A nuclear magnetic resonance (nmr) investigation of the micellar structure of a long-chain non-ionic surfactant

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Peak integrals, peak widths at half-height ($\Delta\nu_{\frac{1}{2}}$), spin-lattice relaxation times (T_1), and chemical shifts (δ) of the alkyl and oxyethylene protons of $CH_3(CH_2)_{21}[OCH_2CH_2]_{27}OH$ ($C_{22}E_{27}$) were measured in D_2O at various temperatures. The peak integrals, $\Delta\nu_{\frac{1}{2}}$, and δ values of the alkyl protons showed a large dependence on temperature below 313K, while the values for the oxyethylene protons were unaffected by temperature. These observations were explained by considering an intrusion of some oxyethylene groups into the hydrocarbon core of the micelle.

The liquid nature of the micellar core of a variety of surfactants has been demonstrated by several workers using different techniques e.g. Wishnia (1963), Clemett (1970), Kalyansundaram & Thomas (1976), Harada & Nakagawa (1979), Vikingstad (1979), and Yoshioka (1979). A liquid state of the core is necessary to account for the wide variety of hydrocarbon additives that can be solubilized by ionic and non-ionic micelles. In non-ionic surfactants containing a long hydrophobic component, the liquid state of the core may be maintained by the depression of the melting point resulting from the intrusion of some of the oxyethylene groups into the core. The presence of a mixed hydrocarbon–oxyethylene region has been previously suggested by Arnarson & Elworthy (1980, 1981, 1982) and by Elworthy & Patel (1982, 1984) to explain some anomalous properties of long chain non-ionic surfactants. From viscosity data, Elworthy & Patel (1984) suggested that the first member of the mono-alkyl ether series to show intrusion was the octadecyl polyoxyethylene ether. An nmr study is now reported on $C_{22}E_{27}$, which provides evidence for the intrusion hypothesis.

MATERIALS AND METHODS

After purification, docosan-1-ol (BDH) was ethoxylated by ICI Organics Division. Traces of catalyst and polyoxyethylene glycol were removed by extraction (Arnarson & Elworthy 1980) and the product recrystallised from a chloroform–light petroleum (bp 60–80 °C) mixture. Nmr analysis

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(Crooks et al 1974) gave a surfactant composition of $CH_3(CH_2)_{21}[OCH_2CH_2]_{27}OH$, ($C_{22}E_{27}$). The purity of the product was ascertained by tlc (Elworthy & Patel 1982) and elemental analysis (C = 59·9%, H = 10·2%; $C_{22}E_{27}$ requires C = 60·1%, H = 10·2%).

$CH_3(CH_2)_{15}[OCH_2CH_2]_{18}OH$, abbreviated to $C_{16}E_{18}$, has been described by Patel (1982).

Deuterium oxide, D_2O (99·8%), deuterochloroform $CDCl_3$ (99·8%), and precision nmr tubes (Wilmad) were obtained from Fluorochem. 3-(trimethylsilyl)-1-propane sulphonic acid, sodium salt hydrate, DSS (>99%), was obtained from Aldrich. Polyoxyethylene glycols 1000 and 1500 (E_{22} and E_{34} respectively), practical grade, were ex Fluka, and docosan-1-ol (pure grade) was from Koch-Light.

Solutions in D_2O were prepared at concentrations of 1% w/v for the surfactant and 0·8% w/v for the glycols, and contained 0·1% w/v DSS in each case (except where indicated). A 1% solution in D_2O is about 10 000 times more concentrated than its cmc at 298 K (Arnarson & Elworthy 1980) so that the surfactant can be considered to be in the micellar state. Solutions in $CDCl_3$ were of the same concentration, but did not contain an internal standard. 0·5 cm³ of solutions were introduced into the nmr tubes, which were then sealed.

The nmr studies were conducted on a Varian SC300 spectrometer operating in the [1]H-Fourier Transform (FT) mode at 300 MHz. For measurement of signal intensities, line widths and chemical shifts, 16 scans with a pulse delay of 20 s (aquisition time 2·6 s) were accumulated. The total delay of 22·6 s ensured complete relaxation of the protons as judged by the T_1 values (<3 s). $\Delta\nu_{\frac{1}{2}}$ was obtained from expanded spectra. The δ values were measured

relative to the main DSS signal. T_1 values, obtained by the pulsed FT-inversion recovery technique (Abraham & Loftus 1978), gave a coefficient of variation of ⩽2%.

RESULTS

The nmr spectrum of $C_{22}E_{27}$ in $CDCl_3$ showed three main peaks at $\delta = 0.84$ (CH_3), $\delta = 1.20$ (CH_2) and $\delta = 3.60$ (OCH_2), based on $CHCl_3 = 7.25$ ppm (Abraham & Loftus 1978). The chemical shifts in D_2O were similar

Peak integrals. Table 1 shows the relative integrals of the main protons of each compound in the two solvents. In $CDCl_3$ there is no evidence of micellization, and it therefore provided the simplest situation in which to assess the instrument performance. Integrals were within 6% of the expected values derived from the known concentrations of the solutions.

Table 1. (a) Signal intensities in the nmr spectra of E_{22}, E_{34}, docosan-1-ol, and $C_{22}E_{27}$ in $CDCl_3$ at 298 K. (b) Signal intensities in the nmr spectra of E_{22}, E_{34}, and $C_{22}E_{27}$ in D_2O at 298 K.

(a) In $CDCl_3$

Compound	Protons	Integral, % of expected value[a]
Polyoxyethylene glycol 1000 (E_{22})	OCH_2	105
Polyoxyethylene glycol 1500 (E_{34})	OCH_2	100
Docosan-1-ol ($C_{22}H_{25}OH$)	CH_2	94
$C_{22}E_{27}$[b]	OCH_2	104
	$CH_2 + CH_3$	105

(b) In D_2O

Compound	Protons	Integral[c] Observed	Calculated
E_{22}	OCH_2	18.0	18.7
E_{34}	OCH_2	17.8	18.9
$C_{22}E_{27}$[d]	OCH_2	20.9	19.2
	$CH_2 + CH_3$	4.16	7.49

[a] Normalized to $E_{34} = 100\%$. [b] $(CH_2 + CH_3)/OCH_2 = 0.394$, $C_{22}E_{27}$ requires 0.391. [c] Relative to 0.1% DSS as internal standard. [d] $(CH_2 + CH_3)/OCH_2 = 0.199$, $C_{22}E_{27}$ requires 0.391.

The integrals of the water soluble compounds in D_2O (Table 1b), agreed with the expected values except for the alkyl ($CH_3 + CH_2$) protons in $C_{22}E_{27}$. Here the integral accounted for only 56% of the protons.

The oxyethylene signal intensity was invariant with temperature (Fig. 1), and showed fluctuations which are due to the errors in measuring the small DSS peaks; the alkyl signal intensity was highly temperature dependent. The ratio of the

alkyl : oxyethylene signal intensities (Fig. 2) shows how the signal from the alkyl protons increases with temperature up to 313 K, after which the integral is independent of temperature and equal to the value in $CDCl_3$.

A 1% w/v solution of $C_{22}E_{27}$ in D_2O absent from DSS gave results consistent with those of the solution containing DSS (Figs 2, 3);
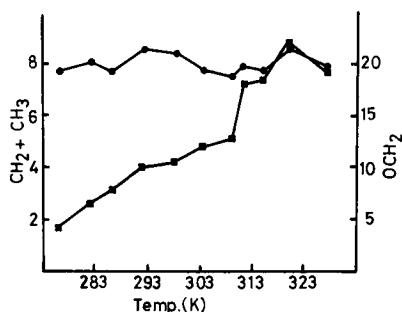

FIG. 1. Temperature dependence of the integrals of the $CH_2 + CH_3$ (■) and OCH_2 (●) protons of $C_{22}E_{27}$ in D_2O. Integrals relative to the DSS peak.
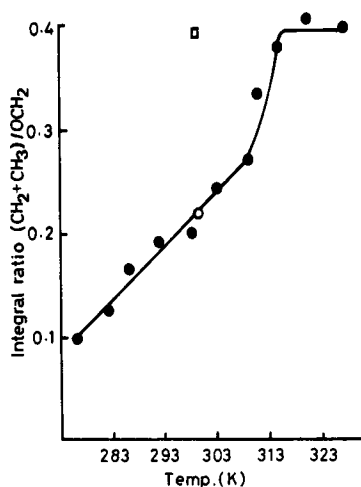

FIG. 2. Temperature dependence of the integral ratio of the $(CH_2 + CH_3):(OCH_2)$ protons of $C_{22}E_{27}$ in D_2O. ● Solution containing DSS, ○ solution without DSS, □ solution in $CDCl_3$.

A 1% solution of $C_{16}E_{18}$ in D_2O at 300 K gave the expected integrals for the alkyl and oxyethylene protons (ratio of integrals 0.394 in D_2O and 0.418 in $CDCl_3$, theoretical 0.419) together with narrow peak widths ($\Delta v_{\frac{1}{2}} \sim 7$ Hz), indicating that this surfactant was not showing the loss of alkyl signal found for $C_{22}E_{27}$ at this temperature.

T_I. Table 2 gives results obtained at 298 and 299 K. Results obtained over the temperature range 276–328 K were used in Arrhenius plots of $\log T_1$ vs $1/T$, giving the activation energies, E_a shown in Table 3.

Table 2. Spin-lattice relaxation times (T_1) of the protons of E_{22}, E_{34}, docosan-1-ol and $C_{22}E_{27}$ in $CDCl_3$ and D_2O.

Compound	Protons	T_1 (s)	
		$CDCl_3$ (299 K)	D_2O (298 K)
E_{22}	OCH_2	0·68	0·61
E_{34}	OCH_2	0·71	0·65
$C_{22}H_{45}OH$	CH_2	1·13	—
	CH_3	2·58	—
	CH_2OH	2·25	—
$C_{22}E_{27}$	OCH_2	0·55	0·53
	CH_2	0·99	0·40
	CH_3	2·24	—

Table 3. Activation energies, E_a ($kJmol^{-1}$), of the protons of E_{34} and $C_{22}E_{27}$ in D_2O and $CDCl_3$ at 298 K.

Compound	Protons	Solvent	
		$CDCl_3$	D_2O
E_{34}	OCH_2	—	20
$C_{22}E_{27}$	OCH_2	11	18
	CH_2	10	11

$\Delta v_{\frac{1}{2}}$. Values for the oxyethylene protons were small (~4 Hz) and showed little change with temperature (Fig. 3). $\Delta v_{\frac{1}{2}}$ for the alkyl protons was temperature dependent, being large at low temperatures but small at temperatures below 311 K.

δ. The chemical shift of the CH_2 peak was temperature sensitive, while that of the OCH_2 peak was insensitive (Fig. 4).

DISCUSSION

The partial loss of signal from the alkyl protons can be explained by considering them in a relatively immobile state. In solids, where motion is considerably restricted, dipole–dipole coupling leads to extensive line broadening, often extending to several KHz (Rushworth & Tunstall 1973). Such peaks would not be evident in the narrow line spectra studied.

As the temperature is increased up to 313 K, an increasing proportion of the alkyl chain becomes relatively mobile. The terms 'mobile' and 'immobile' are used rather loosely, and the latter term means a viscous environment, an ordered structure, where there may be a considerable loss of freedom of motion. Above 313 K the entire alkyl chain is mobile. The oxyethylene protons are relatively mobile at all the temperatures studied. In a region of the micelle where polyoxyethylene has intruded into the hydrocarbon core, congestion is expected due to the juxtaposition of alkyl and oxyethylene chains at the core/mantle interface, a region which is known to be maximally restricted in motion (Ribeiro & Dennis 1976, 1977). It is suggested that the signal from alkyl protons in this region is not seen by the instrument detector. The oxyethylene protons seem unaffected, probably due to similar segmental motions in the intruded and unintruded states. The similar structure of the polyoxyethylene chain in water and in the crystalline state (Bailey & Koleske 1976) may be responsible for this effect.
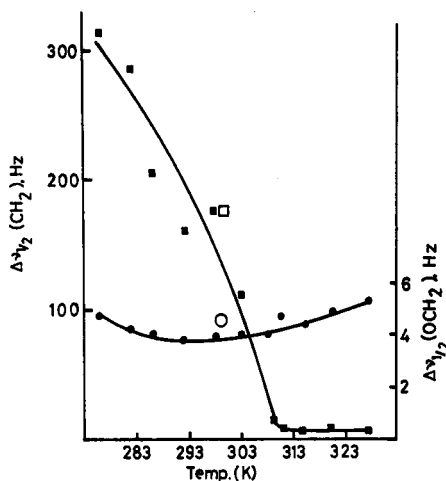

FIG. 3. Temperature dependence of $\Delta v_{\frac{1}{2}}$ of the CH_2 (■) and OCH_2 (●) protons of $C_{22}E_{27}$ in D_2O. (■,● solution containing DSS; □,○ solution without DSS.)

As the temperature increases, the extent of intrusion decreases up to 313 K, where intrusion is absent and the mobility of the alkyl protons is fully restored, as they are in a liquid-like state. This finding is in agreement with the intrusion hypothesis which predicts that intrusion should decrease with increase in temperature, and that it should be absent at temperatures exceeding the melting point of the core. If n-docosane is taken to represent the core, its melting point should be 317 K (Weast 1976). The results indicate a core melting temperature of 313 K, which is in reasonable agreement.

T_1 is determined by the net effect of segmental motion and the overall tumbling of the molecule. The relationship between T_1 and molecular size shows an asymtote at large molecular weights (Heatley 1980) due to the relatively small contribution of the overall tumbling to T_1 in large molecules.
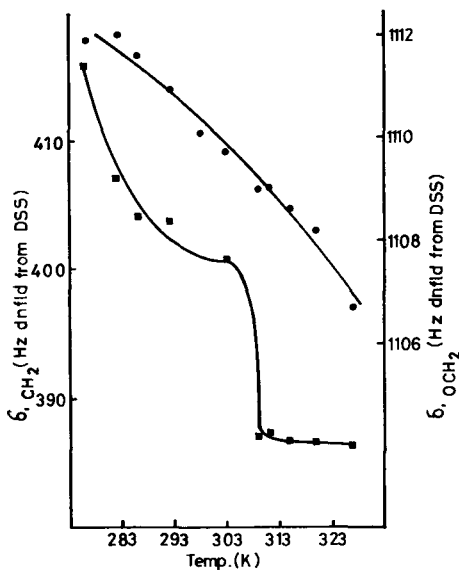
FIG. 4. Temperature dependence of the chemical shifts (δ) of the CH_2 (■) and OCH_2 (●) protons of $C_{22}E_{27}$ in D_2O.

T_1 is almost the same for E_{22} and E_{34} indicating that the relaxation is determined by the relatively fast segmental motions. The oxyethylene protons of $C_{22}E_{27}$ gave similar T_1 values in $CDCl_3$ and in D_2O, despite the fact that micelles are formed in D_2O. The alkyl protons give a lower T_1 in D_2O compared with $CDCl_3$ (0·40 and 0·99 s respectively). This indicates that the segmental mobility of these protons is decreased on micellization. Since this relaxation time derives from the mobile part (about half) of the alkyl chain, the result indicates that even the mobile part of the micellar core experiences some restriction in motion. E_a values (Table 3) for the oxyethylene protons of E_{34} and $C_{22}E_{27}$ in D_2O are similar, which indicates a similar resistance to motion for the two molecules. A similar result was obtained by Clemett (1970) for E_8 and $C_{10}E_5$. The smaller value of E_a for the oxyethylene protons of $C_{22}E_{27}$ in $CDCl_3$ suggests that 'hydrogen bonding' is absent in $CDCl_3$ but present in D_2O. The small values of $\Delta v_{\frac{1}{2}}$ for the oxyethylene protons and for the alkyl protons at high temperatures are indicative of the fast molecular and segmental motions seen in liquids. The increasing value of $\Delta v_{\frac{1}{2}}$ with the decrease in temperature indicates that the motion of even the mobile part of

the alkyl chain is being increasingly restricted. The transition temperature of 311 K is close to the value obtained from the integral measurements, and is interpreted as the temperature below which intrusion occurs and above which micelles behave conventionally.

δ values (relative to DSS) show a large dependence on temperature for the alkyl protons but a smaller dependence for the oxyethylene protons. The results cannot be readily interpreted because of the variety of factors affecting δ (Emsley et al 1966), and the complication of the large changes in $\Delta v_{\frac{1}{2}}$.

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