Isolated Fluid Polyhedral Vesicles

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We report the spontaneous conversion of spherical vesicles of octyltrimethylammonium perfluorooctanoate, $C_7F_{15}COO^-C_8H_{17}N^+$-$(CH_3)_3$ (OTAPFO) into isolated polyhedral (faceted) vesicles. The above compound constitutes a salt-free catanionic system or "true" ion-pair amphiphile (IPA),[1,2] in which the anion and cation, which comprise mutually incompatible hydrophobic chains are, by definition, in equimolar proportions. Most remarkable is the fact that the bilayers remain in the fluid state in the polyhedral vesicles.

The only previous example of regular polyhedral vesicles is that of the micrometer-sized *crystalline* icosahedra made from myristic acid/cetyltrimethylammonium hydroxide mixtures (MA/CTAOH) reported by Dubois et al.[1,3,4] Obtaining these faceted vesicles required that an excess of myristic acid be present. The driving force for their formation was the cocrystallization of the two amphiphiles in the bilayer, which resulted in the expulsion of part of the anionic species, which segregated and concentrated into pores located at the vertices of the icosahedra.

One first fundamental difference is that the bilayers of the polyhedra reported here are in the *fluid* state. The shortness of the chains of our catanionic system does not allow a gel-to-fluid transition at room temperature. A second critical difference is that in the previous work the authors needed to use an excess of the anionic species,[3] while OTAPFO is a true IPA. The nature of the objects (disks, polyhedra, punctured planes) varied with the stoechiometry.[3–5] By contrast, our system self-adjusts on the surface of the vesicle's bilayer, likely owing to the mutual incompatibility of the fluorinated chains with the hydrogenated chains, to produce the segregated nanodomains that lead to facets formation. The observation of a transformation of spherical vesicles into polyhedral vesicles is also novel. Finally, the new polyhedral objects are smaller by an order of magnitude than the earlier reported ones.

A few examples of unilamellar[6] and multilamellar[7] spherical vesicles have been obtained from other salt-free catanionic systems, but no polyhedral structures were reported. Fluorinated amphiphiles have a more pronounced tendency than their hydrogenated analogues to self-assemble in water, collect at interfaces, and induce nanocompartmentation.[8–12] Only a few studies have involved hybrid hydrocarbon/fluorocarbon IPAs. The rheology of some alkylammonium perfluorocarboxylates has been studied,[13] but the nature of any aggregates present was not determined. Alkyldimethylamine oxide dihydroperfluorooctanoic acid[14] and sugar-based fluorocarbon/hydrocarbon[15] IPAs were shown to form vesicles and coiled membranes in water, but no faceted vesicles were reported.

Aqueous solutions of OTAPFO (11 mmol L⁻¹) were prepared in distilled water (pH = 7.4) and sonicated for 1 min to ensure efficient dispersion. Immediately after preparation, well-defined aggregates with an average diameter of ∼200 nm (polydispersity
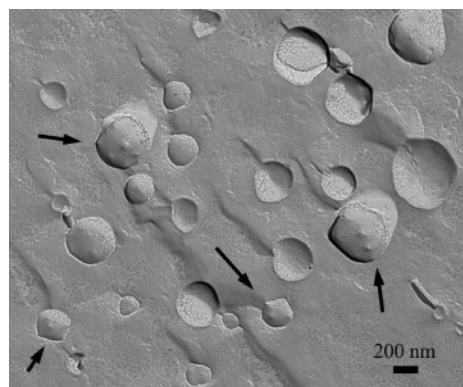
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Figure 1. FF-TEM of self-assemblies formed by the octyltrimethylammonium perfluorooctanoate IPA system in water (11 mmol L⁻¹) one week after preparation. Spherical vesicles coexist with some faceted vesicles (arrows).

index $\sigma = 0.20$) were detected by dynamic light scattering (DLS). When analyzed by freeze fracture transmission electron microscopy (FF-TEM) one week after preparation, the samples were seen to consist in majority of spherical vesicles. However, some faceted polyhedral vesicles were also present (Figure 1).

After 1 month at 25 °C, the samples were composed in a large majority of faceted, polyhedral vesicles, as assessed by both FF-TEM and cryogenic transmission electron microscopy (cryo-TEM) (Figure 2; large field micrographs are provided in Supporting Information). As assessed by DLS, the average diameter of the vesicles increased during the first month, then leveled off at ∼300 nm ($\sigma = 0.25$), in agreement with the mean diameter measured on cryo-TEM images.

ζ-Potential determinations at 25 °C gave values of -80 ± 2 mV, immediately after sample preparation, and did not change significantly after 1 month. This value corresponds to an almost negligible negative surface charge density of approximately -0.01 μC cm⁻² (Supporting Information).

Differential scanning microcalorimetry experiments (Micro DSC III Setaram calorimeter: heating/cooling rate, 0.1 °C min⁻¹; cell volume, 0.7 mL) were performed on aqueous dispersions of OTAPFO (11 mmol L⁻¹) after a 1-month storage at 25 °C, that is, of samples consisting essentially of faceted vesicles. No peak was observed for temperatures ranging from 5 to 80 °C, showing that no transition had occurred (Figure 3). Under the same conditions, a freshly prepared dispersion of dipalmitoylphosphatidylcholine vesicles (DPPC, 11 mmol L⁻¹) shows the well-documented pretransition and gel-to-fluid transition at 35 and 42 °C, respectively.

One substantial difference with the catanionic system investigated by Dubois et al. is that the ions that compose the OTAPFO−IPA system both have a much shorter chain than the MA/CTAOH mixture components (C7−C8 vs C14−C16), causing the OTAPFO
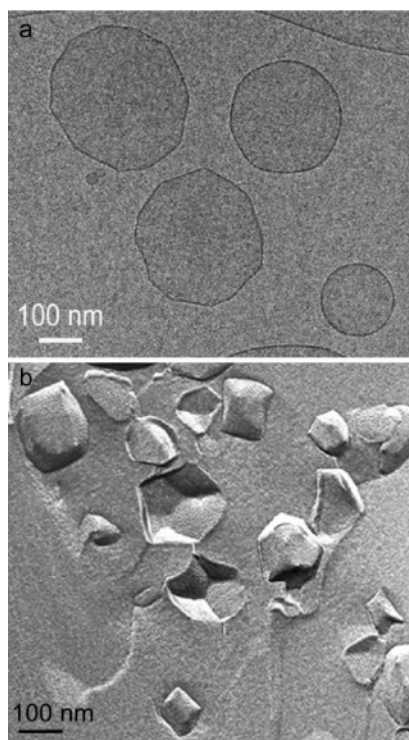
Figure 2. (a) Cryo-TEM and (b) FF-TEM of self-assemblies formed by the OTAPFO−IPA system in water (11 mmol L^{-1}). Faceted polyhedral vesicles were the majority in all the micrographs after 1 month at 25 °C.
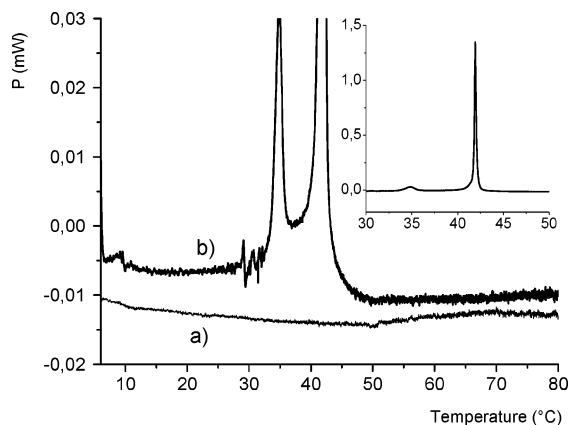

Figure 3. Micro-DSC heating curves of (a) a 1 month-aged aqueous suspension of OTAPFO vesicles (11 mmol L^{-1}; heating rate, 0.1 °C min^{-1}) and (b) freshly prepared DPPC vesicles (11 mmol L^{-1}). The DPPC curve has been offset by 0.003 mW to prevent overlap with the OTAPFO curve. The complete thermogram of DPPC is given in the inset.

bilayer to be in the fluid state at 25 °C. Another key difference is that the OTAPFO vesicles have a negligible surface charge.

A possible mechanism for the formation of faceted polyhedra vesicles with fluid bilayers and essentially null surface charge would involve a transbilayer flip-flop transfer that would lead fluorinated anions and hydrogenated cations to segregate and form nanodomains located at the inner and outer rim of the bilayer leaflet, respectively (Scheme 1). Because of their respective packing parameters (P ≈ 1.4 for C$_7$F$_{15}$COO$^-$ and 0.39 for C$_8$H$_{17}$N$^+$(CH$_3$)$_3$), the hydrogenated
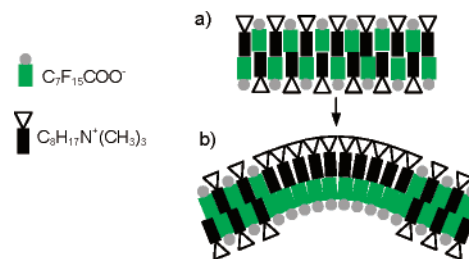
^{a} (a) Symmetrical bilayer membrane formed by the OTAPFO ion pair (zero spontaneous curvature). (b) The flip-flop of a few molecules would induce bilayer asymmetry, resulting in the formation of an angle (nonzero spontaneous curvature) and consequently of a faceted vesicle.

cationic surfactants are expected to be located on the outer rim of the bilayer (positive curvature) and the fluorinated ionic surfactants on the internal rim (negative curvature). A flip-flop of a few molecules would be sufficient to locally induce an asymmetry in the bilayer with a nonzero spontaneous curvature. Between the angles that would be formed, the bilayer portions would have a zero spontaneous curvature and could therefore be planar without energetic penalty. The time scale for flip-flop transfers is typically several days,[16] which is in agreement for the observed time of conversion of the spherical into faceted vesicles

Supporting Information Available: Experimental procedures, a large field micrograph, and calculations for packing parameters and surface charge density. This material is available free of charge via the Internet at http://pubs.acs.org.

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