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OPTICALLY ACTIVE SURFACTANTS - I - THE FIRST SYNTHESIS AND PROPERTIES OF SODIUM BIS [(S) ETHYL-2-HEXYL] SULFOSUCCINATES ("AEROSOL OT")

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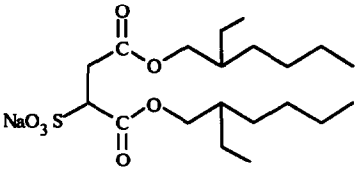
Abstract : *Optically pure (S) ethyl-2-hexan-1-ol (S)4 is prepared for the first time from (S) ethyl-2-hexanoic acid. Nucleophilic addition of sodium bisulfite on the bis [(S) ethyl-2-hexyl] maleate gives rise to an equimolar mixture of two optically active sodium bis [(S) ethyl-2-hexyl] sulfosuccinates diastereoisomers. The critical micelle concentration of these new optically active surfactants is almost identical to those of the well known racemic "Aerosol OT"*

Separation techniques based on chiral surfactants like micellar chromatography or liquid-liquid extraction afford new attractive means for racemate resolution [1]. The enantioselective ability of chiral micelles or other surfactant aggregates has been mostly applied in micellar catalytic hydrolysis in aqueous solutions [2] as well as in organic solvents by using reverse micelles or reverse water in oil microemulsions.[2b-c,3] Although various surfactants or mixture of surfactants and cosurfactants have been studied, relationships between the location of the surfactant chirality and the enantioselective ability of the resulting aggregates have not yet been established. Our approach to this problem is to use a single surfactant with, alternatively or simultaneously, an optical activity on the hydrophobic chain or near the polar head group. We have chosen a well known and widely used[4] surfactant molecule 1 [bis(ethyl-2-hexyl) sodium sulfosuccinate : "Aerosol OT"] containing three chiral carbon atoms, two on the lipophilic ethyl-2-hexyl susbtituents and one on the sulfosuccinate hydrophilic skeleton, which in fact has always been used as a mixture of eight diastereoisomers.

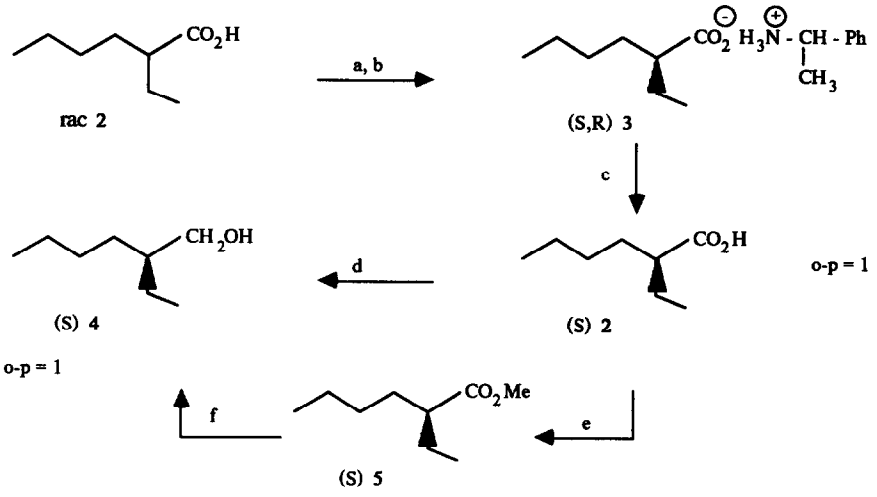


1 : "Aerosol OT"

In this paper, we wish to describe the first synthesis [5] of optically pure (S)ethyl-2-hexan-1-ol and its use for the preparation of "Aerosol OT" 1 with a lipophilic optical activity.

- **Synthesis of (S)ethyl-2-hexan-1-ol**

(S)ethyl-2-hexan-1-ol 4 is prepared from the commercially available racemic ethyl-2-hexanoic acid 2 (Scheme 1).



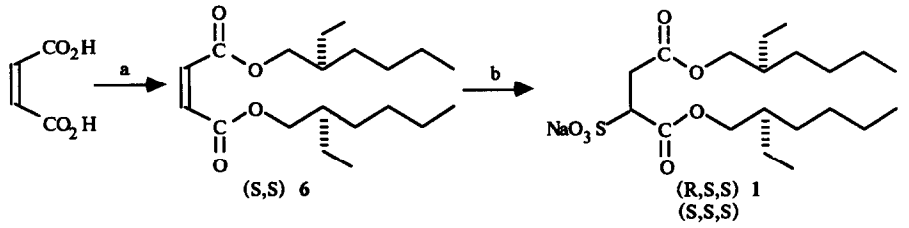
a : (R)α-methylbenzylamine (1 eq), CH_3CN, N_2, RT. then standing 3 weeks at 15°C, filtration of crystallized impure (R,S) 3 ; b : five recrystallisations in CH_3CN ; c : HCl 1N, ether, 24 h ; d : BH_3-Me_2S (1 eq), THF, - 20°C then RT overnight followed by distillation ; e : BF_3-MeOH, reflux, 72 h ; f : $LiAlH_4$ (1 eq), ether, 1 h at 0°C then 2 h at RT followed by distillation.

Scheme 1

The diastereoisomeric salts of (R)α-methylbenzylamine are separated by selective crystallisation in acetonitrile. The pure (S,R) ammonium salt 3 ($[\alpha]_D$ = + 7.7°, H_2O, 25 g.l^{-1}), isolated with 51 % yield after successive recrystallisations, is hydrolyzed with diluted hydrochloric acid in biphasic water-ether medium thus affording optically pure (S)ethyl-2-hexanoic acid (S) 2 ($[\alpha]_D$ = + 8.2°, neat) [7] with 97 % yield. The optical purity of (S) 2 is confirmed by ^{13}C NMR spectroscopic study of its quinine salt.[8] (S)ethyl-2-hexan-1-ol (S) 4 is obtained either by direct reduction of (S)-2 with BH_3 (path d, 73 % yield) or by reduction of the methylester (S) 5 with $LiAlH_4$ (path e, 72 % overall yield). Whatever the reduction procedure, the alcohol, purified by distillation, exhibits the same specific rotation ($[\alpha]_D$ = + 3.3°, $CHCl_3$, 55g.l^{-1}). The optical purity of (S) 4 is confirmed by ^{13}C NMR study of its ester of R(+)MTPA (Mosher's ester)[9] : the spectrum of the MTPA ester of racemic alcohol shows two pairs of peaks respectively at 30.27-30.18 ppm and 23.71-23.63 ppm corresponding to carbon atoms of each diastereoisomer while unique peaks are observed for the MTPA ester of (S) 4.

- **Preparation of optically active "Aerosol OT" 1**

The synthesis of the sulfosuccinic diester **1** is achieved by a slight modification of the usual procedure in two steps from maleic acid and (S)ethyl-2-hexan-1-ol (S) **4** (Scheme 2).



a : (S) **4** (1.9 eq), PTSA (0.05 eq), toluene-dioxane (75/25), reflux, 72 h ; b : $NaHSO_3$ (2 eq), water-isopropanol (50/50), 90°C, 24 h.

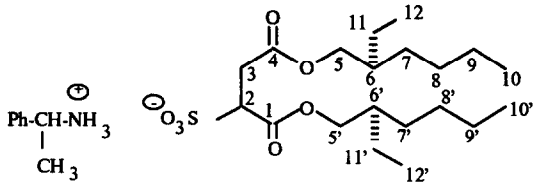
Scheme 2

The bis [(S)ethyl-2-hexyl] maleate (S,S) **6**, obtained by esterification of maleic acid by (S) **4** catalyzed by PTSA, is sulfonated with sodium bisulfite in water-isopropanol [10]. The sulfonation product, which is a mixture of two diastereoisomers, is isolated with 77 % yield after purification by column chromatography on silica gel ; the unique side product is unreacted **6** and under our experimental conditions hydrolysis of the sulfosuccinic diester does not occur. The specific rotation of **1** depends to a large extent on the solvent and on the wavelength : the specific rotation is higher in non polar solvents and increases when the wavelength is decreased (Table 2).

The addition of bisulfite on the activated double bond of maleate (S,S) **6**, which in our conditions involves an ionic mechanism[11], is not enantioselective and gives rise to an equimolar mixture of two diastereoisomers with R and S configuration of the carbon bearing the sulfonate anion. Since no discrimination between the two sodium salt diastereoisomers could be observed by usual methods, the presence of equimolar amounts of each diastereoisomer has been demonstrated by NMR spectroscopic study of their (R) α-methylbenzylammonium salts **7**.

The bis [(S)ethyl-2-hexyl] (R) α-methylbenzylammonium sulfosuccinates **7a** and **7b** are easily and quantitavely obtained by a cation exchange between the amine hydrochloride and **1** in biphasic system.[12]

Both the ^{1}H and the ^{13}C NMR spectra of this mixture of ammonium salts show a diastereoisomeric discrimination. In the ^{13}C NMR spectrum, the discrimination is mainly observed for the secondary carbon of the sulfosuccinic part (C_3 : 33.36 and 33.44 ppm) and the two carbonyl nuclei (C_4: 168.92 and 169.06 ppm ; C_1 : 171.01 and 171.05 ppm). The ^{1}H NMR spectrum shows a discrimination between the two diastereotopic nuclei H_a and H_b (see experimental section). In all cases, the two peaks corresponding to nuclei of each diastereoisomer are of equal intensity thus demonstrating the presence of equimolar amounts of each diastereoisomer.

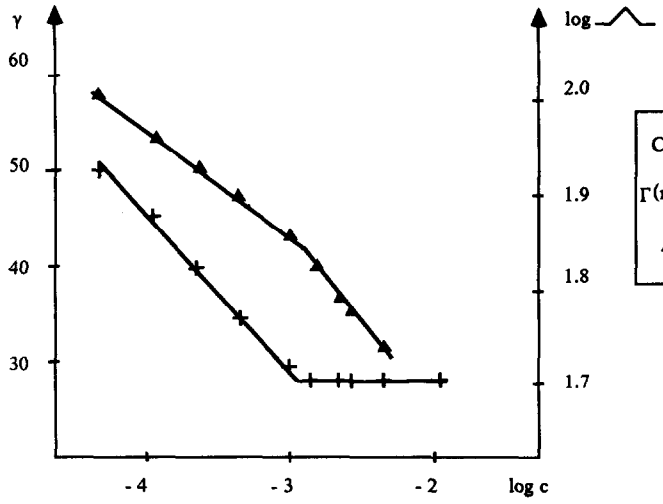


7a (R,R,S,S)

7b (R,S,S,S)

- **Surfactant properties of the new optically active "Aerosol OT" 1**

The critical micelle concentration (CMC) of optically active "Aerosol OT" 1 has been determinated by conductivity and surface tension measurements (Figure 1). Within the accurancy of the measurement the CMC value (1.4 mM) is almost identical to those of racemic "Aerosol OT" 1 (1.1 mM) prepared and purified by the same procedure. Moreover, the similarity of the molar surface excess Γ and of the areas per molecule A at the air-water interface calculated for racemic and optically active "Aerosol OT" (Table 1) demonstrates that the optical activity on the lipophilic chains does not significantly affect the interfacial properties and the process of micellization. The similar properties determined here for diastereoisomeric surfactants are in good agreement with previously described comparative studies of other enantiomeric surfactants.[13]



	(rac) 1	optically active 1
CMC (mM)	1.1	1.4
Γ(mole.m^{-2})	1.2 10^{-6}	1.3 10^{-6}
A (nm^2)	1.4	1.3

Table 1

Figure 1 : Surface tension and equivalent conductivity vs log (concentration) (mol.l^{-1}) for aqueous solutions of optically active 1

(a) : (+ - + - +) surface tension γ (mN.m^{-1})

(b) : (▲-▲-▲) log equivalent conductivity (ms.l.cm^{-1} . mol^{-1})

- Conclusion

The synthesis of (S)ethyl-2-hexanol described here for the first time is useful for large scale preparations and affords means to prepare optically active surfactants such as "Aerosol OT" with enantiomerically pure chiral lipophilic chains. The mixture of two "Aerosol OT" diastereoisomers, resulting from the non enantioselective addition of bisulfite anion to the optically pure maleate diester, exhibits the same surfactant properties than the racemic compound. Further studies are currently being developed in our Laboratory to estimate the enantioselective ability of optically active AOT agregates in chemical reactions or in racemate resolution and to separate the surfactant diastereoisomers.

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EXPERIMENTAL SECTION

Commercial grade reagents were used without purification. Solvents were distilled by conventional methods. NMR spectra were recorded on a Jeol FX 90Q [^1H (89.55 MHz) and ^{13}C (22.50 MHz)] and a Brucker AM 300 MHz [^1H (300 MHz) and ^{13}C (75.47 MHz)] (Centre de Mesures Physiques de l'Ouest). The substitution of the carbon atoms were deduced from DEPT ^{13}C NMR spectra. High resolution mass spectra have been obtained by using a Varian MAT 311 spectrometer (Centre de Mesures Physiques de l'Ouest). Polarimetry measurements were performed on a Perkin-Elmer 241 MC apparatus. Surface tension measurements were obtained by the ring method with a Krüss K10T tensiometer. Conductivity measurements were carried out by using a radiometer CDM 80 equiped with a CDC 104 type radiometer electrode. Gas chromatography analysis were performed with a Carlo Erba FTV series 4000 instrument with a RSL 150 (apolar), 25 m long, capillary column ; temperature programme : isotherm at 40°C for 4 min, then increased at a rate of 10°C/min to 200°C and isotherm at 200°C ; detector and injector temperatures : 250°C and 210°C ; carrier gas N_2, pressure : 90 kPa. HPLC analysis were performed with a Waters 600E system equipped with a RP18 5µm, 25cm length (chrompack) column ; UV detection at 254 nm (LDC spectromonitor) ; eluant : methanol, 1ml.mn^{-1}. Elemental analysis were obtained from the "Service Central d'Analyse" (CNRS Vernaison). The results of elemental analysis are not significant for the hygroscopic compound 1 because the hydration number depends on the rapidity of the analysis.

- (S)ethyl-2-hexanoic acid : (S) 2

(S)ethyl-2-hexanoic acid was obtained by recrystallisation of its (R) phenyl-1-ethylamine salt according to the procedure previously mentionned[7]. A solution of 12.6 g (0.104 mole) of (R) phenyl-1-ethylamine in 420 mL of acetonitrile has been added dropwise (addition time : 30 mn) under nitrogen to a solution of 15 g (0.104 mole) of ethyl-2-hexanoic acid in 420 mL of acetonitrile. A gentle stirring has been maintained for two hours. The mixture was then allowed to stand at 15°C for 21 days. The precipitate of impure (S,R) salt 3 was separated by filtration, dried at 50°C overnight and recrystallized five times in acetonitrile. (S, R) 3 : Isolated yield 7.06 g (51 %) ; $[\alpha]_D$ = + 7.7° (water, c = 25 g.l^{-1}) ; ^1H NMR (89.55 MHz, D_2O, δ ppm) : 0.85 (t, J = 7 Hz, $2CH_3$), 1.26 (m, $4CH_2$), 1.65 (d, J = 7 Hz, CH_3), 2.11 (m, CH), 4.74 (q, J = 7 Hz, CH) ; 7.49 (s, ArH) ; ^{13}C NMR (22.5 MHz, D_2O, δ ppm) : 14.22 (CH_3), 15.82 (CH_3), 22.26 (CH_3), 24.62 (CH_2), 28.44 (CH_2), 32.01 (CH_2), 34.80 (CH_2), 53.36 (CH), 53.49 (CH), 128.90 (C ortho), 131.37 (C para), 131.64 (C meta), 140.96 (C ipso), 188.60 (CO) ; Elemental analysis found : 72.51 % C, 9.97 % H, 5.44 % N, 11.72 % O, calculated : 72.41 % C, 10.17 % H, 5.28 % N, 12.06 % O.

(S) 2 has been isolated by hydrolysis of (S,R) 3 salt according to the following procedure : 125 mL of 1M chlorhydric acid and 250mL of ether were added to 7.06 g (26.6 mmole) of (S,R) 3 salt and the resulting mixture vigourously stirred for 24h. The organic layer was separated by decantation and the aqueous phase washed three times with 100 mL of ether. The combined organic phases have been washed twice with 250 mL of brine and dried over sodium sulfate. (S) 2 has been isolated after removal of the solvent under vacuum : 3.72 g (97 %), liquid. $[\alpha]_D$ = + 8.2° (neat) ; litt[7] : + 8.2° ; GC T_R = 10.85 mn, 100 % ; ^1H NMR (89.55 MHz, $CDCl_3$, δ ppm) :

0.88 (t, J = 7 Hz, CH_3), 0.94 (t, J = 7 Hz, CH_3), 1.20-1.80 (m, $4CH_2$), 2.25 (p, J = 7 Hz, CH), 10.30 (broad, CO_2H) ; ^{13}C NMR (22.55 MHz, $CDCl_3$, δ ppm) : 11.71 (CH_3), 13.88 (CH_3), 22.68 (CH_2), 25.22 (CH_2), 29.58 (CH_2), 31.51 (CH_2), 47.25 (CH), 183.25 (CO_2H) ; elemental analysis found : 66.89 % C ; 11.16 % H ; calculated : 66.67% C ; 11.11 % H.

- **Determination of the optical purity of (S) 2**

The optical purity of (S) 2 has been determinated according to the previously described procedure[8] by ^{13}C NMR spectroscopic study of its quinine salt. The quinine salts of (rac) 2 and (S) 2 have been prepared as follow : a solution of quinine (0.9 g, 2.77 mmole) in 60 mL acetone was added to a solution of (rac) 2 or (S) 2 (0.4 g, 2.77 mmole) in 20 mL acetone ; the reaction mixture was allowed to stand for 12 hours at 0°C. The quinine salts were isolated after concentration under vacuum. The ^{13}C NMR spectra (75.47 MHz, $CDCl_3$) of (rac) 2 and (S) 2 quinine salt shows respectively a pair of peaks at 25.72 and 25.88 ppm for the corresponding carbon atoms in each diastereoisomer and only one peak at 25.88 ppm corresponding to unique diastereoisomer.

- **(S)ethyl-2-hexan-1-ol : (S) 4**

(S)ethyl-2-hexan-1-ol has been prepared by two independent ways :

- Reduction of (S) 2 with borane

Two borane sources have been tested ($BH_3.Me_2S$ and BH_3.THF). The reduction with the sulfur complex is more efficient. A solution of $BH_3.Me_2S$ (6.9 mmole) in 10.5 mL THF was added dropwise under nitrogen to a solution of (S) 2 (1g, 6.9 mmole) in 7 mL THF previously cooled at -20°C. When the addition was complete (5mn), the reaction mixture was allowed to stir at room temperature overnight. A mixture of 25 mL THF and 25 mL water, was then added at 0°C, THF was then partially removed under vacuum and the resulting mixture extracted three times with 50mL ether. The combined organic phases were then washed with 50 mL of dilute sodium bicarbonate (30 %) and dried over sodium sulfate. (S) 4 has been isolated after concentration under vacuum : 0.66 g (73 %) ; liquid ; $[\alpha]_D$ = +3.4° ($CHCl_3$, 58 $g.l^{-1}$) ; GC : t_R = 7.7 mn, 90 %.

- Reduction of the methyl ester (S) 5 with $LiAlH_4$

The methyl ester (S) 5 has been obtained either by acid catalyzed reaction of methanol with (S) 2 or reaction of BF_3.MeOH with (S) 2 the respective yields were 71 % and 75 %. The first procedure is more efficient for large scale preparations. (S) 5 : liquid, $[\alpha]_D$ = + 7.6 ($CHCl_3$, 75 $g.l^{-1}$) ; GC : t_R = 8.73 mn, 100 % ; ^1H NMR (89.55 MHz, $CDCl_3$, δ ppm) : 0.88 (t, J = 7 Hz, $2CH_3$), 1.10-1.80 (m broad, $4CH_2$), 2.24 (p, J = 7 Hz, CH), 3.67 (s, OCH_3). Mass spectrometry (EI, 70 eV) : $M^{+\bullet}$(calc) : 158.1307, $M^{+\bullet}$(found) : 158.1304 (0.3 %) ; presence of fragments resulting from a Mac-Lafferty rearrangement at $M^{+\bullet}$- C_2H_4 (calc) : 130.0994, $M^{+\bullet}$- C_2H_4 (found) 130.0995 and at $M^{+\bullet}$-C_4H_8 (found) : 102.0.

$LiAlH_4$ (1.85 g, 48.5 mmole) was slowly added at O°C to a solution of (S) 5 (7.7 g, 48.5 mmole) in 100mL ether. The reaction was allowed to stir at 0°C for 1 hour, at room temperature for 2 hours and then filtrated. A saturated aqueous NH_4Cl solution (1L) was added to the organic filtrate. After addition of few drops of concentration HCl, the aqueous phase was extracted twice with 200 mL ether. The combined organic phases were washed twice with 200 mL brine and dried over sodium sulfate. (S) 4 has been isolated after removal of the solvent under vacuum and distillation under reduced pressure : 5.82 g (92 %), bp = 60°C (7 mbar), $[\alpha]_D$ = + 3.3° ($CHCl_3$, 53 $g.l^{-1}$), GC : t_R = 8.97 mn, 100 % ; ^1H NMR (89.55 MHz, $CDCl_3$, δ ppm) : 0.89 (t, J = 7 Hz, $2CH_3$), 1.28 (m broad, $4CH_2$ and CH), 1.34 (s, OH), 3.55 (d, J = 3.5 Hz, CH_2) ; ^{13}C NMR (22.55 MHz, $CDCl_3$, δ ppm) : 11.01 (CH_3), 13.99 (CH_3), 23.06 (CH_2), 25.35 (CH_2), 29.11 (CH_2), 30.15 (CH_2), 41.99 (CH), 65.10 (CH_2-O). Mass spectrometry (EI, 70 eV) : $M^{+\bullet}$-H_2O (calc) : 112.1252, $M^{+\bullet}$- H_2O (found) : 112.1244 ; $M^{+\bullet}$- CH_3OH (calc) : 98.1095, $M^{+\bullet}$- CH_3OH (found) : 98.1094 ; $M^{+\bullet}$not observed. Elemental analysis found : 73.98 % C, 13.93 % H ; calculated : 73.85 % C, 13.85 % H.

- **Determination of the optical purity of (S) 4 :**

The optical purity of (S) 4 has been determined by NMR spectroscopy of its Mosher's ester. (R) [2-methoxy-2-phenyl-2-(trifluoromethyl) acetic] esters of (S) 4 and (rac) 4 have been prepared by reaction of MTPA (500mg, 2.1 mmole) with (S) 4 or (rac) 4 (290 mg, 2.1 mmole) in the presence of catalytic amount of PTSA (40 mg) in toluene at reflux for 24 h, followed by usual washing with water. The ^{13}C NMR ($CDCl_3$, 75.47 MHz) spectrum of Mosher's ester of (rac) 4 shows two pairs of peak respectively at 30.27-30.18 ppm and 23.71-23.63 ppm corresponding to carbon atoms of each diastereoisomer while unique peaks are observed in the spectrum of (S) 4 Mosher's ester. The spectroscopic data (δ ppm) are : (rac) 4 MTPA ester : 10.89 (CH_3), 13.98 (CH_3), 22.90 (CH_2), 23.63 and 23.71 (CH_2, (R,S) and (R,R) diastereoisomers), 28.79 (CH_2), 30.18 and 30.27 (CH_2, (R,S) and (R,R) diastereoisomers), 38.69 (CH), 55.41 (OCH_3), 68.59 (OCH_2), 123.42 ($^1J_{C-F}$ = 288 Hz, CF_3), 127.96 (CH, aromatic), 128.39 (CH, aromatic), 129.58 (CH, aromatic), 132.47 (C ipso), 166.78 (CO).
(S) 4 MTPA ester : 10.89 (CH_3), 13.98 (CH_3), 22.91 (CH_2), 23.64 (CH_2, (R,S) diastereoisomer), 28.81 (CH_2), 30.28 (CH_2, (R,S) diastereoisomer), 38.71 (CH), 55.41 (OCH_3), 68.60 (OCH_2), 123.43 ($^1J_{C-F}$ = 288 Hz, CF_3), 127.41 (CH, aromatic), 128.39 (CH aromatic), 129.58 (CH, aromatic), 132.49 (Cipso), 166.78 (CO).

- **bis [(S)ethyl-2-hexyl] maleate : (S,S) 6**

2.70 g (23.3 mmole) of maleic acid, 0.14 g of PTSA, 5.77 g (44.0 mmole) of (S) 4 in 15mL of dioxan and 50mL of toluene were refluxed with azeotropic removal of water using a Dean-Stark apparatus for 72 hours. After concentration under vacuum the mixture was treated with 250 mL ether and washed with 120 mL of a saturated aqueous solution of $NaHCO_3$, twice with 150 mL of NaOH 0.1 N and with water to neutral pH. The organic phase was then dried over sodium sulfate ; removal of the solvent under vacuum afforded crude (S,S) 6 which was then purified by column chromatography on silica gel (eluent : hexane-ether 60/40, Rf = 0.71) : 6.3 g (84 %), liquid, CG : t_R = 24.8 min, 100 %, $[\alpha]_D$ = + 4.3° ($CHCl_3$, 74.4 $g.l^{-1}$), ^1H NMR (89.55 MHz, $CDCl_3$, δ ppm) : 0.89 (m broad, 4 CH_3), 1.25 (m broad, 8 CH_2 and 2 CH), 4.09 (d, J = 5.4 Hz, 2 CH_2-0), 6.22 (s, 2 CH=) ; ^{13}C NMR (22.55 MHz, $CDCl_3$, δ ppm) : 10.71 (CH_3), 13.80 (CH_3), 22.79 (CH_2), 23.58 (CH_2), 28.75

(CH_2), 30.18 (CH_2), 38.56 (CH), 67.43 (CH_2-O), 129.57 (CH =), 165.11 (CO). Mass spectrometry (EI, 70 eV) : $M^{+\bullet}$(calc) : 340.2613, $M^{+\bullet}$(found) : 340.2619 (calc). Elemental analysis found : 71.04 % C, 10.67 % H ; calculated : 70.53 % C, 10.58 % H.

- **bis [(S)ethyl-2-hexyl] sodium sulfosuccinates : 1**

The sulfonation of the maleate has been performed following the previously described procedure[10]. A solution of sodium bisulfite (1.77 g, 17 mmoles) in 28 mL of water was added under nitrogen at room temperature to a solution of maleate 6 (2.91 g, 8.5 mmoles) in 38 mL of 2-propanol. The mixture was then heated at 80°C for 48 hours. The reaction was monitored by thin layer chromatography (eluent : ethylacetate-methanol 80/20, 6 Rf = 0.84, 1 Rf = 0.49). The crude reaction mixture was then concentrated to dryness under vacuum, treated with 200 mL of ether and the inorganic precipitate removed by filtration. The organic filtrate was dried over sodium sulfate. Crude 1, obtained by removal of the solvent under vacuum has been purified by column chromatography on silica gel (eluent : ethylacetate-methanol 80/20). Traces of water were removed by drying a solution of 1 in chloroform over sodium sulfate followed by removal of the solvent and heating the resulting paste at 40°C under reduced pressure (5 mmHg) for 48 h. 2.70 g (77 %), paste. ^{1}H NMR ($CDCl_3$, 89.5 MHz, δ ppm) : 0.88 (m broad, CH_3), 1.25 (m broad, CH_2), 3.15 (m broad, -C<u>H</u>$_2$-CHSO$_3$Na), 3.92 (d, $^3J_{H-H}$ = 5 Hz, O-C<u>H</u>$_2$-CH), 4.08 (d, $^3J_{H-H}$ = 5 Hz, O-C<u>H</u>$_2$-CH), 4.33 (m, C<u>H</u>-SO$_3$Na). ^{13}C NMR ($CDCl_3$, 22.5 MHz, δ ppm) : 10.84 (CH_3), 14.07 (CH_3), 23.00 (CH_2), 23.39 (CH_2), 23.60 (CH_2), 28.97 (CH_2), 30.10 (CH_2), 30.29 (CH_2), 33.1 (<u>C</u>H$_2$-CO$_2$-), 38.47 (CH), 38.69 (CH), 61.36 (-<u>C</u>H-SO$_3$), 67.59 (O-C<u>H</u>$_2$), 68.83 (O-<u>C</u>H$_2$), 169.73 (C=O) ; 171.63 (C=O). HPLC : t_r = 3 min (100%).
1 is slightly hygroscopic and must be stored in an exsiccator.

Polarimetric measurements must be performed on dilute solutions in order to ensure a sufficient transmission of light and to avoid turbidity. The specific rotation of 1 depends both on the wavelength and the polarity of the solvent (Table 2).

Solvent	Ethanol [c] (24 g.l^{-1})	Cyclohexane [c] (4.4 g.l^{-1})	Benzene [c] (4.4 g.l^{-1})
589 nm [a]	+ 2.5	+ 4.5	-
578 nm [b]	+ 3.2	+ 4.9	-
546 nm [b]	+ 3.6	+ 5.4	-
435 nm [b]	+ 6.3	+ 9.0	+ 9.7
365 nm [b]	+ 9.0	+ 14.4	+ 14.4

(a) : $[\alpha]_D$, Na lamp ; (b) : Hg lamp ; (c) : length = 1 dm.

Table 2

- **bis [(S)ethyl-2-hexyl] (R) phenyl-1-ethylammonium sulfosuccinates 7**

A solution of (R) phenyl-1-ethylamine hydrochloride (110 mg, 0.7 mmole) in 1 mL of water and a solution of 1 (300 mg, 0.7 mmole) in 50 mL of hexane were vigourously stirred with a magnetic stirrer for 24hours. The organic phase was separated by decantation (the low concentration of AOT avoids the formation of an emulsion), washed with water, dried over sodium sulfate.The diastereoisomeric ammonium salts 7 are isolated by removal of hexane under vacuum 0.34 g (93 %), oil. ^{13}C NMR (75.47 MHz, $CDCl_3$, δ ppm) : 10.78 (CH_3, 7a or 7b), 10.85 (CH_3, 7b or 7a), 10.89 (CH_3, 7a or 7b), 10. 93 (CH_3, 7b or 7a), 14.05 (CH_3, 7a and 7b), 20.91 ($\underline{CH_3}$-CH-N, 7a and 7b), 22.70 (CH_2, 7a and 7b), 22.99 (CH_2, 7a and 7b), 23.46 (CH_2, 7a and 7b), 23.67 (CH_2, 7a and 7b), 28.90 (CH_2, 7a or 7b), 28.92 (CH_2, 7a or 7b), 28.97 (CH_2, 7b or 7a), 30.08 (CH_2, 7a or 7b), 30.12 (CH_2, 7b or 7a), 30.32 (CH_2, 7a and 7b), 33.36 (CH_2-CO-, 7a or 7b), 33.44 ($\underline{CH_2}CO$, 7b or 7a), 38.51 (CH, 7a or 7b), 38.57 (CH, 7b or 7a), 38.74 (CH, 7a and 7b), 51.58 ($\underline{CH}$-N, 7a and 7b), 61.75 ($CH\text{-}SO_3^-$, 7a and 7b), 67.44 (CH_2-OCO, 7a and 7b), 68.46 (CH_2OCO, 7a or 7b), 68.50 (CH_2OCO, 7b or 7a), 126.75 (CH aromatic, 7a and 7b), 128.58 (CH aromatic, 7a and 7b), 128.97 (CH aromatic, 7a and 7b), 138.99 (Cipso, 7a and 7b), 168.92 (CO, 7a or 7b), 169.06 (CO, 7b or 7a), 171.01 (CO, 7a or 7b), 171.05 (CO, 7b or 7a). The separated peaks corresponding to carbon atoms of each diastereoisomers are always of equal intensity. ^1H (300 MHz, $CDCl_3$, δ ppm) : 0.88 (m, $4CH_3$, 7a and 7b), 1.27 (m, $8CH_2$, 7a and 7b), 1.55 (m, 2CH, 7a and 7b), 1.60 (d, J = 6.8 Hz, $\underline{CH}\text{-}CH_3$, 7a and 7b), 2.85 (dd, $^2J_{a\text{-}b}$ = 17.5 Hz, $^3J_{a\text{-}c}$ = 3.3 Hz, CH_2 (Ha), 7a or 7b), 2.86 (dd, $^2J_{a\text{-}b}$ = 17.5 Hz, $^3J_{a\text{-}c}$ = 3.3 Hz, CH_2 (Ha), 7b or 7a), 3.06 (dd, $^2J_{a\text{-}b}$ = 17.5 Hz, $^3J_{b\text{-}c}$ = 6.5 Hz, CH_2 (Hb), 7a or 7b), 3.10 (dd, $^2J_{a\text{-}b}$ = 17.5 Hz, $^3J_{b\text{-}c}$ = 6.5 Hz, CH_2 (Hb), 7b or 7a), 3.95 (d, J = 6 Hz, CH_2-O, 7a and 7b), 4.04 (m, CH (Hc), 7a and 7b), 4.40 (q, J = 6.8 Hz, $\underline{CH}\text{-}CH_3$, 7a and 7b), 7.39 (m, ArH, 7a and 7b). HPLC : t_r = 3 min. Elemental analysis found : 62.32 % C, 9.20 % H ; calculated : 61.85 % C ; 9.08 % H.

- **Critical micelle concentration of optically active 1**

The critical micelle concentrations of optically active 1 [(R,S,S) and (S,S,S)] and of the full racemic AOT (rac) 1 (obtained and purified by the same experimental procedure) have been determined by surface tension and conductivity measurements of aqueous solutions of various precise concentrations of optically active 1or (rac) 1 ranging from 10^{-5} M to 10^{-2} M.

- Surface tension measurements

The superficial tensions γ ($mN.m^{-1}$) of the aqueous surfactant solutions mentionned above were measured at 20°C until constant values (the equilibrium is usually reached after 10 to 15 min). The plot of γ versus log (concentration) shows a break at the cmc : below the cmc γ decreases linearly with the log of concentration according to Gibbs' equation (equation (1)), above the cmc the superficial tension remains unchanged (Figure 1).

(1) $$\Gamma = -\frac{C}{2RT}\frac{d\gamma}{dC}$$

The superficial excess Γ and the molecule area A at the water-air interface have been determined from the slope of γ = f (log concentration) below the cmc. (equations (2) and (3)).

(2) $$\Gamma = -\frac{1}{2.3 \times 2\,RT} \cdot \frac{d\gamma}{d(\log C)}$$

(3) $$A = \frac{1}{N\Gamma}$$ (N : Avogadro's Number)

- Conductivity measurements

The conductivity X ($\mu S.cm^{-1}$) of the aqueous surfactant solutions mentionned above were measured at 20°C. The variation of the equivalent conductivity Λ ($mS.l^{-1}.cm.mol^{-1}$) (obtained from equation (4)) versus the square root of the concentration shows a break at the cmc.

(4) $$\Lambda = \frac{X \cdot 10^{-3}}{\bar{C}}$$ ($\bar{C}$: equivalent concentration $mole.l^{-1}$)

For brevity requirements, the variation has been plotted with a logarithmic scale in Figure 1.

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