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Order of Polyoxyethylene Chains in the Lamellar Phase of a Nonionic Surfactant

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Order of Polyoxyethylene Chains in the Lamellar Phase of a Nonionic Surfactant

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Lamellar samples of aqueous tetraethylene glycol *n*-dodecyl ether in varying degrees of selective deuteration were studied by ^2H NMR spectroscopy. Order parameter profiles for both the alkyl and oxyethylene head group chain have been obtained. A maximum in the order of the surfactant molecules was found to occur 3–4 methylene segments from the alkyl/headgroup interface on the alkyl chain. Order decreased rapidly with position on either side of this region giving an approximately symmetrical profile.

INTRODUCTION

Nonionic surfactants of the type represented by tetraethylene glycol *n*-dodecyl ether ($C_{12}EO_4$) have been shown[1] to incorporate large amounts of hydrocarbons into their aqueous lamellar phase. This is in contrast to ionic surfactants[2] and phospholipids[3] which have a more limited (ca. 6% w/w) solubilization capacity for such oils. The inherent interest in such systems has recently[4–6] led to the use of ^2H NMR spectroscopy to investigate the dynamic order of solubilized molecules in these systems. Information was obtained using deuterated oil molecules; hence, any deduction about the perturbations induced in the amphiphile molecules by the presence of the solubil-

izate molecules were necessarily inferred indirectly. This prompted a program to investigate the amhiphile behaviour directly by use of selectively deuterated analogues of $C_{12}EO_4$ to obtain a complete order parameter-chain position profile. Many such studies have been made[7-10] of amphiphiles with charged headgroups, but to the best of knowledge the data presented here represents the first complete profile for a nonionic lyotropic liquid crystal system.

EXPERIMENTAL

The perdeuterated surfactants were synthesized from $C_{12}D_{25}OH$ (Cambridge Isotopes ltd.) and monochloroacetic acid followed by methanolysis of the acid and reduction of the methyl ester by $LiAlH_4$ to yield the monoethylene glycol derivative. The reactions were repeated on the mono-, di- and triethylene glycol derivatives to ultimately yield the desired compound. In the case of the selectively deuterated headgroup compounds the same procedures were adopted except using $C_{12}H_{25}OH$ and $ClCD_2CO_2H$ and reductions with $LiAlD_4$. Analysis by GLC and NMR methods indicated purities >98%.

^2H NMR spectra were recorded using a JEOL FX90Q multinuclear Fourier Transform spectrometer operating at a resonance frequency of 13.7 MHz. Sweep widths of up to 40 KHz were used and between 10^3 and 10^4 transients averaged. All spectra were recorded at 298 K in standard 10 mm (o.d.) NMR tubes with a coaxial tube containing the lithium lock material.

Samples were prepared as described previously[5] by thorough mixing and centrifugation and checking sample homogeneity with crossed polarizers.

RESULTS AND DISCUSSION

The order parameter for the C—D bonds, S_i, is related to the observed quadrupolar splitting, $\Delta\nu$, in unoriented lamellar dispersions as

$$\Delta\nu = \frac{3}{4}\chi|S_i| \qquad (1)$$

where χ is the quadrupolar coupling constant with a value of 167 KHz[11] for CD_2 groups in alkyl chains. A plot of order parameter for all 20 carbon positions is shown in Figure 1, with the structure and

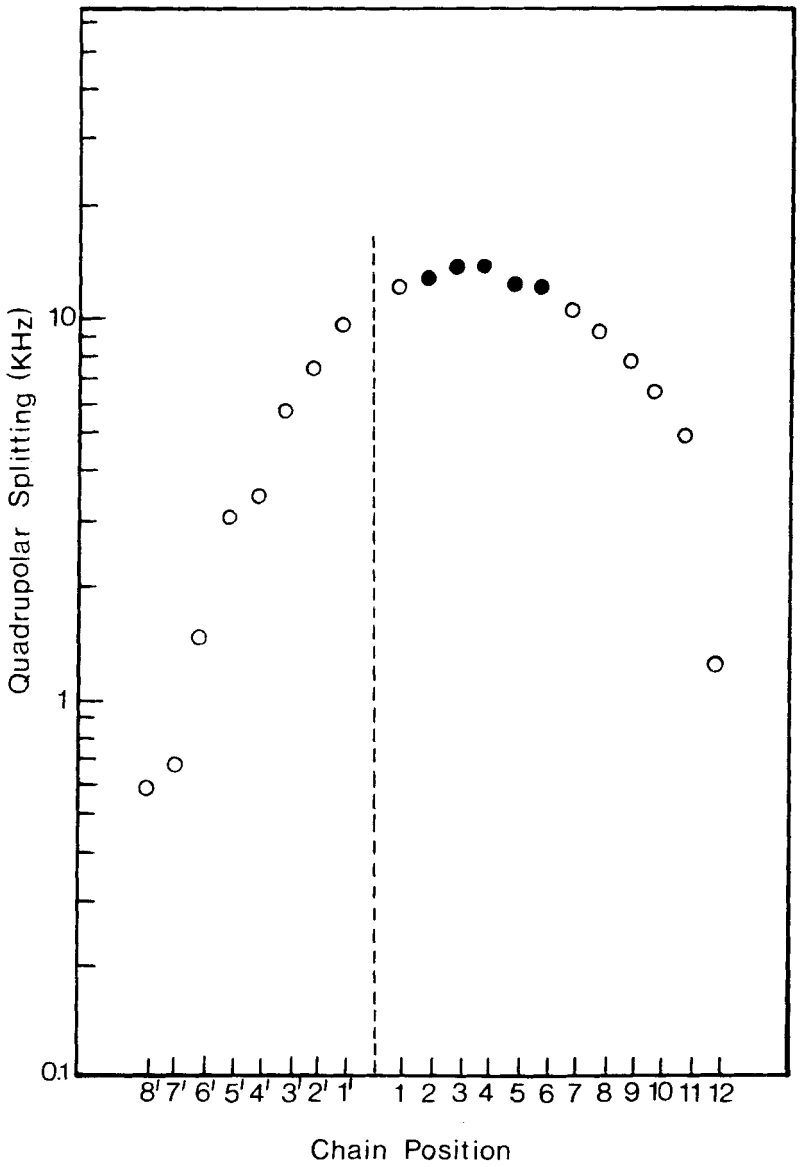
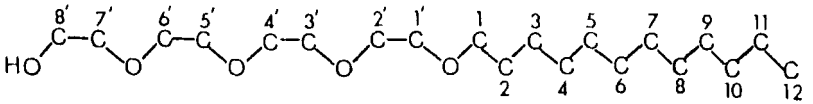


FIGURE 1 Order Profile for tetraethylene glycol *n*-dodecyl ether in the aqueous lamellar phase (60:40 w/w surfactant/water) at 298 K in terms of quadrupole splittings. Filled symbols refer to positions not uniquely assigned.



tetraethylene n-dodecyl glycol ether

FIGURE 2 Numbering system adopted for the surfactant.

numbering shown in Figure 2. Positions 4–6 have not been uniquely assigned, but the variation of S_i in this region is relatively small (ca. 10%) and does not significantly affect the shape of the profile. It can be seen that the 1-position is not the most ordered as found in charged surfactant systems e.g. the potassium laurate/water system[7] where there is a strong electrostatic interaction at the micelle/solvent interface. In this respect, the alkyl chain profile of $C_{12}EO_4$ behaves similarly to charged systems with flexible interfaces.[12–14] The data presented here is for a sample with area/amphiphile in the bilayer surface of 43 Å^2; comparison with S_i values observed in the potassium laurate/water system[7] at a comparable area/amphiphile shows that they are similar for both systems. This implies that the packing and alkyl chain disorder inside the $C_{12}EO_4$ bilayers is essentially the same as that found in ionic systems.

Consideration of the profile of the tetraoxyethylene headgroup chains shows a rapid monotonic decrease in S_i on passing from the headgroup/alkyl chain interface to the terminal oxyethylene group (Figure 1). In fact the rate of decrease is greater than that seen in the 6–12 portion of the alkyl chain ranging from ca. 10 KHz to ca. 0.5 KHz for the 8′-position. About 50% of the observed decrease has occurred within the first two oxyethylene groups next to the alkyl chain (positions 1′ through 4′). The number of molecular conformations accessible to the chain as it projects into the aqueous interlamellar layer is high and the approximately exponential decrease is that expected for a free chain.[14] The profile observed overall is that expected for a continuous chain molecule which is maximally constrained near its center of gravity with terminal segments experiencing a high degree of rotational disorder.

A calculation of the average molecular length of the surfactant molecule, $\langle L \rangle$, can be made[15] using the relationship

$$\langle L \rangle = 1.25\,(n - 0.5\Sigma\, P_{ib}$$

where

$$P_{ib} = (1 - S_{mol})/1.125$$

and $S_{mol} = -2\ S_{CD}$ for methylene groups or $-3S_{CD}$ for methyl groups. S_{CD} is the order parameter derived from the observed quadrupolar splitting (Eq. [1]).

The present example gives $\langle L \rangle$ of 22.5 Å, if the 4 C—O—C distances of 2.476 Å are included, predicting a lamellar bilayer thickness of 45 Å. Previous X-ray data[1] indicates a bilayer thickness of 32.5 Å. The difference between these values may be a consequence of either the axis of the surfactant molecules being tilted at an average angle of ca. 42° with respect to the director or that a proportion of the tetraoxyethylene chain should not be included in the calculation. There is some evidence for the first of these possibilities from the X-ray data[1] and from the compositional dependence of the order of *n*-alkanes solubilized in this system.[4-6] A calculation using only the order parameters of the alkyl chain would give a thickness of 14.6 Å which is clearly too small to be consistent with the X-ray determination.

CONCLUSION

The order profile of $C_{12}EO_4$ molecules in the lamellar phase is consistent with that of a continuous chain with essentially freely moving ends. Packing constraints limit both cis-trans isomerizations and molecular fluctuations with respect to the director producing maximum ordering in the 3–5 positions of the alkyl chains. The methylene segment adjacent to the alkyl/oxyethylene chain junction is not, therefore, the most ordered position. This observation is in line with the view that the bilayer interface in these systems is highly flexible which may be the origin of their enhanced solubilizing power.

References

1. N. Moucharafieh, S. E. Friberg and D. W. Larsen, *Mol. Cryst. Liq. Cryst.*, **53**, 189 (1979).
2. P. Ekwall, *Adv. Liq. Cryst.*, **1**, 1 (1975).
3. S. H. White, *Ann. N. Y. Acad. Sci.*, **303**, 273.
4. A. J. I. Ward, S. E. Friberg, D. W. Larsen and S. B. Rananavare, *J. Phys. Chem.*, **88**, 286 (1984).
5. A. J. I. Ward, S. E. Friberg and D. W. Larsen, ACS Symposium Series #272, *American Chem. Soc.*, Washington, D.C., (1983).
6. A. J. I. Ward, S. E. Friberg, D. W. Larsen and S. B. Rananavare, *Langmuir*, **1**, 24 (1985).
7. B. Mely, J. Charvolin and P. Keller, *Chem. Phys. Lipids*, **15**, 161 (1975).
8. J. Seelig, *Prog. Colloid Polym. Sci.*, **65**, 172 (1978).
9. N. Boden, P. Jackson, Y. K. Levine and A. J. I. Ward, *Chem. Phys. Lett.*, **37**, 100 (1976).

10. J. Charvolin and B. Mely in "Magnetic Resonance in Colloid and Interface Science," H. A. Resing & C. G. Wade, Eds.; ACS Symposium Series 34: American Chem. Soc., Washington, D.C., 1976.
11. L. J. Burnett and B. M. Muller, *J. Chem. Phys.*, **55**, 5829 (1971).
12. T. Klason and U. Henriksson in "Solution Behaviour of Surfactants," Vol. 1 (Eds. K. L. Mittal and E. J. Fendler), Plenum Press, 1982.
13. W. Niederberger and J. Seelig, *Ber. Bunsenges. Physik. Chem.*, **78**, 947 (1974).
14. P. Bothorel, J. Belle and B. Lemaire, *Chem. Phys. Lipids.*, **12**, 161 (1975).
15. J. Seelig, *Quart. Rev. Biophys.*, **10**, 353 (1977) and references cited therein.