Gemini surfactants: studying micellisation by 1H and 19F NMR spectroscopy

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For some cationic Gemini surfactants, exchange between the bulk solution and micelles or other aggregates occurs slowly on the NMR timescale; thus NMR spectroscopy provides an efficient tool for studying micelle formation and mixing of various surfactants.

Among the various aggregates amphiphilic molecules form in water, micelles are by far the most common and the most thoroughly studied.1 The critical micelle (aggregation) concentration (c.m.c.), or the threshold concentration above which monomers co-operatively assemble into micelles (or other aggregates), can be determined by surface tension measurements or conductimetry.1 Above the c.m.c. rapid exchange aggregates), can be determined by surface tension measure-
monomers co-operatively assemble into micelles (or other tration (c.m.c.), or the threshold concentration above which monomers co-operatively assemble into micelles (or other aggregates), can be determined by surface tension measurements or conductimetry.1 Above the c.m.c. rapid exchange occurs between amphiphiles in the bulk and in the micelles (Fig. 1). For single chain surfactants, characteristic times for this exchange are generally of the order of 1 ns to 1 ms and fast techniques such as ultrasonic absorption are required for their measurements.2,3 Slower techniques such as NMR show averaged signals for the surfactant molecules in their various states.4 Both c.m.c. values and exchange rates between surfactants in the bulk and in the micelles depend critically on the size of hydrophobic groups in the surfactants. In most cases, simple laws can be expressed between these physical parameters and the number of CH2 groups in the hydrophobic part of the surfactants.2,5,6

Fig. 1 Schematic representation of surfactant exchange between micelles and bulk phase.

Dimeric (Gemini) or oligomeric surfactants, which consist of two or more conventional surfactant units linked at their polar head groups by a spacer, are attracting a lot of attention in the area of surfactant research because of the many unusual properties that they feature.7,8 A direct consequence of the presence of two hydrophobic tails in dimeric surfactants is a sharp and uniform decrease in the c.m.c. values, which are 1 to 2 orders of magnitude lower than that of their monomeric counterparts.7 For the same reason, slower exchange between dimeric surfactants in the bulk and in the aggregates could be anticipated. We now report on such unusually slow exchange and the consequent occurrence of separate 1H and 19F NMR signals for surfactants in the bulk and in micelles.

The surfactants studied here belong to the series of n-2-m bis-quaternary ammonium bromides whose structures are shown below.9 Hydrocarbon, fluorocarbon as well as hybrid hydrocarbon–fluorocarbon10 surfactants were tested.

Thus, the 1H NMR spectrum of 14-2-14 in D2O below its c.m.c. shows one set of sharp signals corresponding to the monomer in the bulk (Fig. 2c). Above the c.m.c. the lines broaden and a second set of signals appears, corresponding to the micelles (Fig. 2a and 2b). The intensity of the micelle signals increases linearly with the surfactant concentration, whilst the intensity of the monomer signals levels off above the c.m.c. The protons belonging to the polar head are deshielded up to 0.2 ppm in the micelles, and are very distinct from the monomer signals. This downfield shift is likely to be the result of the proximity between the cations in the micelles. For the protons belonging to the alkyl chains, chemical shifts are not so different and the various signals partly overlap.

The c.m.c. value can be estimated by integrating the monomer signals and comparing these with an internal standard, or more accurately determined by diluting the sample after the disappearance of the monomer signals and plotting the signal intensities as a function of concentration. For 14-2-14, the value measured upon dilution in D2O (0.12 mM) matches well that obtained using conductimetry in H2O (0.16 mM). The slight discrepancy may be attributed to expected differences between H2O and D2O.

Line-shape analysis of the broadened signals gives the lifetimes of monomeric and aggregated species at various concentrations, and the characteristic time of exchange τ.11† For 14-2-14, τ (0.1 s) is orders of magnitude longer than for single chain surfactants.3 In a series of n-2-m surfactants, τ increases with n + m. The chain length difference n − m does not considerably affect the exchange, and similar spectra are obtained for 18-2-8 and 16-2-10 (n + m = 26), or for 18-2-10, 16-2-12 and 14-2-14 (n + m = 28). The borderline between fast and slow exchange on the NMR timescale at 25 °C lies between n + m = 24 and n + m = 26. As shown in Fig. 2b, two sets of

Fig. 2 Part of the 400 MHz 1H NMR spectra of dimeric surfactants at various concentrations in D2O (25 °C). The signals observed are those of the N(CH3)4+ protons for molecules in the bulk phase (3.92 ppm) and in the micelles (4.03–4.13 ppm). (a) [14-2-14] = 0.25 mM; (b) [14-2-14] = 0.167 mM; (c) [14-2-14] = 0.125 mM; (d) [18-2-8] = 0.5 mM; (e) [12-2-12] = 1.25 mM.


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signals are present for 18-2-8 above its c.m.c. (0.3 mM). These signals are broader than those of 14-2-14, indicating faster exchange (τ = 0.04 s). Coalescence occurs for 12-2-12 (c.m.c. = 0.95 mM), and a single broad signal representing a weighted average of monomers and aggregated surfactants is seen (Fig. 2e). For all these dissymmetric surfactants, the aggregates formed over a large range of concentration above the c.m.c. have been shown to be micelles. In the case of 14-2-14, slopes of conductivity versus concentration suggest that micelles are also formed above the c.m.c., at least over a short concentration range. Bilayers were observed at 5 mM.9

Such slow exchange on the NMR timescale between monomeric and aggregated amphiphiles has been reported once for a neutral fluorinated surfactant, forming hydrogen bonds in an aggregated state.12 These authors recognised the presence of large aggregates (not micelles), and suggested that this may be of importance in the large values of the measured lifetimes.12 Lipids are much more hydrophobic than usual detergents and also exchange slowly between monomeric and vesicular states.2-13 However, their critical aggregation concentrations are in the nanomolar range and below,13 and are too small for NMR investigations. To the best of our knowledge our observations, using micelle-forming hydrocarbon cationic amphiphiles for which no forces other than the hydrophobic effect stabilise the aggregates, are unprecedented.

19F and 1H NMR spectra of the fluorocarbon Gemini surfactant C8F2C4-C8C4 and the hybrid hydrocarbon–fluorocarbon surfactant C8F2C4-12 also show distinct signals for monomers and aggregated surfactants (Fig. 3a).10 The c.m.c. values deduced from dilution experiments or integration against a CF3CH2OH internal standard are 0.03 and 0.2 mM respectively, compared to 0.028 and 0.2 mM measured by conductimetry. For the hybrid surfactant C8F2C4-12, conductivity and cryo-TEM observations confirm that the aggregates formed are micelles.10 For the fluorocarbon surfactant C8F2C4-2-C8C4 vesicles seem to form even at such low concentrations, and the c.m.c. is probably a critical vesicular concentration.10 The high sensitivity to the environment of fluorine chemical shifts results in large differences between the signals in the bulk and in the aggregates (up to 2.2 ppm for the terminal-CF3 group). The 19F nuclei located in the hydrophobic part of the molecules are shielded in the micelles and their signals shift upfield, whereas signals of the 1H nuclei close to the polar heads shift downfield.

Slow exchange renders NMR studies of co-micellisation of various surfactants very tractable. The example of C8F2C4-12 and 12-12-12 shown in Fig. 3b represents a good illustration. When C8F2C4-12 and 12-2-12 are mixed in different proportions, it can clearly be seen that the hybrid fluorocarbon–hydrocarbon surfactant exists predominantly in the micellar state at concentrations close to, and even below, its c.m.c. At such low concentrations, C8F2C4-12 molecules remain in micelles consisting for the most part of 12-2-12 molecules. The co-micellisation can be traced by following the 19F chemical shifts of C8F2C4-12 (Fig. 3b). As the mixed micelles become richer in 12-2-12, the fluorocarbon chains are less shielded than with pure C8F2C4-12, and the signal intensity of the downfield shift of the fluorine signals may result from the distribution of micelle composition, and not from faster exchange with 12-2-12 rich micelles. A 1H NMR spectrum of these mixed micelles presents the original pattern of an aggregate with which one surfactant exchanges slowly, and the other rapidly. A more thorough investigation of the exchange rates for these surfactants is now in progress.

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Notes and references

† Determination of the characteristic time of exchange τ may be performed using 1D polarisation transfer or 2D exchange spectroscopy. An estimate can be very simply obtained from line shape analysis of a sample at a concentration twice the c.m.c. At this concentration the lifetimes of monomeric and aggregated species are both equal to τ, whose value is then given by 1/τ = πΔντ, where Δν is the linewidth difference between the monomer signal at twice the c.m.c. (broadened by the exchange) and below the c.m.c. (no exchange), as obtained from a least-square analysis of the spectra. The τ values can be measured as long as separate signals are observed, which requires 1/τ < |νm – νv|, where νm and νv are the monomer and the aggregate signal frequencies.

Fig. 3 Part of the 400 MHz 19F NMR spectra of C8F2C4-12 as a function of concentration in 9:1 H2O-D2O (25 °C). The region covers the signals of the terminal-CF3 groups in the bulk and in micelles. (a) no additives; (b) in the presence of 12-2-12 at constant total concentration, [C8F2C4-12 ] + [12-2-12] = 2 mM. The c.m.c. of 12-2-12 is 0.95 mM.

10 A full account of the synthesis and aggregation behaviour of these new fluorinated compounds is in preparation.