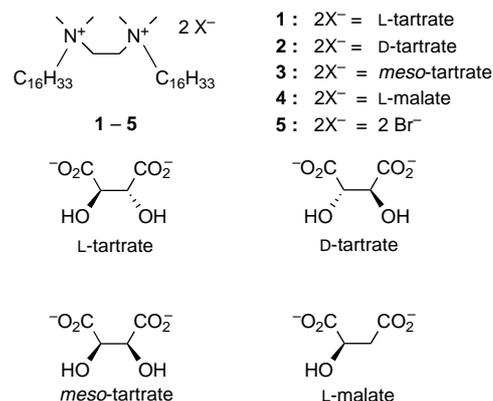[32] a) B. L. Goodall, W. J. Kroenke, R. J. Minchak, L. F. Rhodes, *J. Appl. Polym. Sci.* **1993**, *47*, 607; b) M. McCann, D. McDonnell, B. L. Goodall, *J. Mol. Catal. A* **1995**, *96*, 31; c) L. F. Rhodes (B. F. Goodrich, USA), EP-B 0435146 A2, **1990** [*Chem. Abstr.* **1991**, *115*, 184150]; d) A. M. Mazany (B. F. Goodrich, USA), EP-B 0755938 A1, **1995** [*Chem. Abstr.* **1997**, *126*, 200209].

1 : 2 X⁻ = L-tartrate	
2 : 2 X⁻ = D-tartrate	
3 : 2 X⁻ = *meso*-tartrate	
4 : 2 X⁻ = L-malate	
5 : 2 X⁻ = 2 Br⁻	

Gemini Surfactants as New, Low Molecular Weight Gelators of Organic Solvents and Water**

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During the last decade a number of reports have described the solution-state self-assembly of small molecules into elongated aggregates such as rods, ribbons, helices, or tubules. When these structures are sufficiently long and entangled they may entrap the solvent molecules in a network and lead to the formation of gels.[1] Although the organization of the aggregates has rarely been elucidated at the molecular level,[2] it is generally agreed that the process of aggregate elongation in water or in organic solvents arises from one or more of several factors: the presence of chiral centers often induces helicity and decreases the crystallinity observed for racemates;[1] directional attractive interactions such as hydrogen bonding[3] or face-to-face π–π aromatic stacking[4] help generate linear arrays of molecules. In gemini[5] (dimeric) surfactants, covalent connections between charged head groups were also shown to promote the formation of wormlike micelles and tubules in water.[6, 7] Herein we show that head-group connection also allows gemini surfactants to gel organic solvents upon their assembly into aggregates similar to those formed in water.

Compounds **1**–**5** consist of dimers of cetyltrimethylammonium ions (CTA) with various counterions. Compounds **1** and **2** form gels in chlorinated solvents (CH_2Cl_2, $CHCl_3$, $Cl_2CHCHCl_2$) that remain unchanged after several months. At temperatures above 40 °C the solutions are completely transparent and fluid. They become translucent and viscous upon standing for several hours at 25 °C. The solvent thickening is so efficient that a gel as dilute as 10 mM (gel point for $CHCl_3$) in a 1 cm diameter test tube can be turned upside down without any flow. This means that one molecule of **1** entraps about 1200 molecules of $CHCl_3$. At concentrations lower than the gel point a gel phase separates, and leaves a layer of free solvent.

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When warm solutions of **1** and **2** are mixed in equimolar proportions no gel forms, and the racemate partially precipitates. The *meso* derivative **3** is poorly soluble in chlorinated solvents, and does not form gels either. Thus, for this system, chirality seems essential for gel formation. The gels are easily disrupted upon the addition of alcohols (5–10% volume%) which suggests that hydrogen bonding also plays a role in gel cohesion. The importance of hydrogen bonds is supported further by the fact that **4**, which lacks one of the hydroxyl groups of **1**, does not form gels with organic solvents. Nevertheless, the residual quantities of water[8] contained in a freshly opened bottle of solvent are necessary to partially solvate the polar groups. In anhydrous solvents **1** and **2** tend to crystallize instead of forming gels.

The most probable structure for these gels is thus an entangled network of long fibers with polar groups at the core of the aggregate, and nonpolar hydrocarbon chains in contact with the solvent, like in an inverted long micelle, or in an inverted ribbon.[9] Yet, hydrogen bonding and chirality are not sufficient to explain the formation of the fibers, and head-group connection between the ammonium ions also plays a critical role. Indeed, the monomeric form (CTA)₂-L-tartrate is freely soluble in chlorinated solvents, and does not form gels. In water, hydrophobic effects dominate the process of surfactant aggregation. Short and rigid covalent connections enforce proximity between charged head groups that would otherwise repulse each other. The result is a change in the spontaneous curvature of the water–surfactant interface, as under the screening effect of salt[10] or of a hydrophobic counterion.[11] In nonpolar media the aggregation is directed by electrostatic forces. A possible effect of head-group connections is the reciprocal bridging of bisanions and biscations, a prerequisite to the assembly of a noncovalent polymeric material.[12]

The texture of the gels were examined with transmission electron microscopy (TEM). The images revealed very regular and long helical fibers (Figure 1A). The pitch is 130 nm for a fiber with a width of 20 nm and a length exceeding one micron. The L-tartrate **1** gives exclusively right-handed helices, and its enantiomer **2** gives left-handed helices. These helices are strongly entangled, and sometimes pack into parallel domains. Although the TEM images do not show the inner structure of the helices, their thickness indicate that they are superstructures, probably consisting of stacked rods or ribbons.
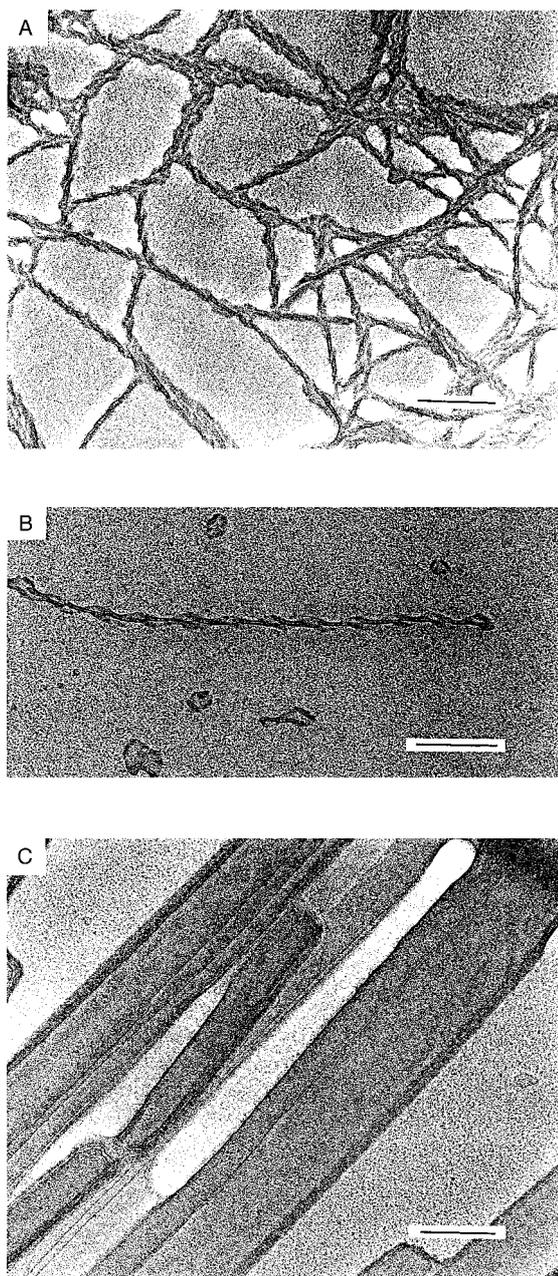
Figure 1. TEM image of the gel formed by **1** in CHCl₃ (A); an individual helix of **1** in water (B); the gel formed by **1+2** in water (C). The scale bar represents 200 nm.

Besides the chlorinated solvents mentioned above, **1** and **2** also form gels with other polarizable solvents such as CCl_4, toluene, xylenes, chlorobenzene, or pyridine, but the gels thicken at slightly higher concentrations (ca. 20–30 mM). Compounds **1** and **2** are not soluble in hydrocarbons, Et_2O, EtOAc, or acetone. No gels are formed in alcohols. However, we found that **1** and **2** are among the rare compounds having the ambidextrous ability to gel water as well as organic solvents.[9a, 13] This could in fact be expected on the basis that the dibromide **5** also forms long tubules in water.[6] For this system, chirality is not required for gelation in aqueous media, and the racemic mixture **1+2** consistently gels water without crystallizing. However, the observation that **3** and **4** are not gelators shows that even in water the number and the orientation of the hydroxyl groups of the tartrate molecules are critical.

No phase separation (gel point) was observed upon dilution of the gels in water. Even at concentrations below 1 mM, the gels were always formed across the entire sample, and simply became more easily and irreversibly disrupted under mechanical stress. Interestingly, the gels formed by **1+2** proved more viscous and less fragile than the gels formed by **1** or **2** alone. With TEM we observed multilayered platelets that are several μm long and 0.1–0.3 μm wide for **1+2** (Figure 1C) and right-handed and left-handed helical multilayered ribbons for **1** and **2**, respectively (Figure 1B). The pitch of the helices is 250 nm; approximately twice the pitch of the helices observed in chloroform. Overall, the structures observed in water very closely resemble those in chloroform. In particular, one enantiomer generates a helix with the same chirality in both water and chloroform.

In view of the data presented here, we propose that the aggregates in water and in organic solvents both have the multilayered structure shown in Figure 2. The cationic head-group layers are held in close contact by bridging bisanions and a network of hydrogen bonds, which involves some water molecules. In water the external layers of the stack expose their polar heads to the solvent, whereas in organic solvents only hydrophobic chains are exposed to the solvent. As a consequence of the similarity of the inner structure of the aggregates in different solvents, a given chiral anion induces similar helicities regardless of the media.

In conclusion, we have described new low molecular weight gelators based on gemini surfactants.[1a] Covalent connections
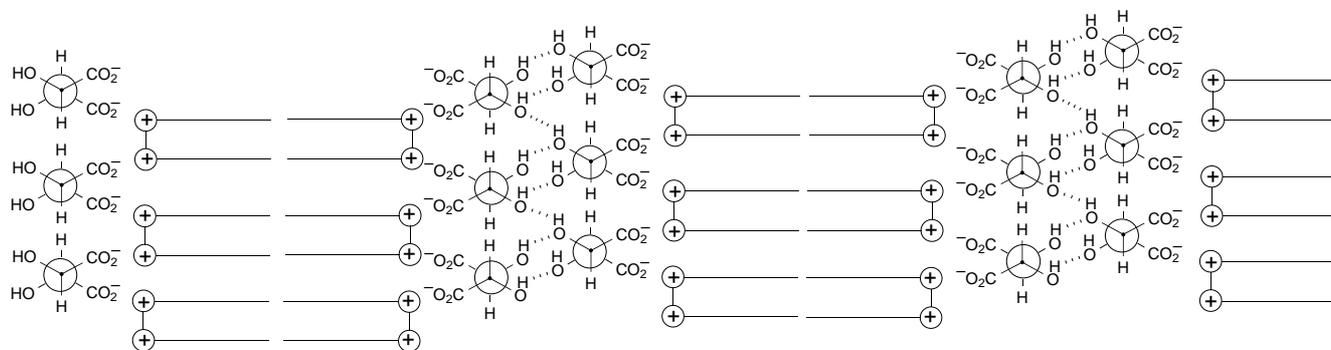

Figure 2. Proposed structure for the aggregates of **2** in water and in organic solvents. The dimeric cations are shown schematically, and the D-tartrate molecules are shown as Newman projections. Other conformers of the tartrate molecules cannot be ruled out, neither can anion bridges across the gap between two cationic layers.

between the charged head groups as well as chiral centers in the counterions are critical factors for determining the morphologies of the aggregates and their ability to gel various solvents.

Experimental Section

Compound **5** was synthesized as described before.[6] Compounds **1 – 4** and the CTA tartrates were prepared from **5** (dissolved in a water/methanol mixture) or cetyltrimethylammonium bromide by elution with water on a strongly basic anion exchange resin (Dowex 1 × 8, 50 – 100 mesh, 10 equivalents). The ammonium hydroxides were mixed with an equivalent amount of a tartaric acid, and the solution was lyophilized. The products were recrystallized from $CHCl_3/Et_2O$ (1/9, v/v) or $EtOH/Et_2O$ (1/9, v/v).

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2-Nitrobenzylarsonium Compounds That Photorelease Heavy-Atom Cholinergic Ligands for Time-Resolved Crystallographic Studies on Cholinesterases**

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Heavy-atom derivatives have found widespread use in macromolecular crystallography, because they are essential in obtaining correct diffraction phases which are required for solving the three-dimensional structure of proteins.[1] Photolabile precursors of biologically interesting molecules, which can be converted rapidly from an inactive form to an active form by light (caged compounds), can provide temporally and spatially controlled release of enzyme substrates or receptor ligands by rapid photolysis,[2] and are thus important tools in the time-resolved crystallographic studies[3] of structural changes at the atomic level during an enzymatic reaction. Here we present 2-nitrobenzylarsonium compounds **1 – 3** (Scheme 1) as photolabile precursors of cholinergic ligands
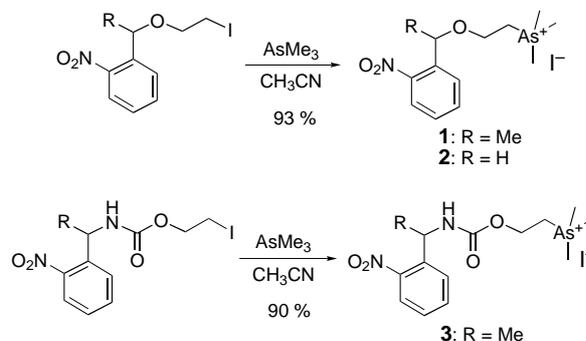
Scheme 1. Synthesis of **1 – 3**.

that contain arsenic as a heavy-atom. They were prepared to facilitate an investigation of the catalytic process of cholinesterases by time-resolved crystallography.

Both acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE) hydrolyze the neurotransmitter acetylcholine very rapidly to acetate and choline.[4] Although the three-dimensional structures of AChE[5] and of several AChE-inhibitor complexes[6] have been solved, questions concerning the traffic of substrate and products to and from the active

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