

Cationic amphitropic gemini surfactants with hydrophilic oligo(oxyethylene) spacer chains

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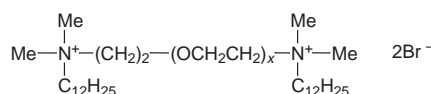
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New gemini diammonium surfactants have been synthesized

in which the spacer chain consists of oligo(oxyethylene) units and which exhibit thermotropic liquid crystalline lamellar α and β as well as lyotropic mesophases.

Surfactant molecules usually consist of a hydrophilic headgroup attached to a hydrophobic alkyl chain. They self-assemble into micellar and lyotropic liquid crystalline mesophases when mixed with water. If the self-organization process occurs on heating, thermotropic liquid crystalline phases are often observed. Many amphiphilic compounds can form thermotropic as well as lyotropic mesophases, and therefore they are labelled as amphitropic.¹ Recently, bis(quaternary ammonium) surfactants ('gemini surfactants') have been prepared, in which two hydrophilic headgroups are linked *via* a hydrophobic alkylene or heteroatom-modified spacer chain.^{2,3} Here we report on a new series of amphitropic gemini surfactants (12-EO_x-12) in which hydrophilic headgroups as well as hydrophilic spacer chains are simultaneously present for the first time. A study of the effect of the hydrophilic oligo(oxyethylene) spacer length on the amphitropic aggregation is presented.

Gemini surfactants 12-EO_x-12 with $x = 2-5$ were obtained in



two steps *via* bromination of the corresponding oligo(oxyethylene)glycols HO-(CH₂)₂-(EO)_x-OH (0.1 mol) with PBr₃ (0.15 mol) in dry dioxane.⁴ The resulting dibromides (0.06 mol) were quaternized with *N,N*-dimethyldodecylamine (0.13 mol) under reflux in anhydrous EtOH for two days. Evaporation yielded white solids which were recrystallized at least three times from ethyl acetate to give the desired products in good yields (50–70%). For comparison, 12-EO_x-12 with $x = 0$ or 1 were also prepared.^{2,3a} The purity of all compounds was confirmed by elemental analysis and ¹H NMR spectroscopy.[§]

The thermotropic behaviour of the surfactants was characterized using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The surfactants with $x \leq 4$ form one or two mesophases on heating, either an L_β (viscous neat) or an L_α (smectic A) phase. The transition temperatures as well as the transition enthalpies are compiled in Table 1. The results were taken from the first DSC heating runs because the compounds are thermally unstable at high temperatures and partially decompose. Subsequent DSC scans are therefore significantly changed, as similarly observed by Fuller *et al.* for a series of conventional gemini surfactants.^{5a} The first heating scans were always reproducible. For 12-EO₀-12, two mesophases were observed, while 12-EO₁-12 shows only one mesophase. For 12-EO₂-12, again two mesophases occur. 12-EO₃-12 and 12-EO₄-12 show a single mesophase each and clearing temperatures much lower than those of the compounds with shorter spacer chains. For 12-EO₅-12, no thermotropic mesophase was observed. This may be due to the higher flexibility of the spacer chains introduced by the

additional oxygen atoms.

In Fig. 1, the first DSC heating run for 12-EO₂-12 is shown as a typical example. The four phase transitions are clearly recognizable. The occurrence of the mesophases was further identified by the characteristic textures to be seen in the POM. In the case of 12-EO₀-12 and 12-EO₁-12, the optical textures are not easily discernable, since the materials exhibit a very high viscosity. Only after long thermal or mechanical treatment, birefringent cloudy textures occurred resembling that of a viscous neat phase. This effect was also reported for gemini surfactants with hydrophobic spacer chains.^{5a} In contrast, the textures formed immediately for the compounds with x being 2–4. In Fig. 2(a) and (b), the fan-like textures of the viscous neat phase of 12-EO₂-12 at 120 °C and the mosaic texture of its smectic A phase at 180 °C are shown. Upon shearing, the mosaic texture at 180 °C is converted into oily streak textures.

The assignment of the mesophases was confirmed using XRD. The XRD spectrum of Fig. 3 indicates that the crystalline phase of 12-EO₂-12 has a layered structure with a period of 24.8

Table 1 Transition temperatures^a (°C) of compounds 12-EO_x-12 and ΔH (kJ mol⁻¹) in parentheses determined by DSC at heating rate 10 °C min⁻¹

x	K ₁	K ₂	L _β	L _α	I
0	● 88.7 (64.8)	● 97.4 (19.2)	● 151.5 (9.3)	● 204.0 (nd)	●
1	●	● 31.3 (70.9)	●	● >230 (nd)	●
2	● 33.1 (1.0)	● 82.7 (104.9)	● 150.5 (13.0)	● 196.7 (5.2)	●
3	● 31.3 (1.1)	●	● 55.4 (67.2)	● 79.4 (1.0)	●
4	● 34.2 (1.7)	● 83.0 (26.5)	●	● 120.8 (73.3)	●
5	● 32.9 (1.1)	●	●	● 81.9 (64.4)	●

^a K = crystal; L_β, L_α = lamellar mesophases; I = isotropic liquid; nd = not determined.

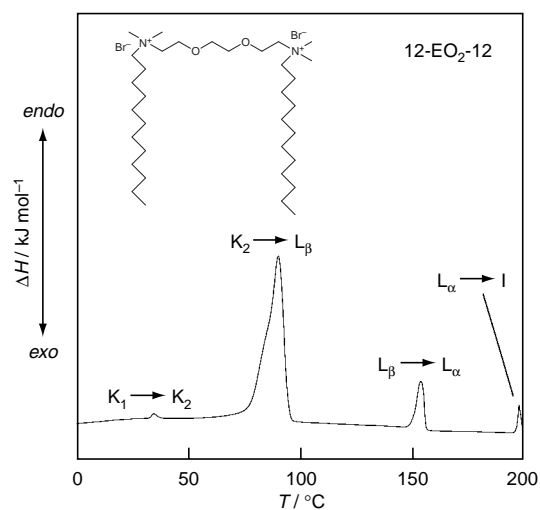


Fig. 1 First DSC heating scan of 12-EO₂-12 at 10 °C min⁻¹

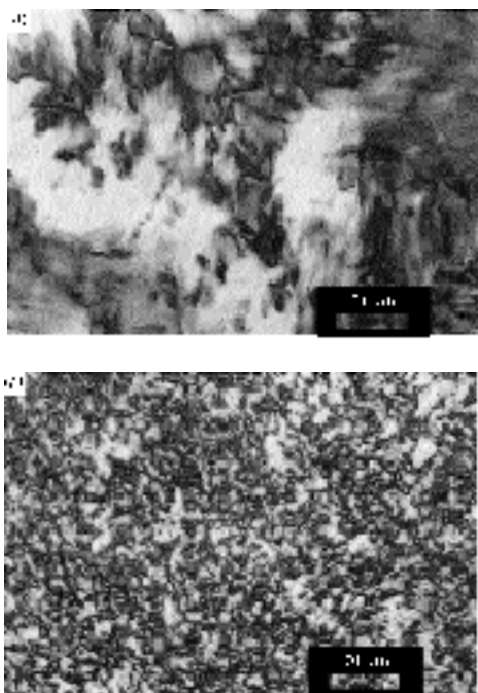


Fig. 2 Polarizing micrographs of the fan-like texture of 12-EO₂-12 at 120 °C (a) and of the mosaic textures at 180 °C (b)

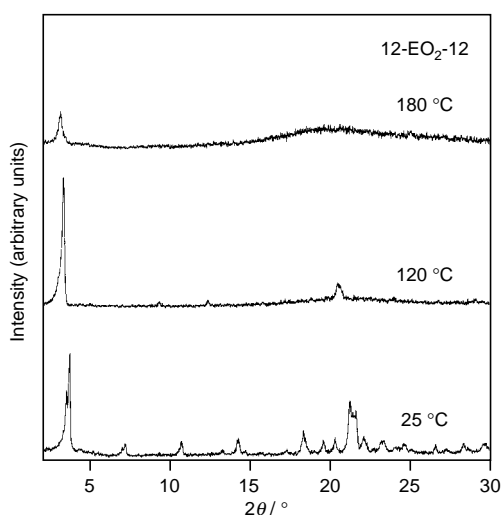


Fig. 3 XRD spectra of 12-EO₂-12 at 25, 120 and 180 °C

phase of 12-EO₂-12 has a layered structure with a period of 24.8 Å. The splitting of the low angle peak may indicate the presence of two coexisting crystalline modifications. At 120 °C, the typical diffraction pattern of an L_β phase is apparent,⁶ indicating that the alkyl chains attain a hexagonal packing with fully extended chain conformation. The layer period is increased to 26.7 Å. At 180 °C, 12-EO₂-12 adopts a smectic A structure⁶ indicating a disordered, liquid-like conformation of the alkyl chains and a layer period of 28.6 Å. Compared with a fully extended molecule (45.4 Å) or two extended C₁₂ chains (33.4 Å), the repeat distance is much smaller. Therefore, we assume an interpenetrating bilayer structure, as similarly proposed for conventional gemini surfactants⁵ and U-shaped benzimidazolium salts reported recently.⁷ For the L_α-phase of 12-EO₃-12, a period of 29 Å was found, while 12-EO₄-12 has a layer spacing of 25.2 Å in the viscous neat phase. Both values are very similar to that of 12-EO₂-12 and indicate the same structural arrangements in the mesophases.

For all compounds, hexagonal (H₁), cubic (V₁) and lamellar (L_α) lyotropic mesophases were observed in water at certain concentration intervals in the temperature range from 25 to 100 °C using the contact preparation technique. Lyotropic phase behaviour sets in at concentrations above 36 (x = 0) to 66 wt% (x = 5). The hexagonal phase is stable in the whole temperature range for all surfactants except for x = 0, where it disappears above 50 °C. The bicontinuous cubic phase is formed for 12-EO_x-12 with x = 2–4 between 25 and 100 °C, for x = 0 only above 35 °C, and for x = 1, 4 above 50 °C. For x = 0, the lamellar phase occurs above 65 °C, for x = 1 above 50 °C and for x = 2 above 40 °C. For x = 4 it is stable during the whole temperature range and for x = 3, 5, only until the transition to the isotropic melt occurs (see Table 1).

In summary, the mesophase behaviour of the 12-EO_x-12 compounds is rather complex. Compared to geminis with short and hydrophobic spacer units, the 12-EO_x-12 compounds with x ≥ 2 form thermotropic liquid crystalline phases quite readily, which can be easily identified. Therefore, such compounds may be useful as solvents for chemical reactions or as templating agents in the synthesis of inorganic materials. The lyotropic mesophase behaviour of the surfactants is also of considerable interest, since gemini surfactants with a hydrophobic spacer chain have been found to form ternary polymerizable microemulsions with styrene in water.⁸ Gemini surfactants with hydrophilic oligo(oxyethylene) spacer are expected to exhibit similar or even improved properties due to a higher flexibility.

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Notes and References

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§ Selected data for 12-EO₂-12: C₃₄H₇₄N₂O₂Br₂ (702.28) (Calc. C, 58.11; H, 10.61; N, 3.99. Found C, 57.97; H, 10.75; N, 4.13); δ_H(300 MHz, CDCl₃) 0.85 (t, 6 H), 1.22, 1.32 (s, m 36 H), 1.7 (m, 4 H), 3.40 (s, 12 H), 3.54 (m, 4 H), 3.75 (s, 4 H), 3.90 (m, 4 H), 4.10 (m, 4 H); 12-EO₃-12: C₃₆H₇₈N₂O₃Br₂ (746.84) (Calc. C, 57.90; H, 10.53; N, 3.75. Found C, 57.48; H, 10.54; N, 3.76); δ_H(300 MHz, CDCl₃) 0.85 (t, 6 H), 1.22, 1.32 (s, m 36 H), 1.70 (m, 4 H), 3.41 (s, 12 H), 3.54 (m, 4 H), 3.61 (m, 4 H), 3.72 (m, 4 H), 3.90 (m, 4 H), 4.08 (m, 4 H). 12-EO₄-12: C₃₈H₈₂N₂O₄Br₂ (790.89) (Calc. 57.71; H, 10.45; N, 3.54. Found C, 57.81; H, 10.60; N, 3.67); δ_H(300 MHz, CDCl₃) 0.85 (t, 6 H), 1.22, 1.32 (s, m 36 H), 1.70 (m, 4 H), 3.42 (s, 12 H), 3.6 (m, 12 H), 3.72 (m, 4 H), 3.88 (m, 4 H), 4.08 (m, 4 H). 12-EO₅-12: C₄₀H₈₆N₂O₅Br₂ (834.94) (Calc. C, 57.54; H, 10.40; N, 3.36. Found C, 57.37; H, 10.59; N, 3.44) δ_H(300 MHz, CDCl₃) 0.85 (t, 6 H), 1.22, 1.32 (s, m 36 H), 1.70 (m, 4 H), 3.42 (s 12 H), 3.6 (m, 16 H), 3.72 (m, 4 H), 3.88 (m, 4 H), 4.08 (m, 4 H).

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