography on silica gel using chloroform+acetone mixtures as eluents, followed by vacuum-distillation.

SAMPLE PREPARATION

Either doubly distilled water or I.C.I. 99·7 % D_2O was used for sample preparation. Samples were made up by weight and mixed at a temperature at which an isotropic fluid was formed. They were either prepared directly in 5 mm ext. diam. Varian sample tubes or introduced by suction into 1 mm ext. diam. Pyrex capillary tubes. After sealing, the capillaries were mounted concentrically inside Varian tubes by two Teflon bushes.

For relaxation time measurements, samples were made up on a vacuum line. After de-oxygenation by repeated freeze-thaw cycles, the water was distilled into a Varian sample tube containing a known quantity of solute, de-oxygenated in a similar fashion. The composition of these samples was checked by integration of the n.m.r. spectra. The criterion for effective de-oxygenation of the water was a relaxation time of greater than 4 sec at 30°C.

N.M.R. MEASUREMENTS

The n.m.r. measurements were obtained using a Varian DA60 system (external proton lock) operating at 60 Mc/sec. All chemical shifts are quoted in parts per million *downfield* of tetramethylsilane (TMS). As TMS altered the positions of the mesomorphic phase boundaries, the resonance of the terminal methyl group of the alkyl chain was adopted as an internal reference. In those regions in which mesomorphic phases were not formed, the separation between this signal and the TMS resonance was, in common with other systems,[8] independent of both temperature and composition. Chemical shifts for capillary tube samples were determined relative to external TMS+CCl_4 (2 %) contained in the annulus between the capillary and Varian sample tube. The bulk susceptibility correction for this system was experimentally determined by measurements of the terminal chain methyl group resonances. It was 0·017 p.p.m. at all temperatures of observation. Using the external field lock and pre-calibrated chart paper, the accuracy (500 c/sec scale) is within ±0·008 p.p.m.

The spin-lattice (longitudinal) relaxation times T_1 were determined from the signal behaviour after saturation or adiabatic rapid passage, to an accuracy of ±100 msec. In all cases, the signal changes were simple exponential functions of the time.

The standard temperature control system was modified by the addition of an automatic heater power control which kept the gas stream around the sample at a constant chosen temperature. The relationship between the sample and gas stream temperature was determined by inserting a calibrated thermistor into a spinning liquid sample. The system enabled temperatures to be selected and maintained to ±0·1°C in the range 15-90°C.

X-RAY MEASUREMENTS

The capillary tube samples used in the n.m.r. measurements were examined by low-angle X-ray diffraction using the evacuated flat-plate camera described previously.[9]

RESULTS

CHEMICAL SHIFTS

ISOTROPIC SOLUTIONS

The spectra of C_8E_6 in D_2O (33 % w/w, 32°C) and C_8E_6 itself are shown in fig. 1 together with an assignment of the various signals. Those originating from the polyoxyethylene head group (EO) were assigned by comparison with the spectrum of C_8E_3 and triethylene glycol. The spectra of the other C_xE_y compounds are similar. The $C_xE_yC_1$ spectra have an additional signal ~0·1 p.p.m. upfield of the EO signal group due to the methoxyl protons. In all these compounds in aqueous solution, the alkyl chain shifts are independent of concentration, whereas the water proton signal shows a shift variation over 1 p.p.m. and the EO signals show a smaller, but significant (~0·13 p.p.m.) change. In fig. 2 the shift of the water proton signals for C_8E_3, C_8E_6 and $C_8E_6C_1$ and in fig. 3 the EO group signals of C_8E_6 are shown as functions of the mole fraction of the solute species. The initial slopes of the water proton shift curves for a number of these compounds are given in table 1.

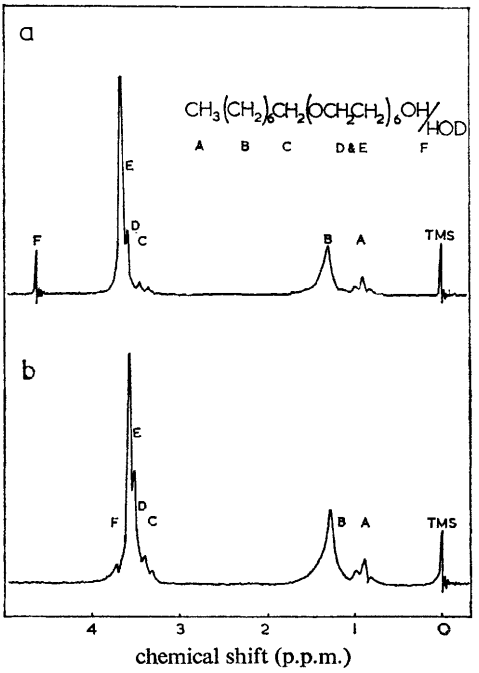

FIG. 1.—Spectra of (*a*) 33 % w/w C_8E_6 in D_2O and (*b*) pure C_8E_6, at 32C°.

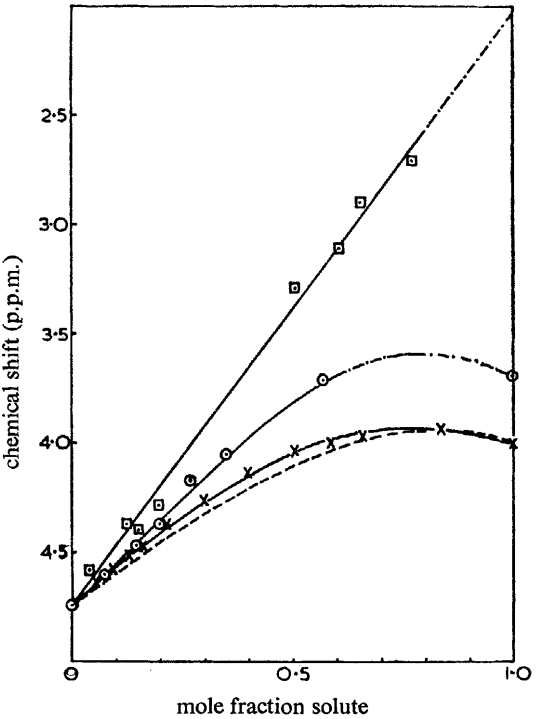

FIG. 2.—Chemical shift of the water protons in solutions of $C_8E_6C_1$, ⊡; C_8E_6, ⊙; C_8E_3, ×, at 32°C. The calculated relationship for C_8E_3 is shown by the broken curve.

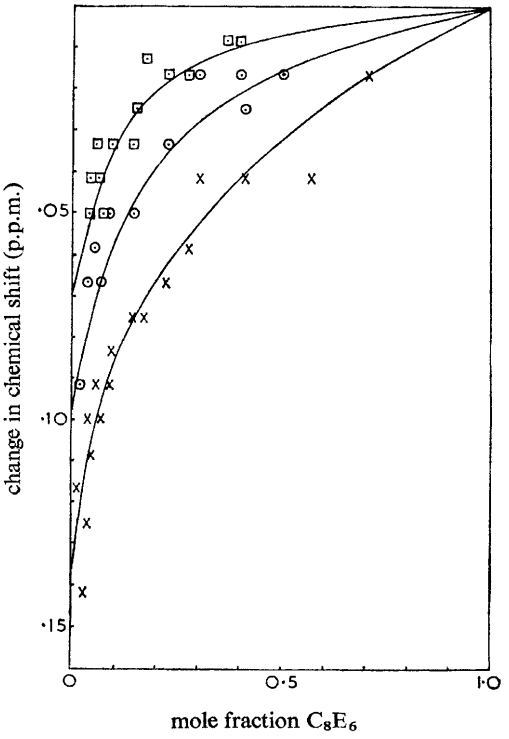

FIG. 3.—Chemical shifts of the ethoxide chain signals for C_8E_6 in water, relative to the values in pure C_8E_6, (C), ⊡; (D), ⊙; (E), × of fig. 1 at 32°C.

TABLE 1.—SLOPES (p.p.m./unit mole fraction) FOR INITIAL LINEAR PORTIONS OF CHEMICAL SHIFT-CONCENTRATION CURVES (±0·08)

	alkyl chain length			
head group	C_6	C_8	C_{10}	C_{12}
E_3	1·63	1·52	—	—
E_3C_1	—	1·92	—	—
E_6	2·07	2·02	1·92	2·00
E_6C_1	—	2·72	2·85	—

MESOMORPHIC PHASES

In both the middle and neat mesophases given by the $C_{12}E_6+H_2O$ system* only one signal, arising from the water protons, is observed under high resolution conditions. In the 5 mm tubes, the signals appeared to contain several overlapping components with a total width at half-height of 5-15 c/sec., depending in no obvious way upon the thermal and mechanical history of the sample. With capillary samples, much more reproducible behaviour was observed, with a clear correlation between the sample treatment and the n.m.r. spectra.

The capillary samples were cooled slowly (0·5°C/h) from the isotropic region into the appropriate mesomorphic phase state at room temperature (20°C). The n.m.r. water signal and corresponding X-ray pattern for a neat phase sample are

* For phase diagram, see fig. 1, *Trans. Faraday Soc.*, 1969, **65**, 287.

shown in fig. 4*a*. The annealed samples were then centrifuged back and forth in the capillary tube (5,000 ***g***) and the n.m.r. and X-ray determinations repeated. The results of this treatment are shown in fig. 4*b* for the same sample. Qualitatively similar results were obtained from middle phase samples. In all cases the annealed samples gave oriented X-ray diffraction patterns and n.m.r. signals that were narrower and further downfield than those from the centrifuged samples, which showed no preferred orientation.

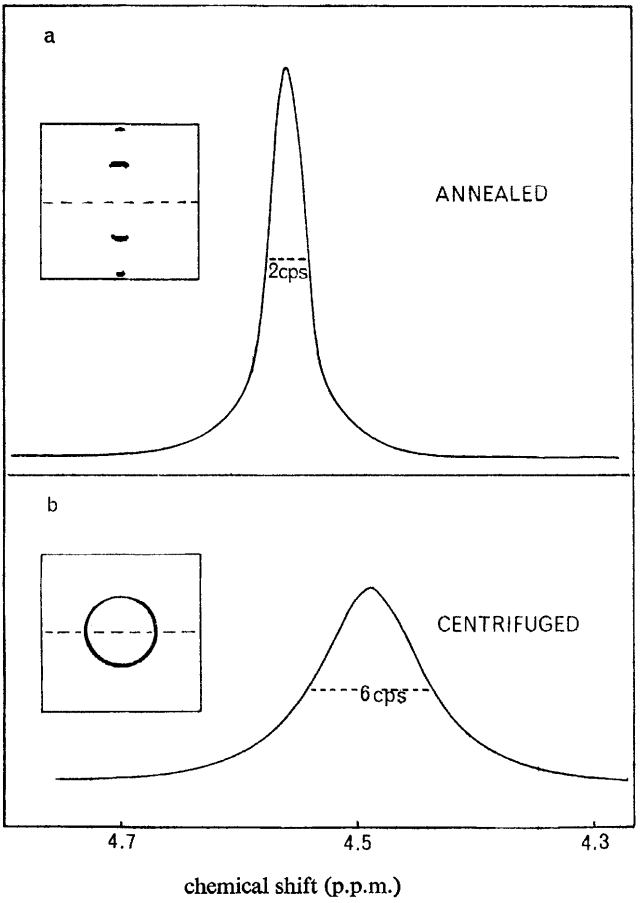

FIG. 4.—Water signals and X-ray diffraction patterns (schematic inset) for $C_{12}E_6+H_2O$ neat phase (72 % w/w) at 32°C. (*a*), annealed sample, (*b*), centrifuged sample.

The position of the water signal is strongly temperature dependent, moving upfield with increasing temperature, irrespective of the phase and its treatment. At the mesophase/isotropic phase boundaries discontinuities in the shift against temperature curves are observed, large for the annealed samples, small for the centrifuged samples. Typical results for neat and middle phases are shown in fig. 5. As the transition region is approached a second water signal appears and grows in intensity, accompanied by the signals characteristic of the solute (fig. 6). The temperature range in which a double water signal is observed corresponds to the two phase co-existence region in the binary phase diagram.

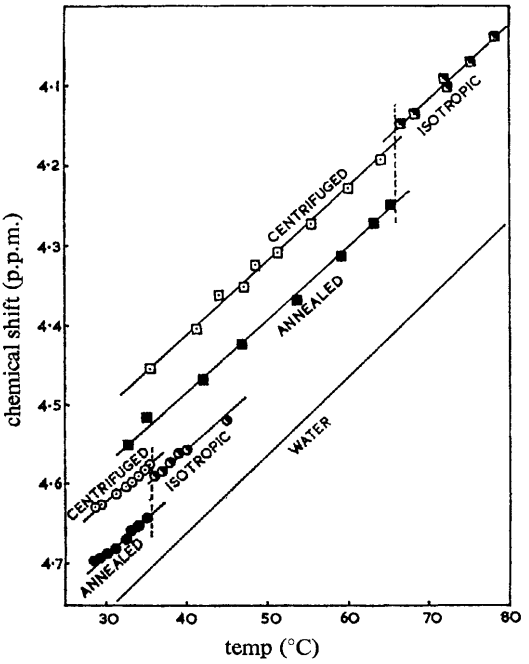

FIG. 5.—Temperature dependence of the water chemical shift in the $C_{12}E_6+H_2O$ system. 72 % w/w $C_{12}E_6$: neat, ⊡, ■; isotropic, ◹. 45 % w/w $C_{12}E_6$: middle, ⊙, ●; isotropic, ◑. The dependence for water is shown by the solid line. Transition temperatures are indicated by vertical broken lines.

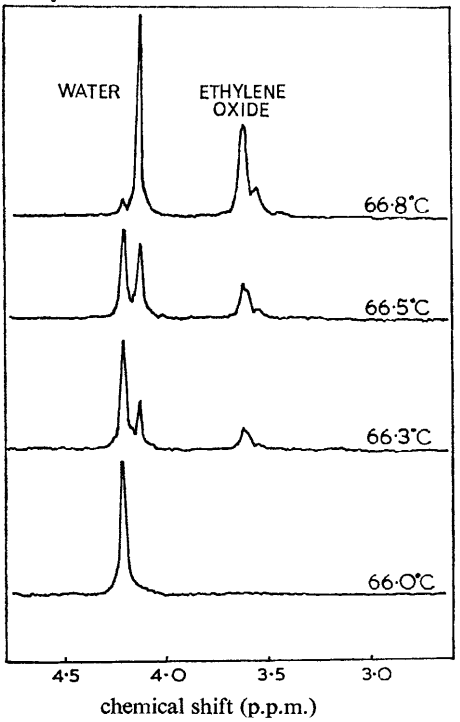

FIG. 6.—Spectra of a 72 % w/w $C_{12}E_6+H_2O$ sample in the neat to isotropic phase transition region.

RELAXATION TIMES

The water signal intensities from capillary samples were too small to give accurate data and measurements of T_1 were conducted on samples in 5 mm tubes. The results obtained were independent of the sample treatment, although the line shapes were extremely variable. In fig. 7, log T_1 is shown as a function of the reciprocal temperature ($1/T$) for neat and middle phase samples and for pure water. The transition temperatures for the mesomorphic phases are marked with dotted lines. There are no detectable discontinuities in the relaxation times on passing from the mesomorphic to the fluid isotropic states.

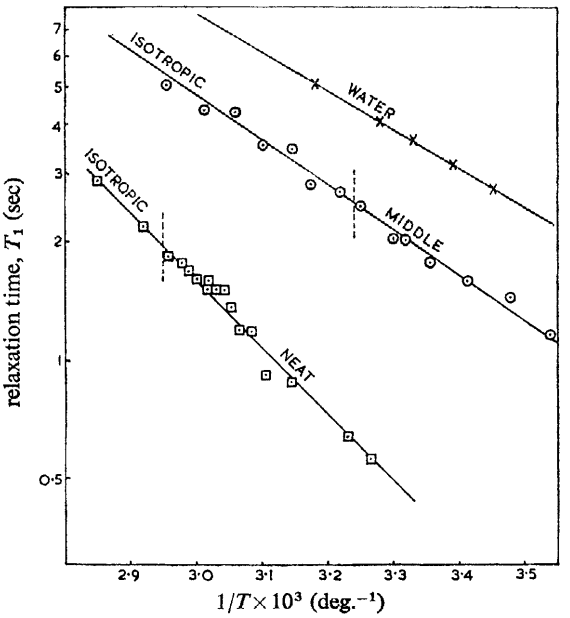

FIG. 7.—The temperature dependence of the water proton relaxation time T_1 in the $C_{12}E_6$+H_2O system: water, ×; 45 % w/w $C_{12}E_6$, ⊙; 72 % w/w $C_{12}E_6$, ⊡. The transition temperatures are indicated by the broken lines.

DISCUSSION

ISOTROPIC SOLUTIONS

In hydrogen-bonded systems, the chemical shift of the protons involved is generally downfield with respect to the unassociated species.[10] For water, the difference in shift between the liquid and vapour states has been determined to be 4·66 p.p.m. at 0°C.[11] The introduction of solute molecules into water leads to two effects, the disruption of water-water hydrogen bonds and the establishment of solute-solvent interaction. The effect on the chemical shift of the water protons is usually an upfield change relative to the pure liquid, even with many ionic solutes.[12] Although the energy of interaction of the solute with the solvent may be greater than that of the solvent hydrogen bond, the observed chemical shift change appears to be dominated by the extent of hydrogen-bond disruption. For a solute in which chemical exchange of protons can take place with the solvent, the chemical shift will be further modified. If the exchange is rapid, a single signal will be observed at a position determined by the solute and solvent shifts in the absence of exchange and the relative proportions of the sites available for exchange.

In the $C_xE_yC_1$ systems, where there is no solute-solvent proton exchange, there is an approximately linear upfield shift of the water signal with increasing solute concentration (fig. 2). For $C_6E_6C_1$ and $C_8E_6C_1$ total water shifts are 2·9 p.p.m. and 2·7 p.p.m. respectively, which are comparable with the value of 2·6 p.p.m. obtained by Satake *et al.*[13] for water in dioxane. In both the C_xE_y and $C_xE_yC_1$ systems the methylene protons of the head group have chemical shifts that are dependent on composition (fig. 3) indicating that the electron distributions around the ether oxygens are perturbed by interaction with the water. The results for the $C_xE_yC_1$ series are thus due to progressive replacement of water-water hydrogen bonds by water-ether oxygen interactions that involve a smaller change in chemical shift relative to unassociated solvent.

The results for the C_xE_y compounds may be analyzed on the basis of chemical exchange between the terminal OH-proton and water which has already undergone hydrogen bonding changes due to the presence of the solute. Chemical exchange leads to a single signal of chemical shift $\bar{\delta}$ given by

$$\bar{\delta} = [\delta_s x+2\delta_w(1-x)]/[2-x], \tag{1}$$

where x is the solute mole fraction and δ_s and δ_w are the solute and water chemical shifts in the absence of exchange. The data for the $C_xE_yC_1$ series suggest a linear change in the water chemical shift, hence, approximately

$$\delta_w = \delta_w^\circ - \alpha x, \tag{2}$$

where δ_w° refers to pure water and α is a constant. The effect of composition on δ_s is difficult to assess, but the results of Gillberg and Ekwall [14] for the decanol+water system suggest that, in the absence of exchange, the decanol OH-proton shift is nearly independent of composition, hence δ_s has been taken as a constant δ_s°, the value for pure solute. On combining these assumptions with (1) we obtain

$$\bar{\delta} = [2\delta_w^\circ+(\delta_s^\circ-2(\alpha+\delta_w^\circ))x+2\alpha x^2]/[2-x]. \tag{3}$$

The gradient of this curve as x approaches zero is given by

$$g = 0{\cdot}5(\delta_s^\circ-\delta_w^\circ)-\alpha. \tag{4}$$

Both δ_w° and δ_s° can be accurately determined but α obtained from eqn. (4) is less exact as the initial gradient g is difficult to estimate. Insertion of the appropriate values of δ_w° and δ_s° (fig. 2) and α obtained from g (table 1) into eqn. (3) for the C_8E_3+ water system leads to

$$\bar{\delta} = [9{\cdot}48-7{\cdot}78x+2{\cdot}30x^2]/[2-x]. \tag{5}$$

The agreement between the calculated relationship for $\bar{\delta}$, shown as a broken curve in fig. 2, and the observed relationship is reasonable in view of the simplified nature of the treatment, the maximum discrepancy being 0·06 p.p.m. at $x = 0{\cdot}5$. Similar agreement has been obtained for the other systems studied, although with the C_xE_6 compounds the coincidence of the solvent and head group signals in the region of the maximum upfield shifts prevents a complete comparison.

In this investigation the minimum concentrations were well in excess of the respective critical micelle concentrations, hence all data refer to solute in the micellar state. For the same head group, the chemical shift curves were superimposable and thus independent of the alkyl chain length as reflected by the data given in table 1. It has been suggested that the hydrophobic chain adjacent to the head group may still be in contact with the solvent in the micellar state.[5] Our results indicate that the amount of water involved is independent of chain length, at least above C_6. The increase in the magnitude of g in passing from the E_3 to the E_6 series reflects

the greater solvent perturbation due to the larger head group. The replacement of the hydroxyl by the methoxyl group (E_y to E_yC_1) also leads to an increase in g, due more to the removal of the hydroxyl group, with its associated downfield shift effect, as for hydrogen peroxide [15] and alcohols [1] than to any intrinsic disruptive effect of the methyl group.

The decrease in longitudinal relaxation time T_1 with increasing solute concentration at a given temperature may be attributed to the restriction of the solvent motion in the vicinity of the head groups (fig. 7). The increase in the temperature coefficient of T_1 with increasing solute concentration implies that the micro-viscosity in the region of the head groups decreases more rapidly with temperature than in water itself. In contrast, the temperature coefficient of chemical shift is only weakly dependent upon solute concentration (fig. 5) showing that the thermal disruption of water-water hydrogen bonds is scarcely affected by the presence of solute.

MESOMORPHIC PHASES

In the mesomorphic state, the signals characteristic of the solute are too broad to be observed under high-resolution conditions. We may attribute this to a decrease in the extent of motion of the solute molecules relative to the isotropic solution on the formation of the mesophase.[6] The solvent resonance, however, remains similar to that observed in the fluid isotropic state and therefore appears to retain a similar degree of mobility (fig. 6). The double signal observed in the two-phase region indicates that chemical exchange between the co-existing phases is slow. Both line width and δ for water in the mesomorphic phases depend upon the method of preparation of the sample and are clearly correlated with the ordering indicated by the X-ray diffraction data (fig. 4). The diffraction photographs of the slowly cooled mesomorphic phase samples exhibit equatorially disposed arcs. The structure of neat phase is lamellar,[16, 17] consisting of bimolecular sheets of surface-active molecules separated by the solvent, with the head groups oriented towards the solvent. The sharp diffraction spots arise from lamellae arranged parallel to the capillary walls. The effect of centrifugation is to produce a continuous diffraction ring with the same characteristic spacing, corresponding to a random arrangement of the lamellae. In neat phase the long axes of the solute molecules are essentially normal to the lamellar plane, hence in the ordered samples, these will be oriented perpendicularly to the capillary axis. Thus, in an orthogonal co-ordinate system, if we take the static magnetic field to be directed in the Z-direction, and the capillary axis to be the Y-direction, then the solute long axes lie in the XZ plane. For annealed middle phase the axes of the cylindrical colloid units, arranged in a two-dimensional hexagonal array,[16, 17] show a preferential alignment parallel to the capillary axis. The EO head groups, as in the ordered neat phase, lie in the XZ plane.

The effect of the anisotropy of one molecular species upon the chemical shift of another has been discussed in terms of the variation in the local magnetic field around the anisotropic species due to the anisotropy of its magnetic susceptibility.[18, 19] In general, a rod-like magnetically anisotropic molecule lying parallel to the magnetic field direction induces a downfield shift for the nuclei of a small molecule close to it. In the vicinity of the EO head group the water molecules are in an anisotropic environment and hence the chemical shift will be dependent upon the relative directions of the magnetic field, the axis of the EO group and the position vector of the water molecule with respect to the head group. In a macroscopic sample, there will be exchange of the solvent protons between the various solute sites, in particular between the EO head group region and the interlamellar fluid. The resonance position will thus be determined by the weighted mean of the various site shifts, provided exchange

is sufficiently rapid. In the oriented samples there will be a relative deficiency of EO groups arrayed in the *Y*-direction and hence the anisotropy effect upon the chemical shift of the water close to the head groups will be different from that in a sample in which the EO groups take up all directions. The shift discontinuity in passing from the isotropic solution to the centrifuged mesophases varies in a random fashion between $\pm 0{\cdot}01$ p.p.m., whereas the discontinuity for the ordered samples is much larger ($\sim 0{\cdot}07$ p.p.m.) and is consistently downfield (fig. 5). The slight variability of the results for the centrifuged specimens is probably due to incomplete disorientation.

We may conclude that in the absence of orientation effects the chemical shift-temperature relationship is a continuous function. The temperature coefficient of chemical shift is independent of the nature of the phase, indicating that hydrogen bonding undergoes no radical change with phase transition. The longitudinal relaxation time T_1 is also a continuous function of the temperature (fig. 7), showing the mobility of the water molecules to be independent of phase structure.

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