Unique Interfacial Properties of a Homologous Series of Novel Triple-chain Amphiphiles Bearing Three Anionic Head Groups Derived from 1,1,1-Tris(hydroxymethyl)ethane

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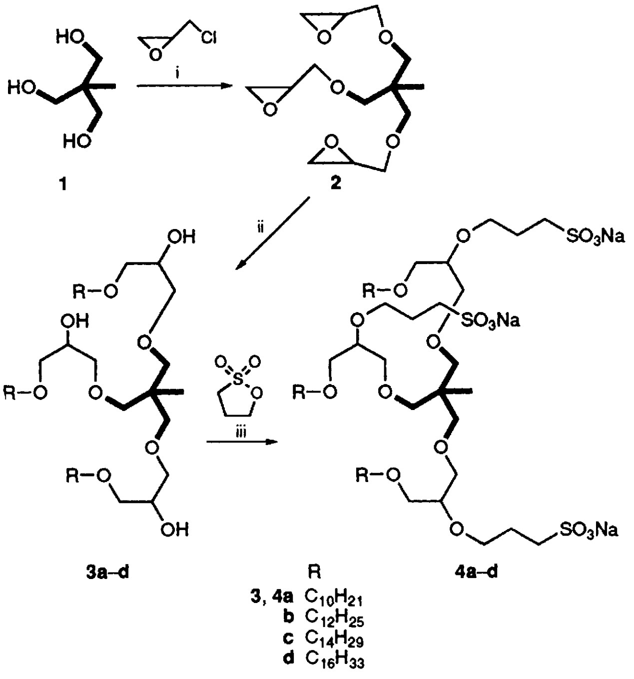
Unusual behaviour in which the critical micelle concentration (CMC) values in water for a homologous series of the title amphiphiles increased with an increase in the number of carbons of the lipophilic alkyl chains was observed when these data were obtained by the common surface tension method using a Wilhelmy tensiometer.

Almost all the established surfactants are amphipathic molecules consisting of one lipophilic chain and one hydrophilic head group. The relation between the interfacial properties and the structural factors of such surfactants has been already systematically summarized in detail.[1] Thus someone who designs an unknown surfactant molecule on paper by combining a lipophilic group and a hydrophilic group should be able to speculate on the surface-active properties of the proposed compound.

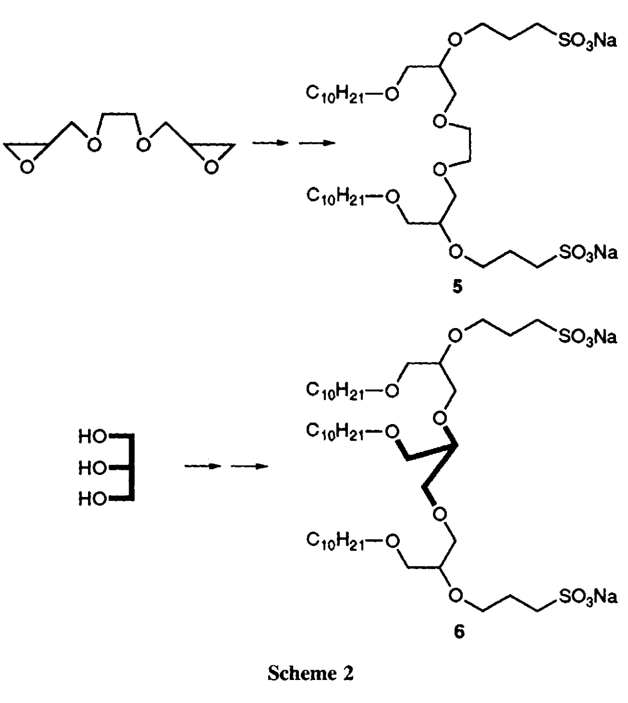
We have found, however, that double-chain amphiphiles bearing two ionic head groups, for which the molecular structure is apparently shaped as a bundle of two typical single-chain surfactants, exhibit various interesting interfacial properties.[2] These properties are not simply an extension of the relation between the interfacial properties and the structural factors of conventional surfactants. As a result we have been investigating the preparation and properties of new amphiphiles consisting of two or three lipophilic chains, two hydrophilic head groups and an appropriate connecting group between the lipophilic part and the head groups.[3,4] Especially, among these compounds, triple-chain amphiphiles bearing two anionic groups derived from glycerol have very small CMC values and great ability to lower surface tension, both of which cannot be achieved by the simple modification of the structure of general single-chain monoanionic surfactants.[3] In this work, we used 1,1,1-tris(hydroxymethyl)ethane **1** as a starting material and synthesized novel triple-chain amphiphiles **4** bearing *three* sulfonate groups. Here we report unusual and interesting interfacial properties observed among these homologues.

Scheme 1 shows the synthetic route for the target triple-chain tris(sulfonate) compounds **4a–d**. The synthetic intermediate, 1,1,1-tris(hydroxymethyl)ethane tris(glycidyl ether) **2**, was prepared according to the previously reported method.[5] Pure compounds **4a–d** were finally isolated as white solids by silica gel column chromatography with a chloroform–methanol eluent.†



Scheme 1 i, KOH–DMSO, room temp., 6 h, 78% yield; ii, ROH/K, 95 °C, 4 d, ≈51% yield; iii, NaH–THF, 50 °C, 2d, ≈47% yield

Although compounds **4a–c** were freely soluble in water at 1 wt% concentration at any temperature, compound **4d** bearing three hexadecyl chains was insoluble even in boiling water. Therefore, the interfacial properties in water were measured for **4a–c**. The surface tension of the amphiphile solutions was measured at 20 °C with a conventional Wilhelmy tensiometer using a glass plate. Table 1 summarizes the data for their CMC, γ_{CMC} (the surface tension at CMC) and pC_{20} (the efficiency of adsorption at the air/water interface)[6] values which are obtained from each surface tension *vs.* concentration (on a log scale) curve. The corresponding data for double-chain bis(sulfonate) **5** derived from ethylene glycol diglycidyl ether[7] and triple-chain bis(sulfonate) **6** derived from glycerol[3] are also included in Table 1 as reference amphiphiles (Scheme 2).



Scheme 2

Surprisingly, in the homologous series of the compounds **4**, the increasing order of CMC is: **4a** < **4b** < **4c**, indicating that the CMC values increase with an increase in the length of the lipophilic alkyl chain. This result is contrary to the common recognition that the CMC values for a homologous series of general single-chain surfactants decrease with an increase in the length of the alkyl chain up to about a hexadecyl group.[8] In the case of the homologous series of reference compound **5** or **6**, this unusual tendency of the CMC values was not observed within the range of our study.[3,7]

Moreover, there are two noteworthy points concerning the measurement of surface tension for compounds **4a–c** by the Wilhelmy method. First, very long ageing time was required (from 24 h to 48 h) until the surface tension of the aqueous solution of these compounds reached a constant value at lower concentrations than each of their CMC values. Second, the pC_{20} values decreased with an increase in the length of the alkyl chain as shown in Table 1. The pC_{20} value is proportional to the standard free energy of adsorption at the air/water interface, $-\Delta G^\circ_{ad}$.[6] The pC_{20} values generally increase linearly with an increase in the number of carbons in a straight-chain lipophilic group of conventional single-chain surfactants.[6] However, the pC_{20} values for the homologous series of compounds **4** showed an opposite tendency to this rule, in other words, indicating that an increase in the length of the alkyl chain causes a negative contribution to the adsorption of the compounds **4** at the air/water interface.

Information obtained from the Wilhelmy method reflects the behaviour of an amphiphile not in the bulk phase but at the surface. Thus we additionally tried to measure the CMC for compounds **4** by another method, the dye method,[9] the results of which reflect the behaviour of an amphiphile in the aqueous bulk phase. Ultraviolet (UV) spectra of the aqueous solutions of compounds **4a–c** and **5** at various concentrations (with 5×10^{-7} mol dm^{-3} of pinacyanol chloride as dye probe) were measured. The absorbance change in the γ-band of the probe at λ_{max} = 490 nm was monitored. It has been reported that the absorbance of the γ-band decreases with the formation of aggregates of amphiphiles in the bulk phase.[9] The determination limit of the amphiphile concentration was *ca.* 2×10^{-6} mol dm^{-3} under the experimental conditions of this work. The relation between the amphiphile concentration and the surface tension as measured by the Wilhelmy method is shown in Fig. 1(*a*) and by the dye method in Fig. 1(*b*) for compounds **4a–c** and **5**.

Table 1 The CMC, γ_{CMC}, and pC_{20} values of amphiphiles **4a–c** and the reference compounds measured by the Wilhelmy method at 20 °C in water

Surfactant	CMC/mol dm^{-3}	γ_{CMC}/mN m^{-1}	pC_{20}
4a	6.8×10^{-6}	31.5	7.4[a]
4b	5.0×10^{-5}	33.0	5.8
4c	2.5×10^{-4}	34.0	4.8
5[b]	3.2×10^{-5}	30.0	5.2
6[c]	1.4×10^{-5}	28.0	6.6[a]

[a] Estimated value. [b] Ref. 7. [c] Ref. 3.

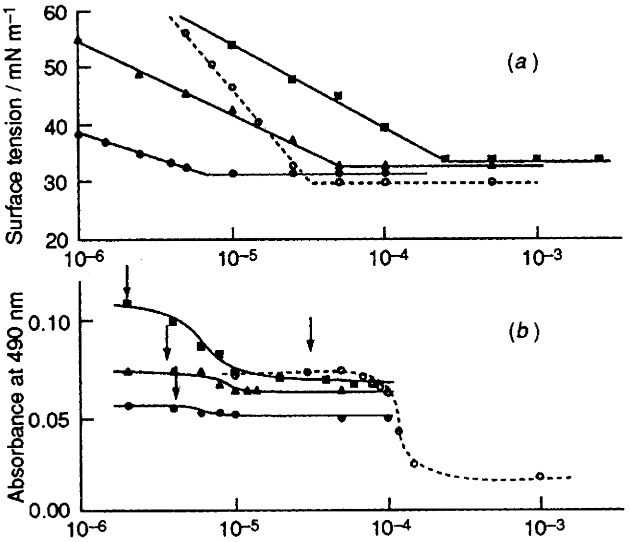


Fig. 1 CMC measurements by (*a*) the Wilhelmy method and (*b*) by the dye method; (●) **4a**, (▲) **4b**, (■) **4c** and (○) **5**. Arrows indicate estimated CMC values.

For compound **5**, the CMC values obtained by the two different methods are almost the same. For compounds **4a–c**, however, the absorbance change attributed to aggregation in water was observed at much lower concentrations than each CMC estimated from the Wilhelmy method. It appears that the absorbance of **4c** is already changing at the minimum amphiphile concentration of this experiment.

These results imply that compounds **4a–c** could form molecular aggregates, so called 'pre-micelles', at lower concentrations than indicated by their CMC values as estimated by the Wilhelmy method. Recently, Menger *et al.*[10] have also reported that some 'gemini surfactants', which are amphiphiles possessing, in sequence, a long lipophilic chain, an ionic head group, a rigid spacer, a second ionic group, and another lipophilic hydrocarbon tail, would be substantially preassembled well below the CMC obtained by the surface tension method.[10] In the case of a homologous series of compounds **4** in this study, it is surmised that the formation of some aggregates in the bulk phase is relatively easier compared with adsorption at the surface. However a more detailed study is required to interpret these unique phenomena precisely.

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Footnote

† Satisfactory spectral and microanalytical data were obtained for all purified compounds **4**. Selected spectroscopic data for **4** are as follows: **4a**; ^{1}H-NMR [JEOL JNM-GSX-400 (400 MHz)], δ 0.88 (t, 12H), 1.09–1.47 (m, 42H), 1.50–1.67 (m, 6H), 1.97 (m, 6H), 2.72–3.08 (m, 6H) and 3.20–3.97 (m, 33H); IR (KBr) 2900, 2860, 1450, 1170, 1110 and 1070 cm^{-1}.

References

1 See for example, M. J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd edn., Wiley, New York, 1989.
2 M. Okahara, A. Masuyama, Y. Sumida and Y.-P. Zhu, *J. Jpn. Oil Chem. Soc.* (Yukagaku), 1988, **37**, 746.
3 Y.-P. Zhu, A. Masuyama, Y. Kirito, M. Okahara and M. J. Rosen, *J. Am. Oil Chem. Soc.*, 1992, **69**, 626.
4 Y.-P. Zhu, A. Masuyama, Y. Kobata, Y. Nakatsuji, M. Okahara and M. J. Rosen, *J. Colloid Interface Sci.*, 1993, **158**, 40.
5 T. Kida, M. Yokota, A. Masuyama, Y. Nakatsuji and M. Okahara, *Synthesis*, 1993, 487.
6 Ref. 1, pp. 84–90.
7 Y.-P. Zhu, A. Masuyama, T. Nagata and M. Okahara, *J. Jpn. Oil Chem. Soc.* (Yukagaku), 1991, **40**, 473.
8 Ref. 1, p. 120.
9 M. L. Corrin, H. B. Klevens and W. D. Harkins, *J. Chem. Phys.*, 1946, **14**, 480.
10 F. M. Menger and C. A. Littau, *J. Am. Chem. Soc.*, 1993, **115**, 10083.
11 Ref. 1, pp. 94–98 and pp. 156–159.