Synthesis and Properties of Three Triple-armed Amphiphiles

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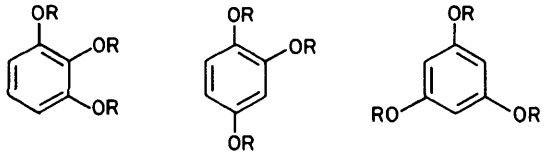
Three new isomeric 'trigapus' molecules, having long ion-terminated chains radiating from an aromatic ring, are only weakly surface active; yet they dramatically lower the critical micelle concentration of an admixed cationic surfactant to produce 'giant' micelles.

'Tentacle' molecules having ion-terminated hydrocarbon chains that radiate from a central unit are described only twice in the literature. Suckling[1] examined benzene-1,3,5-tricarboxylic acid esterified with three $[CH_2]_{11}NR_3^+$ groups. The resulting tentacle molecule forms complexes in acetonitrile with small aromatics. When phenol is enmeshed among the arms, it becomes resistant to chlorination by t-butyl hypochlorite. 'Hexapus' constitutes the second published example;[2] six $[CH_2]_{10}CO_2^-$ chains project from a cyclotriveratrylene framework. Hexapus in water binds tightly to cholesterol, phenol blue, naphthalene, and hydrophobic esters. In the present communication, we describe three new tentacle molecules: 1,2,3-, 1,2,4-, and 1,3,5-tris(10-carboxydecyloxy)benzene [(**1**), (**2**), and (**3**), respectively] called 'trigapus' for brevity.

We were curious about whether one or more of these isomers would form micelles as do, of course, the individual fatty acid chains. Too little is known about ion-terminated tentacle molecules even to speculate on this point. We were also intrigued by the possibility that trigapus, being anionic



(1) (2) (3)

R = $[CH_2]_{10}CO_2^-$

and multi-armed, could interconnect or 'cross-link' cationic micelles.

Synthesis of the trigapus molecules was carried out by treating a trihydroxybenzene in dry dimethylformamide first with NaH and then with ethyl 11-bromoundecanoate (95 °C, 16 h). Hydrolysis of the triester in aqueous ethanol containing NaOH gave, after acidification, the triacid which was identified by elemental analysis, neutralization equivalent, i.r., ^{1}H n.m.r., and mass spectrometry (fast atom bombardment).† Corresponding trigapus molecules with trimethylammonium headgroups were prepared by lithium aluminium hydride reduction of the triester to the trialcohol, methyl sulphonation, and reaction with trimethylamine.

Trigapus compounds display a weak surface activity: 10 mM (**3**) lowers the surface tension of a pH 9.3 buffer by only 12 dyne/cm.‡ This compares, for example, with a 33 dyne/cm change induced by 1.0 mM of a single-chained surfactant, dodecylbenzene-*p*-sulphonate.[3] Packing problems of the trigapus compounds at the 2-dimensional air–water boundary probably reduce interfacial adsorption. Low levels of trigapus do, however, have an impressive effect on the surface activity of an admixed cationic surfactant (decyltrimethylammonium bromide, DTAB). Thus, the 'break point' of the surface tension *vs.* [DTAB] plot [corresponding to the critical micelle concentration (c.m.c.) of DTAB] is lowered from 40 to 4 mM by the presence of 1.3 mM (**3**) in the water. It is as if the trigapus 'seeds' micellization of the cation surfactant.

Rayleigh plots, obtained from light scattering experiments on the trigapus compounds, differ from those of mono-chain surfactants[4] in two respects: (a) the plots are linear up to 10 mM trigapus, indicating that micellization is not occurring precipitously over a narrow concentration range. In other words, trigapus has no c.m.c. as do ω-phenylalkanoic acids.[5] Slopes of the Rayleigh plots are small, indicating that the aggregation numbers (a.n.) are considerably less than the 50—100 associated with conventional surfactants. This is true for both our anionic and cationic trigapus molecules. For example, the mean a.n. for (**1**) in basic water equals only 5 ± 2. Covalent attachment of chains obviously has a dramatic effect on the colloidal properties of amphiphilic molecules.

Since small amounts of trigapus can reduce by 10-fold the c.m.c. of DTAB and thus affect the *propensity* to aggregate, it was interesting to determine whether trigapus could likewise affect the *size* of the DTAB micelles. Figure 1 shows a plot of Rayleigh's ratio for a 90° scattering angle (R_{90}) as a function of [DTAB] in the presence of 1.3 mM (**3**) (pH = 9.3, 23 °C). The plot is seen to rise to a maximum at *ca.* 20 mM DTAB and then fall to values typical of DTAB without trigapus at 50 mM and above. A similar curve was found using 0.25 mM trigapus additive except that R_{90} reached a maximum of only 2.5 × 10^{-2}. Particular attention should be paid to the magnitude of the R_{90} values. The scale of the ordinate is such that a Rayleigh plot for most simple surfactants without any additive would appear as a horizontal line at the base of the graph. Clearly,

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‡ 1 Dyne = 10^{-5} N.

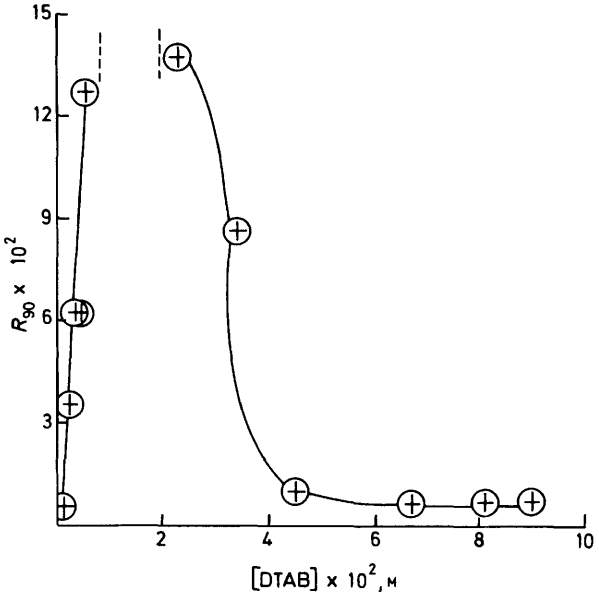

Figure 1. Rayleigh's ratio for a 90° scattering angle *vs.* concentration of DTAB in the presence of 1.3 mM (**3**) (pH = 9.3, 23 °C). Coacervate formation (between the dotted lines) was not observed in similar experiments with (**1**) and (**2**).

low levels of trigapus cause a huge growth of the DTAB micelles. Although there is no simple way to calculate the exact aggregation number from the bell-shaped plot in Figure 1, the DTAB micelles must reach a size of at least 500 [an order of magnitude greater than in the absence of (**3**)]. Each of the anionic trigapus molecules manifests the enlargening effect, with the 1,2,3-isomer giving a somewhat lower maximum than the other two (R_{90} = 4.3 × 10^{-2}). Stabilization of the giant micelles does not require all three ion-terminated arms because the 1,3-double-armed analogue (a weakly surface active material) perturbs the DTAB system similarly. Electrostatic interactions are, however, critical; trigapus molecules with cationic headgroups do not enlarge DTAB micelles.

When the DTAB concentration reaches a sufficient excess over that of the trigapus, the giant micelles disappear (thus leading to the righthand portion of the bell-shaped curve). Apparently, the giant micelles (seeded by 25 or more trigapus molecules) disintegrate if the trigapus is permitted to distribute itself among a multitude of 'normal' DTAB micelles. Note also from Figure 1 the region (dotted lines) in which the solutions are not optically clear owing to coacervate formation. The structure of these trigapus–DTAB coacervates, and all coacervates for that matter, is not understood.

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