Supporting Information

Characterization and stability of catanionic vesicles formed by pseudotetraalkyl mixtures

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To 2 mL of acetic acid 0.66 mL (10x 10⁻³ mols) of chlorosulfonic acid were added at 0-5 °C with stirring. Then 2 gr (8.2 x 10⁻³ mols) of 8-hexadecanol were added drop wise and the mixture was stirred during 30 minutes at 4 °C. After that the reaction mixture was poured on 30 grams of cracked ice and 30 mL of n-butanol were added. The end of the reaction was checked by TLC using as eluent a mixture of ciclohexane/ isopropyl ether/acetic acid (86:14:0.8). Finally the solution was neutralized using sodium carbonate and then sufficient solid sodium bicarbonate was added in order to keep the solution saturated with inorganic sodium salts. The target compound was separated with the butanol layer and the aqueous layer was further extracted four times with butanol. The butanol extract was concentrated under vacuum to remove the water and the inorganic salts were separated by filtration. The butanol was removed under vacuum and the solid obtained was crystalized in methanol/acetonitrile.

Analytical data and spectral assignments:

Yield: 78%, MW: 344.2 g.mol⁻¹, ESI-MS, m/z= 321 corresponding to (M+H)⁺. Elem. Analy. Found: C, 54.3; H, 9.6; S, 8.8; Cal. for C₁₆H₃₃NaO₄S-0.5H₂O, C, 54.3; H,9.8; S, 9.0. ¹HNMR: $\delta_{\rm H}$ (CD₃OD), 0.8 [t, 6H, -C<u>H₃</u> alkyl chain], 1.2-1.4 [m, 24H, -C<u>H₂-, alkyl chain], 1.6 [m, 4H, -C<u>H₂-</u>CH(SO₄Na)-C<u>H₂-], 4.4 [m, 1H -CH(OSO₃Na)-]. ¹³CNMR: $\delta_{\rm H}$ (CD₃OD), 14.4 [<u>C</u>H₃-, alkyl chain], 23.7, 26.1, 30.4, 30.6, 30.7, 30.8, 33.0, [-<u>C</u>H₂-, alkyl chain], 35.2 [-C<u>H₂</u>-CH(SO₄Na)-C<u>H₂-], 80.9 [-C<u>H</u>(SO₄Na)-].</u></u></u>

Methods

The structure of the pure compound was checked by ¹H and ¹³C nuclear magnetic resonance (NMR) analyses which were recorded on a Varian spectrometer at 499.803(¹H) and 125.233 (¹³C) MHz, respectively, using the deuterium signal of the solvent as the lock. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). All measurements were carried out on 0.6 mL samples in 5 mm tubes using a 5 mm indirect broadband probe. ¹³C NMR spectra were recorded under composite decoupling to eliminate ¹³C-¹H coupling.

Mass spectroscopy (MS) spectra with fast atom bombardment (FAB) or electrospray techniques were carried out with a VG-QUATTRO from Fisons Instruments. Elemental analysis of the final compounds was also achieved.



Figure S1. SAXS spectra of DiDAB solutions at 10.0 (squares), 15.0 (circles), 20.0 (up triangles), 25 (down triangles), 30.0 (rhombuses) and 35.0 wt/wt% (cross) in water, at 25.0°C. The solid lines represent the fits obtained by a modified Caillè analysis.

% wt/wt	d (Å)	A _m (Ų/mol)
35	63.0	61
30	76.0	59
25	96.8	56
20	122.9	55
15	167.6	54
10	285.5	49

Table S1. Bragg repetition distances and area per surfactant molecule derived from SAXS spectra of DiDAB solutions in water at different wt/wt% at 25.0 °C.



Figure S2. Conductivity, κ , (μ S/cm) vs DiDAB concentration (mmol/kg) at 25.0 °C. The intersection of the straight lines identified the CMC.



Figure S3. Surface tension, γ , (mN/m) vs DiDAB concentration (mmol/kg) at 25.0 °C. The intersection of the straight lines identified the CMC.



Figure S4. Conductivity, κ , (μ S/cm) vs 8-SHS concentration (mmol/kg) at 25.0 °C. The intersection of the straight lines identified the CMC.



Figure S5. Surface tension, γ , (mN/m) vs 8-SHS concentration (mmol/kg) at 25.0 °C. The intersection of the straight lines identified the CMC.



Figure S6. Electromotive force, emF, (mV) vs 8-SHS concentration (mmol/kg) at 25.0 °C. The intersection of the straight lines identified the CMC.