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Electronic Supplementary Information

Spontaneous catanionic vesicles formed by the interaction between an anionic β-cyclodextrins derivative and a cationic surfactant.

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Experimental section

Materials

Benzyl-*n*-hexadecyldimethylammonium chloride (BHDC, Scheme 1 a), from Sigma (> 99 % purity) was used as received. Ultrapure water was obtained from a Millipore apparatus.

Amphiphilic CDs synthesis: The amphiphilic CDs (Scheme 1b - c, Mod-β-CD14) were synthesized in the laboratory following the procedure descripted previously[1] by the reaction of 2-tetradecen-1-ylsuccinic anhydride and β-CD under appropriated experimental conditions to obtain an average degree of substitution of one alkenyl chain per cyclodextrin molecule. ^{13}C NMR spectroscopy showed a mixture of isomers 1b and 1c as expected.[1]

Catanionic surfactant preparation: The catanionic surfactant ModCD14-BHD (Scheme 1d) was obtained by placing in a round-bottom flask a solution of Mod-β-CD14, BHDC in dimethylformamide (containing 0.8 mmoles of both surfactants) with a 10% molar excess of Na_2CO_3 and mixed in a shaker bath at room temperature for 24 hours. The suspension was filtered to eliminate most of the NaCl precipitate and the solution obtained was freeze-dried. The product, a brown liquid, was suspended in water and the salt impurities were removed by dialysis. The dialysate is a white suspension that yields 80 %a white solid after freeze-drying.

The formation of the catanionic surfactant was confirmed by NMR (Figure S3, supplementary information). ^1H NMR (400 MHz, D_2O) shows the aromatic protons at 7.55 ppm, vinyl protons at 5.41 ppm, the sugar protons at 5.08 and 3.91-3.63 ppm and methyl groups linked to quaternary ammonium at 3.05 ppm. From integrated values of aromatic and anomeric proton signals, we conclude that the catanionic association is 1:1. Using FT-IR spectroscopy (Figure S4, electronic supplementary information), we observed the presence of the carboxylate band at 1580 cm^{-1}.

Fluorescence and induced circular dichroism experiments: To introduce the molecular probe, a 1.0×10^{-3} M solution of PRODAN was prepared in methanol. The appropriate amount of this solution to obtain a given concentration of the probe in water was transferred into a volumetric flask, and the methanol was evaporated by bubbling dry N_2; then water was added to the residue to obtain aqueous solutions of PRODAN. Solutions of ModCD14-BHD $5.0x10^{-4}$M were prepared by dissolving a required amount

of solid ModCD14-BHD with an aliquot of the solution of PRODAN prepared previously.
Spectrofluorimetric analyses were carried out on a Jasco FP 777 spectrofluorimeter using 360 nm as excitation wavelength. The induced circular dichroism spectra were measured using a JASCO J-810 instrument.

DLS experiments: The apparent diameters of ModCD14-BHD vesicles were determined by dynamic light scattering (DLS, Malvern 4700 with goniometer). The laser used is an argon-ion operating at 488 nm and the methodology employed was described elsewhere.[2] The samples were filtered prior to the experiments using an Acrodisc with 0.45 μm nylon membrane (Sigma). To obtain statistic reliable results, 30 independent size measurements were taken for each of the samples. The scattering angle used was ninety degrees. CONTIN was used as the algorithm to obtain the apparent hydrodynamic diameter values. The polydispersity found for the different solutions investigated was always less than 5%.

TEM experiments: Micrographs were obtained with a JEOL 1200 EXII transmission electron microscope at a working voltage of 80 kV. The TEM samples were prepared by the negative-staining method. Phosphotungstic acid solution (2%) was used as the staining agent.

SEM experiments: Scanning electron microscopy (SEM) images of vesicles were obtained with a SIGMA (Carl Zeiss) field emission scanning electron microscope (FE-SEM), using electron irradiation and 8 kV with 100× magnification. SEM experiments were carried out in the Laboratorio de Microscopía Electrónica y Análisis por Rayos X (LAMARX), Facultad de Matemática, Astronomía y Física (FAMAF), Universidad Nacional de Córdoba, Argentina.

Table S1. Apparent hydrodynamic diameter (D_{app}) and polydispersity index (PDI) values of ModCD14– BHD vesicles in water at different surfactant concentrations. T = 25 °C.

Surfactant concentration (10^{-4} M)	**D_{app} (nm)**	**PDI**
1.0	240 ± 12	0.27
1.0 (two weeks later)	239 ± 12	0.22
0.8	223 ± 11	0.24
0.7	233 ± 15	0.26
0.1	240 ± 11	0.25

Figure S1. Photograph of a solution at 5.0×10^{-4} M of BHDC (left) and ModCD14-BHD (right).

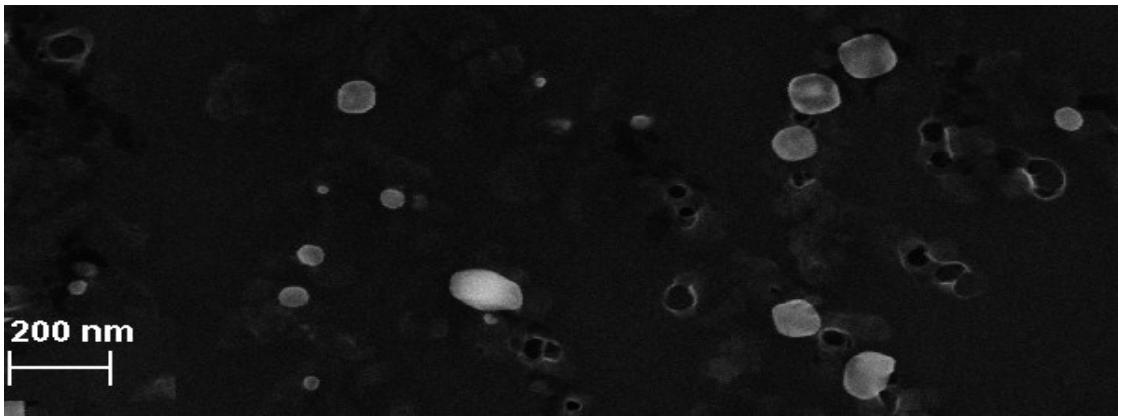

Figure S2. SEM image of ModCD14-BHD vesicles. [ModCD14-BHD] = $5x10^{-4}$ M.

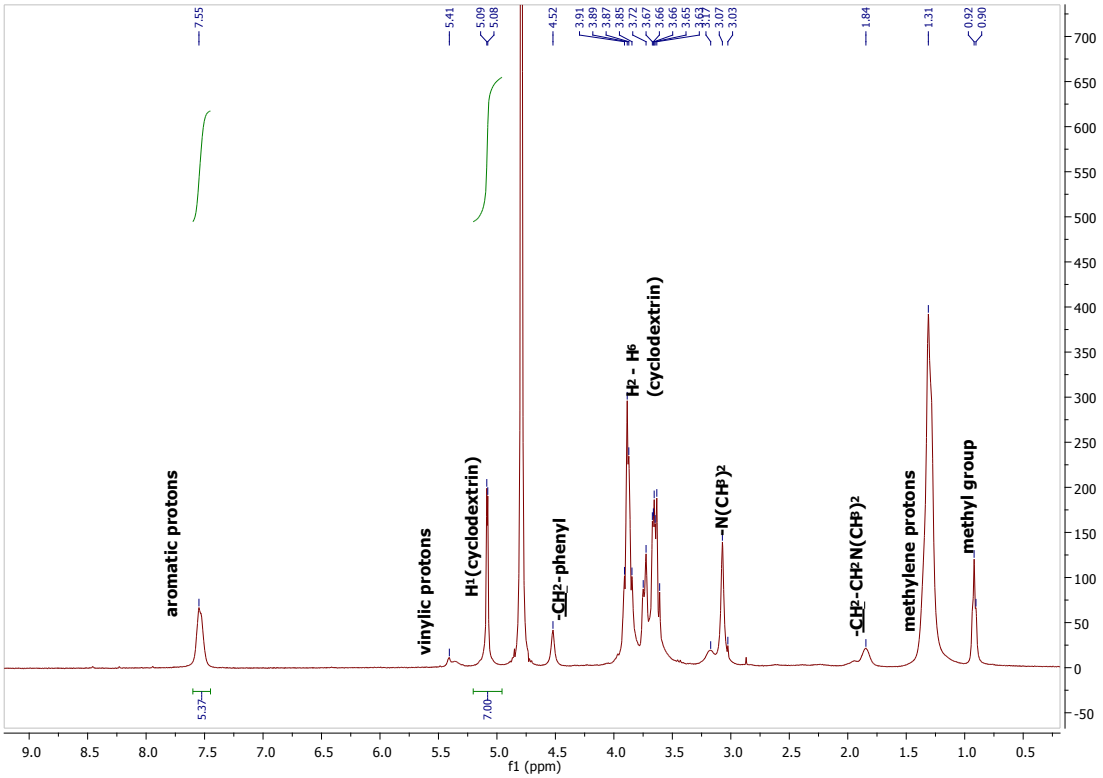

Figure S3. ^{1}H NMR of ModCD14-BHD in D_2O. [ModCD14-BHD] = 5x10^{-4} M.

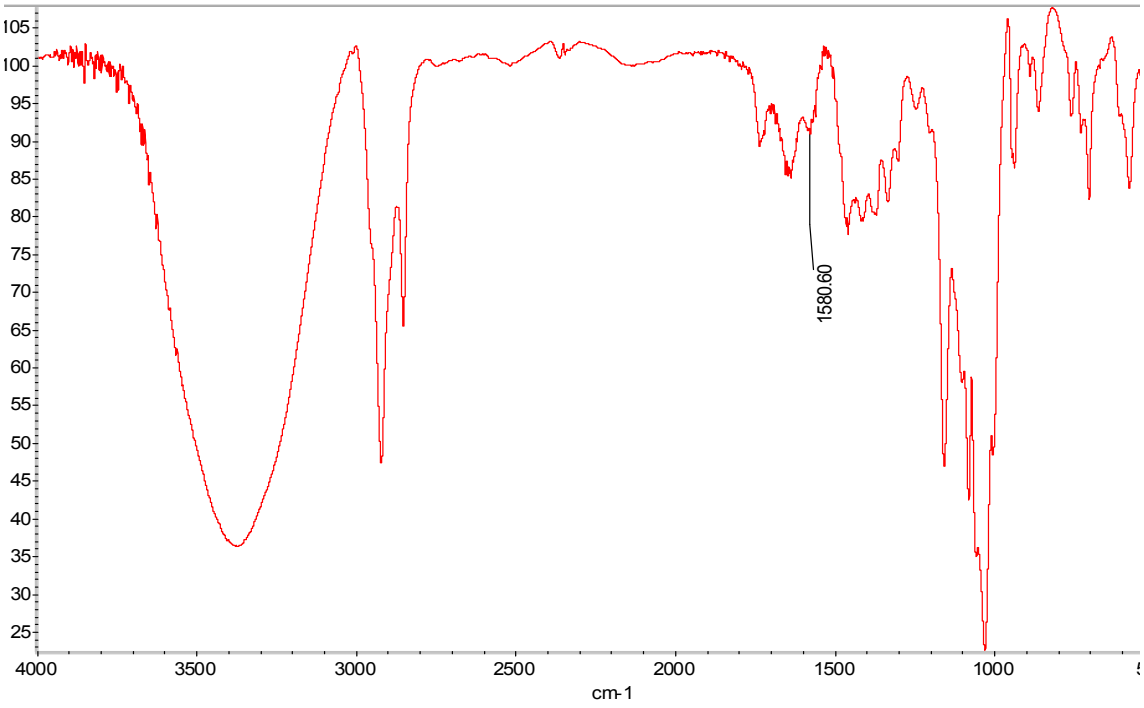

Figure S4. FT-IR (KBr) of ModCD14-BHD.

References

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