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Chirality of Reverse Micelles

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ABSTRACT Four chiral analogues of the surfactant Aerosol-OT (AOT) have been synthesized and characterized. All of them form reverse micelles in apolar solvents in the w_0 range 0–30 (w_0 = [water]/[tenside]). Reverse micellar solutions have been investigated by UV absorption and circular dichroism spectroscopies with the aim of clarifying whether the formation of the macromolecular micellar structure induces the appearance of new chromophoric bands or perturbs the existing ones. Methanolic solutions of the surfactants, in which no micellar aggregates are formed, were taken as references. One of the products 1(S),1′(S)-dimethylbisheptylsulphosuccinate sodium salt (MH-AOT) was capable of forming reverse micelles of relatively high water content (w_0 up to 40) and this process was accompanied by a specific increase in the intensity of the circular dichroism band associated with the ester absorbance of the molecule. As no concomitant changes were seen in the UV absorbance spectrum, it was concluded that this observation reflected conformational events occurring within the surfactant rather than chromophoric perturbation. These results are qualitatively similar to those found recently for lecithin reverse micelles which, however, form gels at sufficiently high water contents. The chiroptical properties of these supramolecular aggregates are compared with those of covalent macromolecular systems such as polypeptides.

KEY WORDS: circular dichroism, 1(S),1′(S)-dimethylbisheptylsulphosuccinate sodium salt, spectroscopy, optical activity, surfactant, chiroptical properties

INTRODUCTION

Macromolecules composed of repeat units each containing one chiral centre may show interesting optical activity effects which become apparent only when one compares the molar rotation of the chain (per mole of repeat unit) with the molar rotation of the monomer or the corresponding low-molecular-weight model compound.[1] Often, there is an enhancement of the optical activity (and an increase in rotational intensity) in the polymer, due to the fact that only a restricted number of conformations are compatible with the macromolecular chain. It is also possible that novel spectroscopic bands or spectroscopic perturbations, that are not visible in the repeat unit alone, appear in the polymer. Thus, in the case of polypeptides which form an α-helix, the rigid conformational relationship between the peptide units brings about exciton coupling, which results in novel absorption and circular dichroic bands in the 190–210 nm region.[2] In the case of isotactic poly-α-olefins bearing an asymmetric carbon atom in the side chain, the classical studies by Pino and coworkers[3,4] showed that there was considerable enhancement of the optical activity with respect to low-molecular-weight model compounds. This enhancement was ascribed to the concurrence of the following features: (1) isotactic vinyl polymers tend to exist in helical conformations in solution, (2) one sense of helix is predominant for a given chirality at the asymmetric C-atom (e.g., a left-handed screw sense for an S absolute configuration), and (3) that only a very few side chain conformations are compatible with a helical main chain conformation.

Whereas these phenomena are well known in macromolecules of the covalently bonded polymer type, very little is known about chirality effects in supramolecular surfactant aggregates such as micelles, liposomes, bilayers, and cubic phases. In this group of structures, monomeric surfactant molecules spontaneously associate, forming geometrically well defined noncovalent polymeric aggregates that offer several points of interest to the chemist.[5–7] In particular, these structures possess a flexibility that allows not only the physiochemical manipulation of their gross macromolecular architecture, but also the introduction, and modulation of the chemical reactivity, of guest molecules, things that are not possible in normal synthetic polymers.

The present paper is devoted to the exploration of chirality effects in one of these types of surfactant aggregates, the reverse micelle, which is formed in or-

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This paper is dedicated to the memory of Prof. P. Pino.

ganic (usually aprotic) solvents by certain surfactants, and which takes its name from its structure, which is "reverse" with respect to the structure of normal aqueous micelles. The polar heads of the surfactant molecules, avoiding contact with the apolar solvent, are directed toward the centre of the micelle, thus forming a polar core that can solubilize water (the "water pool"), with the aliphatic chains being directed toward the solvent.

Reverse micelles can, then, be seen as small water droplets (with radii of the order of 25–100 Å) stabilized in organic solvents by a layer of surfactant; they are thermodynamically stable structures, highly dynamic in nature, rapidly interchanging surfactant molecules and the water pool and its contents upon collision (7). The physical properties of the micelles depend primarily on the molar ratio of water to surfactant, usually defined as w_0 = [H_2O]/[surfactant].

For detailed reviews on the subject, the reader is directed to the specialized literature.[7,8]

EXPERIMENTAL

Materials and Methods

Synthesis of optically active surfactants

Maleic anhydride was esterified with (S)-2-methylbutanol, 1-(S)-phenylethanol, and (S)-2-octanol, in toluene, under reflux, and using sulphuric acid as catalyst. Each raw maleic ester was washed with saturated aqueous sodium chloride, twice with 5% aqueous sodium bicarbonate, again with saturated aqueous sodium chloride, and was then dried over $MgSO_4$. After the toluene had been evaporated, the esters were distilled in vacuo as follows: 2(S),2′(S)-dimethylbisbutylmaleic ester [bp 130–132°C, 0.02 Torr; $[\alpha]_D$ = +7.63, c = 0.1 g liter^{-1} in toluene; 94% yield, ^{1}H-NMR: 0.94 (m, 12H), 1.21 (m, 2H), 1.45 (m, 2H), 1.75 (m, 2H), 4.02 (d, J = 6, 4H), 6.24 (s, 2H), anal. calc. for $C_{14}H_{24}O_4$ (256.28): C, 65.60, H, 9.43; found: C, 64.94, H, 9.11]; 2(S),2′(S)-diphenylbisethylmaleic ester [bp 120–123°C, 0.05 Torr; $[\alpha]_D$ = −27.16, c = 0.05 g liter^{-1} in toluene; 91% yield, ^{1}H-NMR: 1.54 (m, 6H), 4.26 (m, 2H), 6.21 (s, 2H), 7.31 (m, 10H), anal. calc. for $C_{20}H_{20}O_4$ (324.31): C, 74.06, H, 6.21; found: C, 73.26, H, 6.12]; 1(S),1(S)′-dimethylbisheptylmaleic ester [bp 182–184°C, 0.05 Torr; $[\alpha]_D$ = −1.76, c = 0.05 g liter^{-1} in toluene; 92% yield ^{1}H-NMR: 0.87 (m, 12H), 1.28 (m, 20H), 4.25 (q, J = 7, 2H), 6.19 (s, 2H), anal. calc. for $C_{20}H_{36}O_4$ (340.44): C, 70.55, H, 10.66; found: C, 69.72, H, 10.71].

Fumaroyl chloride was esterified with 3(S),7-dimethyloctan-1-ol, obtained by the hydrogenation of 3(S),7-dimethyloct-6-en-1-ol (β-citronellol) in the presence of Pd/C, and the reaction mixture was then hydrolysed by the addition of water at 0°C. Following esterification, the aqueous phase was extracted with dichloromethane and the organic phase thus obtained was extracted with saturated aqueous sodium chloride, aqueous 0.1 *M* NaOH, and, finally, saturated aqueous sodium chloride and was then dried over $MgSO_4$. After evaporation of the dichloromethane, the product, 3(S),3′(S),7,7′-tetramethylbisoctylmaleic ester, was distilled as follows: [bp 200–203°C, 0.3 Torr; $[\alpha]_D$ = −3.86, c = 0.05 g liter^{-1} in toluene; 83.6% yield ^{1}H-NMR: 0.88 (m, 18H), 1.15 (m, 16H), 1.52 (m, 4H), 4.23 (t, J = 4, 4H), 6.84 (s, 2H), anal. calc. for $C_{24}H_{44}O_4$ (396.54): C, 72.68, H, 11.18; found: C, 71.94, H, 11.12].

Methanolic solutions of each of the purified maleic esters were sulphonated with 50% aqueous sodium bisulphite (50:50 water:methanol, v/v) at 100°C until the reaction mixture became water soluble. The mixture was dried and freed from inorganic salts by dissolving in benzene, followed by filtration and evaporation of the benzene. Three of the synthetic optically active surfactants, 2(S),2′(S)-dimethylbisbutyl-

TABLE 1. Optical activity in aggregates

Surfactant	Feature	Reference
Cholesteryl-4-(2-anthyloxy)butanoate (CAB)	Appearance of CD signal in gel state, when tenside is solubilized in organic solvent	9
Dimyristoyl-5′-phosphatidyldeoxycytidine	Spontaneous formation of superhelical strands in aqueous solution	10
Di-C_{12}-L-Glu-$(CH_2)_2N^+(CH_3)_3$ and derivatives in water	Helical structures are formed in aqueous solutions from chiral bilayers	11
Oligo-L-Glu-alkyl derivatives in water dispersions	New CD bands are observed in water upon the formation of highly ordered aggregates	12
CBzAC and CTAB in organic solvent	Enantioselective hydrolysis of amino acid esters	13
1(S),1′(S)-Dimethyl*bis*heptylsulphosuccinate sodium salt (MH-AOT)	Enantioselective hydrolysis of amino acid in chiral reverse micelles	14
Di-C_{12}-L-Glu-$(CH_2)_2N^+(CH_3)_3$ bound to methyl orange	Induced circular dichroism of methyl orange when bound to a chiral membrane in water	15
N-(α-Methylbenzyl)stearamide	Pure enantiomers have higher aggregation energy than racemates in monolayers	16
N-Alkyl-*N*,*N*-dimethyl-(L or D)-alanine hydrobromide	D-Amino acids are more strongly absorbed to the surface of normal micelles consisting of D-surfactants	17
Hexadecyltrimethylammonium bromide in water	L/D stereoselectivity of amino acid derivatives in deacylation step	18

sulphosuccinate sodium salt (MB-AOT) [mp 231–232°C; $[\alpha]_D = +3.45$, $c = 0.1$ g liter^{-1} in toluene; 82% yield, ^{1}H-NMR: 0.87 (m, 12H), 1.17 (m, 2H), 1.41 (m, 2H), 1.68 (m, 2H), 3.16 (d, $J = 4$, 2H), 4.01 (m, 4H), 4.37 (t, $J = 4$, 1H), anal. calc. for $C_{14}H_{25}O_7NaS$ (361.40): C, 46.25, H, 6.97, S, 8.87; found: C, 45.60, H, 6.92, S, 8.80], 2(S),2′(S)-diphenylbisethylsulphosuccinate sodium salt (PE-AOT) [mp 74–75°C; $[\alpha]_D = -19.83$, $c = 0.05$ g liter^{-1} in toluene; 55% yield ^{1}H-NMR: 1.36 (m, 6H), 3.14 (s, 2H), 4.10 (m, 2H), 4.26 (t, 1H), 7.25 (m, 10H), anal. calc. for $C_{20}H_{21}O_7NaS$ (428.35): C, 56.07, H, 4.94, S, 7.48; found: C, 55.38, H, 4.99, S, 7.35], and 1(S),1′(S)-dimethylbisheptylsulphosuccinate sodium salt (MH-AOT) [mp 168–170°C; $[\alpha]_D = -5.12$, $c = 0.1$ g liter^{-1} in toluene; 78% yield, ^{1}H-NMR: 0.87 (m, 12H), 1.26 (m, 20H), 3.10 (d, $J = 6$, 2H), 4.11 (d, $J = 4$, 2H), 4.24 (d, $J = 4$, 2H), 4.86 (t, $J = 6$, 1H), anal. calc. for $C_{20}H_{37}O_4NaS$ (444.45): C, 54.03 H, 8.39 S, 7.21; found: C, 53.89 H, 8.27 S, 7.05] were crystalline, whereas 3(S),3′(S),7,7′-tetramethylbisoctylsulphosuccinate sodium salt (DC-AOT) [mp 213–215°C; $[\alpha]_D = -2.07$, $c = 0.1$ g liter^{-1} in toluene; 77% yield ^{1}H-NMR: 0.87 (m, 18H), 1.14 (m, 16H), 1.50 (m, 4H), 3.13 (m, 2H), 4.06 (t, $J = 6$, 2H), 4.2 (t, $J = 4$, 2H), 4.29 (t, $J = 6$, 1H), anal. calc. for $C_{24}H_{45}O_7NaS$ (500.67); C, 57.58, H, 9.06, S, 6.40; found: C, 56.95, H, 8.97, S, 6.32] was amorphous.

Melting points were determined with a Tottoli (Büchi) apparatus, $[\alpha]_D$ rt with a Perkin Elmer 241 Polarimeter and ^{1}H-NMR spectra were obtained with a Bruker AC 200 P spectrometer in δ (ppm), in $CHCl_3$ relative to TMS.

Phase and temperature stability diagrams for MH-AOT

2-Octanol was used as a cosurfactant in all experiments involving MH-AOT dissolved in heptane (see Results and Discussion section).

Phase diagram. A set of solutions of increasing con-

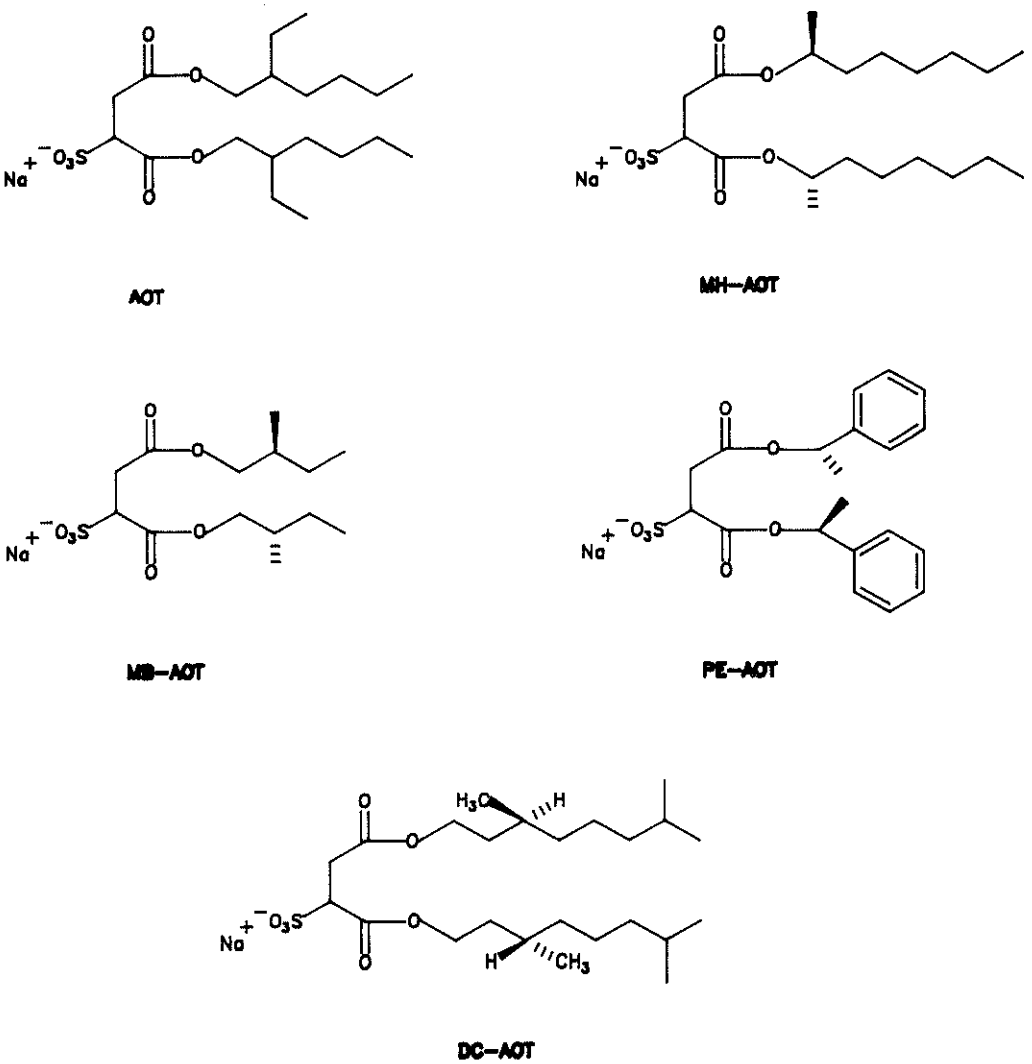


Fig. 1. Chemical structure of the synthetic surfactants: AOT, 2,2′-diethylbishexylsulphosuccinate sodium salt; MH-AOT, 1(S),1′(S)-dimethylbisheptylsulphosuccinate sodium salt; MB-AOT, 2(S),2′(S)-dimethylbisbutylsulphosuccinate sodium salt; PE-AOT, 2(S),2′(S)-diphenylbisethylsulphosuccinate sodium salt; DC-AOT, 3(S),3′(S),7,7′-tetramethylbisoctylsulphosuccinate sodium salt.

centration of MH-AOT in heptane, containing 2-octanol as cosurfactant at the fixed molar ratio [surfactant]/[cosurfactant] = 0.4, was titrated by the stepwise injection of water, with continuous stirring, at 25°C, until turbidity was first detected. This point was characterized by the partial weights of surfactant, solvent, and water present and was denoted as falling on the phase boundary.

Temperature stability diagram. The stability of the micellar state between −40 and +60°C was established as follows: A set of solutions with a fixed MH-AOT concentration of 50 m*M* but with varying w_0 values was prepared. The solutions were placed in a thermostatted bath at −40°C and the temperature was slowly (0.5°C/min) raised until the solution became turbid or, conversely, for those solutions that were initially turbid, until they became clear. Points determined in this way were also denoted as lying on a phase boundary.

Spectroscopic measurements

UV absorption measurements were carried out on a Hewlett Packard 8452A UV/VIS diode-array spectrophotometer using a 0.1 cm pathlength quartz cell. Circular dichroism spectra were recorded with a Jasco J-600 spectropolarimeter interfaced to an IBM AT computer, using a cylindrical quartz, 0.1 cm pathlength cell, with nitrogen gas flushing the sample chamber. Nine to sixteen spectra of each sample were accumulated between 260 and 190 nm at a resolution of 0.2 nm, scan speed 20 nm/min, time constant 1 sec, band width 1 nm, and with a sensitivity range of either 20 to −20 or 50 to −50 mdeg, and the accumulated spectra corrected by subtraction of the relevant solvent blank. All UV and CD measurements were performed at 22 ± 0.2°C, unless otherwise specified.

RESULTS AND DISCUSSION

Characterization of Chiral AOT Analogues

As has already been mentioned, little is known about chirality effects in macromolecular surfactant aggregates and most of the information reported in the literature on the subject is summarized in Table 1.

This table does not, however, include data on lecithins that we have acquired only very recently, which

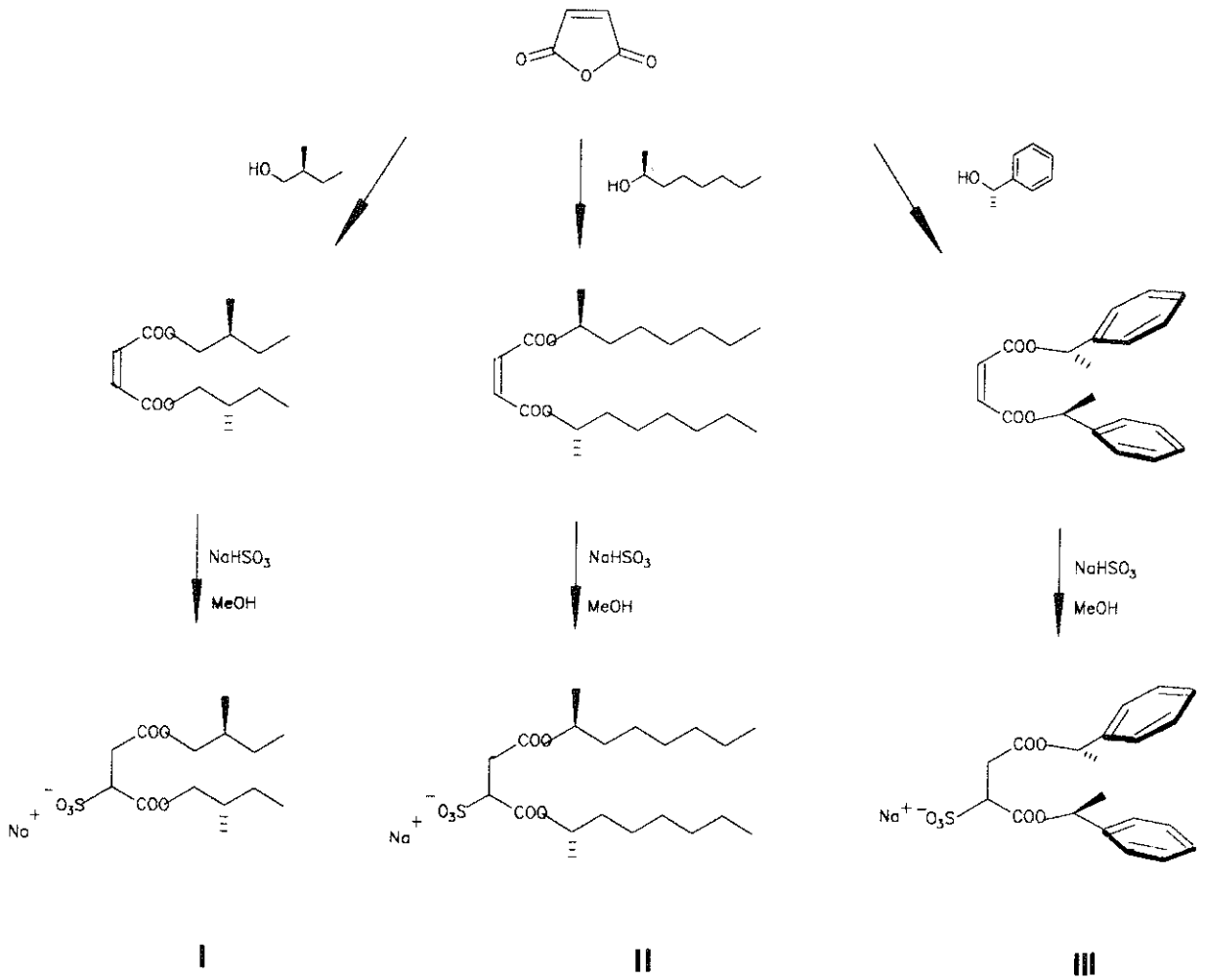
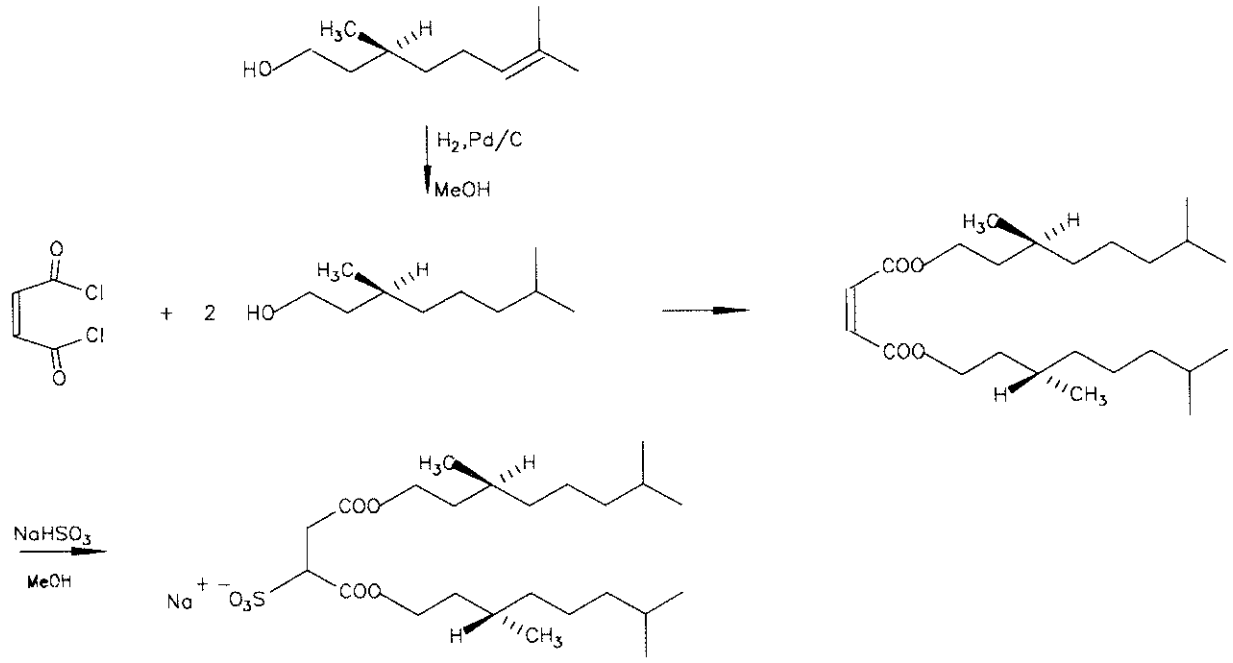


Fig. 2. Synthetic schemes for I, 2(S),2'(S)-dimethylbisbutylsulphosuccinate sodium salt; II, 1(S),1'(S)-dimethylbisheptylsulphosuccinate sodium salt; III, 2(S),2'(S)-diphenylbisethylsulphosuccinate sodium salt.



IV

Fig. 3. Synthetic schemes for IV, 3(S),3′(S),7,7′-tetramethylbisoctylsulphosuccinate sodium salt.

show that these naturally occurring chiral surfactants form reverse micelles and microemulsion gels, characterized by novel features in their CD spectra (19) that are qualitatively similar to those reported in the present paper. We report here on the chiroptical properties of four sulphosuccinate surfactants whose structural formulas are given in Figure 1.

All four are analogues of AOT (2,2′-diethylbishexyl sodium sulphosuccinate), which is the best-studied reverse micelle-forming surfactant.[7,8] In common with the lecithin system, CD signals arising in these compounds are associated with the n–π* transition of the ester chromophores, under the influence of asymmetric carbon atom(s) either in the head group (in the lecithin case) or in the side chains (in the case of the AOT analogues). The formation of reverse micelles has been described[14,20] for each of the AOT analogues used in this study.

AOT is popular first because of the fact that no cosurfactant is needed for the formation of reverse micelles and second because the amount of water that can be solubilized in such microemulsion systems extends up to w_0 ~60. AOT, although it is commonly studied in the racemic form, also contains chiral centres, and we thought that close chiral analogues of AOT would have a good chance of forming stable micelles. The synthesis of the AOT analogues was carried out according to the schemes described in Figures 2 and 3. (Details are reported in the experimental section.)

It was found that all four AOT analogues were able to form reverse micelles in a variety of solvents, and Table 2 summarizes the $w_{0,max}$ (i.e., the maximum amount of water solubilized at a given surfactant concentration) in different solvents, the compound with the maximum solubilizing power for water being 2(S),2′(S)-dimethylbisheptylsulphosuccinate (MH-AOT).

Figure 4 illustrates the temperature stability regions of all four analogues, i.e., the temperature/w_0 regions in which transparent, thermodynamically stable reverse micelles are formed. The phase diagram of the

TABLE 2. Maximal water amount for the synthetized surfactants in different solvent systems[a]

Solvent system	Surfactant				
	MB-AOT	MH-AOT	PE-AOT	DC-AOT	AOT
Chloroform	11	6	12	8	nd
2,2,4-TMP	t	6	t	10	~70
Heptane	t	7	t	7	~70
Cyclohexane	t	20	t	nd	nd
2,2,4-TMP/ $CHCl_3$, 1/1	27	8	t	15	nd
2,2,4-TMP/ hexanol, 9/1	32	8	t	15	~70
Heptane[b]	nd	40	t	nd	nd

[a] $w_{0,max}$ for the synthetic surfactants in various solvent systems always at a concentration of 50 m*M* and at 25°C. 2,2,4-TMP,2,2,4-trimethylpentane; t, indicates a turbid solution after addition of water; nd: not determined. For abbreviations, see text.
[b] In the presence of 125 m*M* 2-octanol.

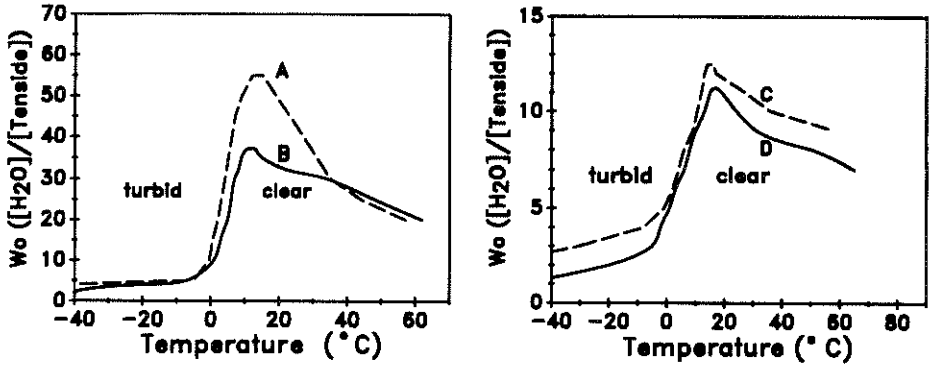


Fig. 4. Temperature stability diagrams. w_0 as a function of temperature for the synthetic chiral surfactants: (A) 1(S),1′(S)-Dimethylbisheptylsulphosuccinate sodium salt (MH-AOT) 50 m*M* in heptane containing 125 m*M* 2-octanol; (B) 2(S),2′(S)-dimethylbisbutylsulphosuccinate sodium salt (MB-AOT) 50 m*M* in 2,2′,4-trimethylpentane/hexanol: 9/1 (v/v); (C) 2(S),2′(S)-diphenylbisethylsulphosuccinate sodium salt. (PE-AOT) 50 m*M* in chloroform; (D) 3(S),3′(S),7,7′-tetramethylbisoctylsulphosuccinate sodium salt (DC-AOT) 50 m*M* in 2,2′,4-trimethylpentane.

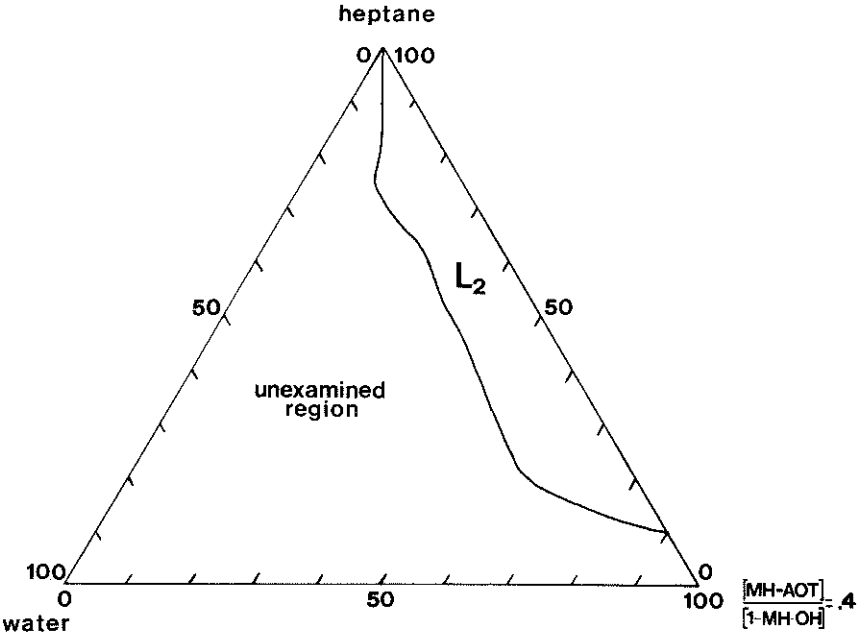


Fig. 5. Phase diagram (at 25°C) for the system 1(S),1′(S)-dimethylbisheptylsulphosuccinate sodium salt (MH-AOT), 2-octanol, heptane, and water at the fixed ratio of [MH-AOT]/[2-octanol] = 0.4. Concentrations are expressed in weight percent.

quaternary system MH-AOT, 2-octanol, heptane, and water at 25°C is then reported in Figure 5. Only that part of the phase diagram where reverse micelles are formed, i.e., the L_2-phase was investigated. Notice that the reverse micellar phase, due to the presence of the cosurfactant, is relatively broad and MH-AOT is able to take up as much as 18% v/v water.

A more extensive investigation of the phase diagrams of these compounds is in progress.

The synthetic analogues, like AOT itself, do not form reverse micelles in methanol and we have therefore used solutions of the surfactant in this solvent as a reference system with which to compare the optical activity of the AOT analogues in other solvents, in which it is known that reverse micelles form. A significant change in the optical activity found in such a solvent with respect to methanol can then be taken as indication of a chirality effect brought about by the creation of the micellar structure.

Of all the AOT analogues synthesized it was only MH-AOT that exhibited changes in chiroptical behaviour upon reverse micelle formation, as shown in Table 3.

The other three analogues of AOT (representative results illustrated in Fig. 6) showed no such behaviour in the limited w_0 range accessible, although they are known to form micelles under the conditions given.

Chiral Properties of MH-AOT

Unlike AOT, the maximum w_0 value that can be

TABLE 3. Ellipticity of the chiral surfactants[a]

Tenside	Solvent system	$w_{0,max}$	$[\theta]_{MeOH}$[b]	$[\theta]_{\lambda,max}$[b]
MB-AOT	2,2',4-TMP/ hexanol, 9/1	32	−117	−110
MH-AOT	Heptane[c]	40	−364	−658
PE-AOT	Chloroform	12	165	150
DC-AOT	2,2,4-TMP/ hexanol, 9/1	15	−122	−131

[a]Ellipticity of the synthetic chiral surfactants in reverse micelles at $w_{0,max}$ and in methanolic solution. In each case the surfactant was at a concentration of 50 m*M*. 2,2,4-TMP is 2,2,4-trimethylpentane.
[b]Ellipticity values are given in deg $dmol^{-1}$-cm^2 and, for the micellar systems, they refer to the value measured at $w_{0,max}$.
[c]In the presence of 125 m*M* 2-octanol.

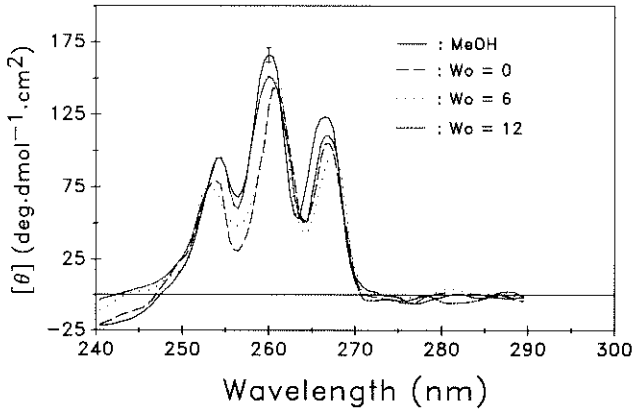


Fig. 6. Circular dichroism spectra as a function of w_0 for 2(S),2'(S)-diphenylbisethylsulphosuccinate sodium salt in chloroform at 22°C.

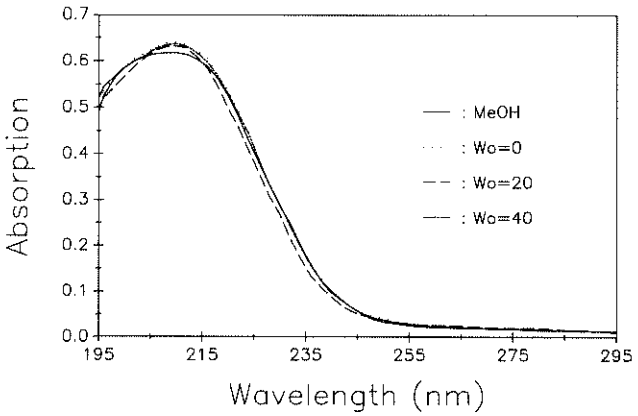


Fig. 7. UV absorption spectra of MH-AOT, 50 m*M* in heptane containing 125 m*M* 2-octanol, as a function of w_0 at 22°C. For comparison, the spectrum of a 50 m*M* solution of MH-AOT in methanol is also shown.

obtained in the MH-AOT system is only about $w_{0,max}$ = 7 ($w_{0,max}$ = 70 for AOT) although this can be increased to $w_{0,max}$ = 40 when 2-octanol is used as a cosurfactant with heptane as solvent. The UV absorption spectrum of MH-AOT in this solvent system (Fig. 7) is not significantly perturbed by the addition of water, which

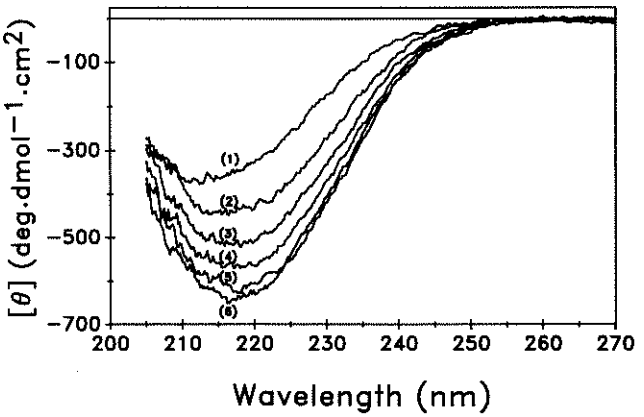


Fig. 8. Circular dichroism spectra of MH-AOT, 50 m*M* in heptane containing 125 m*M* 2-octanol, as a function of w_0 at 22°C. For comparison, the spectrum of a 50 m*M* solution of MH-AOT in methanol is also shown. (1) Methanolic solution; (2) w_0 = 0; (3) w_0 = 5; (4) w_0 = 10; (5) w_0 = 20; (6) w_0 = 40.

means that the CD spectra shown in Figure 8 are of particular interest, as the changes seen upon increasing the water content of the system must reflect conformational (as opposed to chromophoric) effects.

Two important points can be derived from this figure: first, that the formation of micelles induces a specific chiral effect, and, second, that the chiral effect is increased by increasing w_0. Bearing in mind that increasing the amount of water present increases the size of the reverse micelles (the radius of the micelle is directly proportional to w_0[7,21] to a first approximation), this finding suggests that the chiral effect is the more pronounced the larger the dimensions of the micelle.

It is often found that an increase in optical activity is related to an increase of "thermodynamic conformational rigidity,"[22] i.e., it indicates a shift of the conformational equilibrium towards a more restricted number of conformers. Thus, the data of Figure 8 would seem to indicate that the conformational rigidity of the surfactant molecule increases as the micelle grows in size. This idea is supported by the data reported in Figure 9 where the intensity of the dichroic band at 218 nm is shown as a function of temperature in the range −22 to +69°C at constant w_0 (w_0 = 4).

There is a significant increase of the dichroic signal at lower temperatures, i.e., under conditions which should tend to freeze out particularly stable conformers from a conformational equilibrium.

This behaviour is not restricted to only the one solvent system and, as is shown in Figure 10, a similar dependence of the CD signal on both w_0 and temperature is observed when cyclohexane is used as the solvent.

CONCLUDING REMARKS

There is, to the best of our knowledge, no report in the literature describing the peculiar chirality effects that arise as a result of reverse micelle formation. The present study, along with the parallel investigation on lecithin reverse micelles and microemulsion gels,[19]

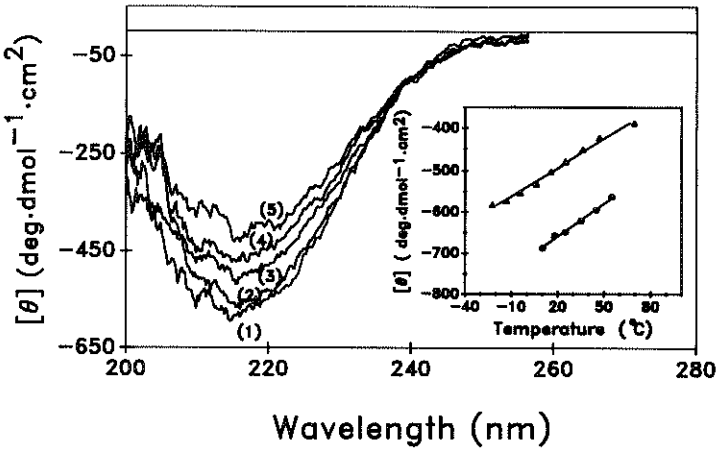


Fig. 9. Circular dichroism spectra of MH-AOT, 50 m*M* in heptane containing 125 m*M* 2-octanol, as a function of the temperature. (1) $T = -22$°C; (2) $T = -4$°C; (3) $T = 15$°C; (4) $T = 36$°C; (5) $T = 69$°C. In the inset the ellipticity at 218 nm of MH-AOT is reported against the temperature, at $w_0 = 4$ (▲) and $w_0 = 20$ (●). The samples were prepared by the injection of 3.6 and 18 μl water, respectively, into 1 cm^3 of the micellar solution in a thermostatted quartz cell.

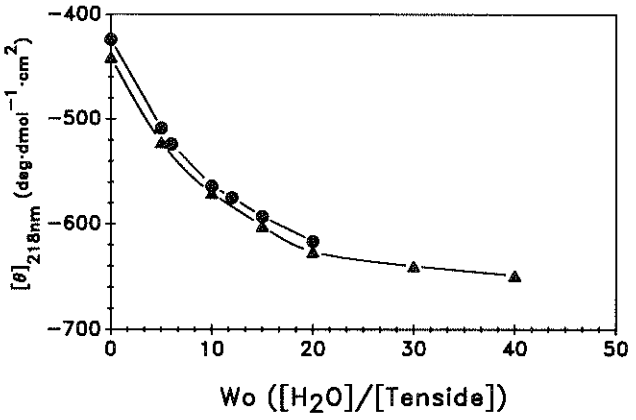


Fig. 10. Influence of w_0 on the ellipticity at 218 nm of MH-AOT in two different solvent systems at 22°C. (▲) MH-AOT, 50 m*M* in heptane containing 125 m*M* 2-octanol and (●) 50 m*M* MH-AOT in cyclohexane.

therefore provides the first evidence that such chirality effects do in fact arise. The interpretation of the lecithin data is relatively difficult because the addition of small amounts of water to lecithin micellar systems not only often produces highly viscous gels, but also causes substantial changes in their UV absorbtion properties. The surfactants studied here, particularly MH-AOT, exhibit neither gelation nor micelle formation-dependent chromophoric modification, which means that the CD effects can be attributed solely to conformational effects.

In order to attempt to explain the origin of the increase in intensity of the CD band at 230 nm, it is appropriate briefly to reconsider the data reported on polymers.[3] As already mentioned, in a covalently linked, stereoregular polymer the repeat units can interact with each other giving rise to unique spectroscopic features. Two types of behaviour can be distinguished: (1) a strong interaction among the chromophores leading to significant perturbation of the electronic transitions in the polymer, when compared with the isolated repeat unit (or the corresponding model compound). This may give rise to novel electronic transitions (e.g., exciton coupling in the polypeptide α-helix) or to a change in UV absorption properties (as is the case in hypochromism in polynucleotides); or (2) there is no strong perturbation of the electronic transition(s), but the ordered structure of the chain imposes severe restrictions on the conformation of the repeat unit (e.g., of the side chain). In this case, there are generally significant changes in the circular dichroism and optical activity without any noticeable change in UV absorption properties.

The two mechanisms are obviously not mutually exclusive and, for example, tight conformational restriction may well lead to strong electronic perturbation. However, the second mechanism can operate in the absence of the first. In this case, an increase of the absolute value of the optical activity is to be expected. Such behaviour has been found, for example, in isotactic poly-α-olefines by Pino and collaborators.[4] It would seem that, in the case of MH-AOT reverse micelles, we are dealing with this second type of mechanism: only one—or a very few—conformation(s) of the surfactant molecule is compatible with the micelle structure and this greater conformational rigidity induces an increase in the intensity of the CD band.

A similar conclusion has been reached for lecithin micelles[19] and one is therefore tempted to generalize the findings: it is probable that only a few of the available conformations of the surfactant molecule are compatbile with the spherical micellar structure. Some of the data presented here, however, appear to be in conflict with this generalization as no chirality effect were observed with three of the four analogues of AOT studied. Why this is so remains for the moment unanswered although it may be that, in very small micelles, individual surfactant molecules experience little or no

steric crowding and that, in these systems, phase separation takes place before there is sufficient molecular packing to lead to any measurable change in the CD signal.

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