Localised Regions of Reduced Mobility in Micelles; ^{13}C N.m.r. Spin-Lattice Relaxation Times of Functional Surfactants in Aqueous Solution

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Summary ^{13}C nuclear magnetic resonance spin-lattice relaxation times of n-alkyltrimethylammonium halides bearing a polar substituent in the chain demonstrate a reduction of molecular motion in the region of that substituent; the site of solubilisation of n-pentanol within the micelle may be influenced by the structure of the surfactant.

Recently there have been several studies of carbon-13 nuclear magnetic resonance spin-lattice relaxation times (T_1) of surfactants in aqueous solution above the critical micelle concentration.[1] They have shown that the micellar interior is quite fluid, with motions of hydrocarbon chains somewhat constrained compared to those of free surfactant molecules. We have been interested in catalysis by chain-functionalised surfactants[2] and have carried out structural studies in parallel. To this end chain-substituted hydroxystearyltrimethylammonium halides have been synthesised‡ and ^{13}C n.m.r. T_1 values recorded for 0·5M aqueous solutions.§ Whilst only the first and last three resonances of the chain are resolved in cetyltrimethylammonium bromide (CTAB)[1c] (**1**), more information is available from the substituted compounds since the hydroxy-group perturbs the chemical shift of five additional carbon nuclei.

$Me(CH_2)_{15}\overset{+}{N}(Me)_3\ \ Br^-$

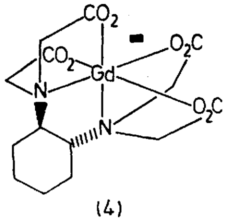
(1)

$Me(CH_2)_{10}CHOH(CH_2)_6\overset{+}{N}(Me)_3\ \ I^-$

(2)

$Me(CH_2)_5CHOH(CH_2)_{11}\overset{+}{N}(Me)_3\ \ X^-$

(3; X = Cl or I)



(4)

With 7-hydroxystearyltrimethylammonium iodide (**2**) the most striking single feature is the reduction in T_1 values close to the hydroxy-group. C(6), C(7) and C(8) are strongly affected, and C(5) and C(9) (β- to the hydroxy-group) have relaxation times close to the average of the inner chain, which is similar to the value for (**1**) determined at 70° and under otherwise identical conditions. A parallel result is obtained for 12-hydroxystearyltrimethylammonium iodide (**3**; X = I) and for the corresponding chloride (**3**; X = Cl). In the latter, relaxation times are higher at all sites by around 35% although ratios, and particularly the extent of reduction in the region of the hydroxy-group, are

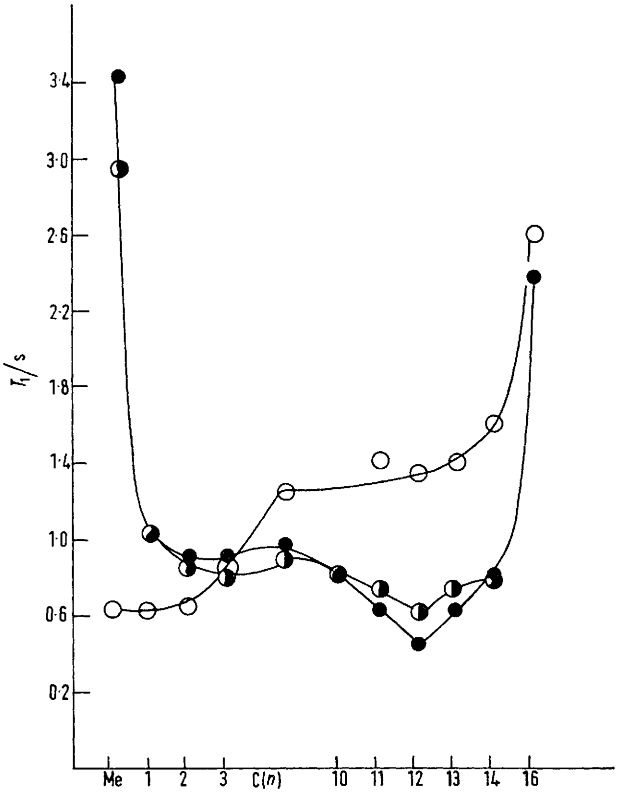


Figure 1. Relaxation times for carbon nuclei, 0·5M, D$_2$O solution, 80°. 12-hydroxystearyltrimethylammonium iodide; ● alone, NT_1 (product of the observed relaxation time and the number of hydrogens attached to that carbon); ◑ plus 0·5M n-pentanol, NT_1; ○ plus 0·025M (**4**), T_1^{para} $\frac{1}{T_1^{\text{obs}}} = \frac{1}{T_1\bullet} + \frac{1}{T_1^{\text{para}}}$

Measurements were carried out on undegassed samples by the inversion-recovery technique (180°, τ, 90, T) with $T > 4\ T_1$ for the slowest relaxing carbons being measured. Typical conditions: pulse width 37 μsec (180° pulse angle frequently calibrated), T = 6·0 seconds, 900 scans, 9 τ readings. T_1 values were estimated from peak heights by a curve-fitting non-linear least-squares procedure. All ● and ◑ runs were carried out in duplicate or triplicate and accuracy is ±10%. C(17) and C(18) relaxed too slowly for T_1 determination by this procedure and in some cases separate experiments with a different set of τ values were applied.

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‡ New compounds were analytically pure crystalline materials with consistent ^{13}C n.m.r. spectra, prepared from the corresponding keto-stearic acids. Critical micelle concentrations for (**2**) and (**3**) in aqueous solution at 45° were respectively $1{\cdot}53 \times 10^{-3}$M and $3{\cdot}46 \times 10^{-3}$M determined conductimetrically. Under the conditions of T_1 experiments, the contribution of non-micellated (**2**) and (**3**) should therefore be negligible.

§ Previous workers[1c] carried out measurements on (**1**) at 34°, but at higher temperatures less viscous solutions and sharper spectra resulted, particularly for (**2**) and (**3**). In our experiments line widths of 3—5 Hz were typical with some broadening apparent close to the *N*-terminus and at the hydroxy-bearing carbon. Assignments were made by reference to standard additive-shift tables and aided by inspection of the spectrum of pentyltrimethylammonium bromide. On this basis it proved necessary to reverse previous[1c] C(2) and C(3) assignments for (**1**).

similar. Iodide ion would be expected to bind more tightly than chloride ion to a cationic micelle since the latter is more lyophilic[3] and this may reduce the overall freedom of motion. In all cases, all remaining carbon atoms (with the exception of the last four atoms of the chain) have internally comparable relaxation times.

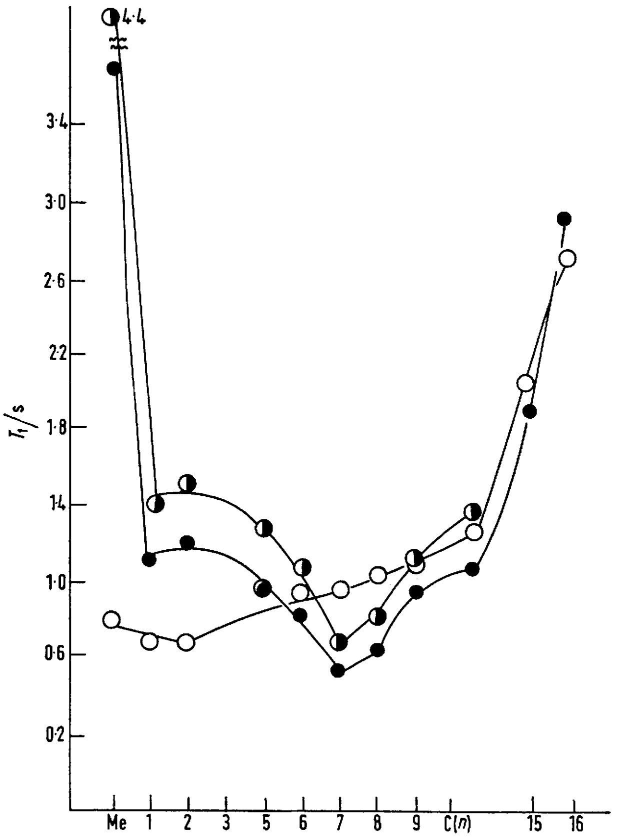

FIGURE 2. 7-hydroxylstearyltrimethyl ammonium iodide, as in Figure 1.

Interpretation of ^{13}C n.m.r. T_1 values for alkyl chains has been widely discussed[4] and in larger molecules and aggregates it is likely that they are governed by dipole–dipole relaxation brought about by internal motion. Whilst small rocking motions (*cf.* T_1 values for α- and β-carbons of proline residues in peptides[5]) enhance T_1 significantly, segmental motion of the chain must be more important. In the crystalline state polymethylene chains are fully extended[6] although amorphous polymers and liquid hydrocarbons[7] have significant populations of *gauche*-butane subunits. Kinking of the micellar chain (a β- or δ-double-*gauche* arrangement) would provide minimum disruption of packing within the micelle. Since the rotational barrier and *trans*:*gauche* population ratio are unlikely to be perturbed by the hydroxy-group,[8] steric explanations for reduced molecular motion are unattractive. We consider that the region of the hydroxy-group is more restricted due to intermolecular hydrogen-bonding, and penetration of water into that region of the micelle. The perturbed region is quite local, and relaxation times beyond the β-carbon are normal. In the presence of 5 mole % of the relaxation reagent (**4**) all T_1 values of (**2**) or (**3**) are reduced, but most particularly those close to the head-group with no special effect in the region of the hydroxy-group; the Figures illustrate the paramagnetic contribution to the overall relaxation. This result demonstrates that the hydroxy-group is buried in the micellar core, rather than appearing close to the surface by chain coiling.

We observe that addition of a molar equivalent of hexane to 0·5M (**1**) in D_2O at 70° uniformly shortens observed values of T_1 by around 20%, whereas a molar equivalent of benzene or n-pentanol has the opposite effect. This implies that hexane is solubilised in the micellar interior, forcing tighter packing and reduced mobility whilst benzene and n-pentanol disrupt micellar structure by binding close to the Stern layer, in accord with previous observations.[9] Similar results obtain with 0·5M n-pentanol and 0·5M (**2**), T_1 increases of 10—20% being observed. With (**3**), the effect of n-pentanol on relaxation times is smaller and the trends suggest that carbons in the region of the head-group are less mobile, whilst those in the regions of the hydroxy-group are more mobile. This suggests penetration by n-pentanol into the micellar interior by hydrogen-bonding to the surfactant hydroxy-group and displacement of attendant water molecules.

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[9] Summarised in E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271. A referee has suggested that hexane may promote the formation of spherical rather than rod-shaped micelles, although the latter are perhaps more likely at 0·5M.