

References

- BELL, L. G. & DABROWIAK, J. C. (1975). *J. Chem. Soc. Chem. Commun.* pp. 512–513.
- CROMER, D. T. & MANN, J. L. (1968). *Acta Cryst.* A24, 321–324.
- GOEDKEN, V. L. & LADD, J. A. (1982). *J. Chem. Soc. Chem. Commun.* pp. 142–144.
- GOEDKEN, V. L., PLUTH, J. J., PENG, S. M. & BURNSTEN, B. (1976). *J. Am. Chem. Soc.* 98, 8014–8021.
- GOULD, R. O. & TAYLOR, P. (1983). *CALC*. Program for molecular geometry calculations. Univ. of Edinburgh, Scotland.
- JÄGER, E. G. (1964). *Z. Chem.* 4, 437.
- LEONI, P., GRILLI, E., PASQUALI, M. & TOMASSINI, M. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2561–2564.
- MALLINSON, P. D. & MUIR, K. W. (1985). *ORTEPII*, interactive version. *J. Appl. Cryst.* 18, 51–53.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure refinement. Univ. of Cambridge, England.
- WARREN, L. F. & GOEDKEN, V. L. (1978). *J. Chem. Soc. Chem. Commun.* pp. 909–910.
- WEISS, M. C., BURNSTEN, B., PENG, S. M. & GOEDKEN, V. L. (1976). *J. Am. Chem. Soc.* 98, 8021–8031.
- WEISS, M. C. & GOEDKEN, V. L. (1976). *J. Am. Chem. Soc.* 98, 3389–3392.

Acta Cryst. (1987). C43, 850–854

Structure of a Triclinic Phase of Sodium Dodecyl Sulfate Monohydrate. A Comparison with Other Sodium Dodecyl Sulfate Crystal Phases

BY V. M. COIRO, M. MANIGRASSO, F. MAZZA* AND G. POCHETTI

Istituto di Strutturistica Chimica 'G. Giacomello', CNR, CP n. 10, 00016 Monterotondo Stazione, Roma, Italy

(Received 9 June 1986; accepted 14 November 1986)

Abstract. Na⁺.C₁₂H₂₅O₄S⁻.H₂O, *M_r* = 306.4, triclinic, *P*1̄, *a* = 10.423 (4), *b* = 5.662 (3), *c* = 28.913 (12) Å, α = 86.70 (4), β = 93.44 (4), γ = 89.55 (4)°, *V* = 1700 (1) Å³, *Z* = 4, *D_x* = 1.20 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 20 cm⁻¹, *F*(000) = 664, *T* = 290–294 K, *R* = 0.11 for 4457 observed reflections. Each asymmetric unit is made up of two water and two sodium dodecyl sulfate (SDS) molecules with different conformations. The SDS molecules form a lamellar structure with regions alternately polar and apolar. Adjacent polar heads of the same monolayer are displaced in a zigzag fashion along the *a* axis forming a rippled structure. Facing monolayers are held together by Coulombic interactions not screened by the water molecules. Weak van der Waals interactions are present in the apolar region. From comparison of the present phase with other SDS crystal phases differing in water content it is possible to deduce that the higher the water content, the larger the average area per polar head and the smaller the lamellar thickness. In all the crystal phases interdigitation of hydrocarbon chains does not take place, whereas the polar heads can give rise to planar or rippled monolayers.

Introduction. The alkali-metal dodecyl sulfates form micellar aggregates in aqueous solutions; in particular sodium dodecyl sulfate forms micelles at concentrations over the critical micellar concentration [8.1 × 10⁻³ mol dm⁻³ (Mukerjee & Mysels, 1971)].

The SDS anion is amphiphilic since it possesses the sulfate group as the polar head and the non-polar hydrocarbon chain ending with a methyl group. Among the micellar systems that of SDS is one of the most studied because of its wide variety of applications as a detergent. The knowledge of the aggregation mode of SDS molecules in micelles is necessary to understand the SDS behaviour in aqueous solution and the role at the molecular level of micelles in fields such as detergency, separation science, micellar catalysis and so on. In fact many important aspects of micellar systems such as shape, size and water content of their interior are not yet clear (Dill, Koppel, Cantor, Dill, Bendedouch & Chen, 1984; Menger & Doll, 1984).

We think that the aggregation model of a surfactant observed in the solid state may be present in micellar solutions (Conte, Di Blasi, Giglio, Parretta & Pavel, 1984). For this purpose we have undertaken the structural determination of those SDS crystal phases that can be obtained from aqueous solutions at different concentrations and temperatures in order to check the corresponding structural units in the study of the micellar solutions.

Experimental. SDS was purchased from Sigma Chemical Co. Single crystals in the form of colourless prisms were obtained by dissolving SDS in water (32 wt%) within a temperature range 290–294 K. A crystal of 1 × 0.5 × 0.05 mm was mounted on an automatic Syntex P2₁ diffractometer equipped with a graphite monochromator and Cu Kα radiation. The unit-cell parameters were determined from a least-

* Also at Dipartimento di Fisica, Università di L'Aquila, 67100 L'Aquila, Italy.

squares fit of the angular settings of 15 reflections in the range $5 < \theta < 20^\circ$. Three different crystals, of about the same dimensions as that used for crystal-data collection, were successively used to complete the intensity-data collection because of their quick and complete X-ray decay. Three data sets at increasing intervals of θ were recorded by the ω -scan technique, with a scan rate varying in the interval $29.3\text{--}2.0\text{ min}^{-1}$ over a scan range of 1.2° in ω up to a maximum 2θ value of 116° . Background counts were taken for a time equal to one third of the scan. For each set of data ϕ -scan curves obtained for two reflections were used to take care of anisotropy of absorption and the correction for X-ray decay was performed by three standard reflections (002, 200 and 203) measured after every 100, which showed a steady decrease; when their intensities decreased to less than 40% of their initial value, a new crystal was used for intensity-data collection. The three sets of data were successively scaled by averaging the intensities of common reflections. After merging equivalent reflections R_{int} was 0.10. A total of 4458 independent reflections with $I > 1.5\sigma(I)$ were obtained ($h\ 0\rightarrow 11, k\ -6\rightarrow 6, l\ -32\rightarrow 33$) and corrected for Lorentz and polarization factors but not for extinction or absorption. 482 unobserved reflections.

The structure was solved by direct methods using the program *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

400 reflections and 4015 \sum_2 relationships were used in the phase-determining procedure. An E map computed with the phases of the set having the highest figures of merit revealed all the non-H atoms, which were refined isotropically and then anisotropically by block-diagonal least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight applied to each observation was $w = (a + |F_o| + c|F_o|^2)^{-1}$ with a and c equal to $2F_{o(\text{min})}$ and $2/F_{o(\text{max})}$ respectively. Since no H atom could be detected from the final Fourier difference map, the H atoms of the hydrocarbon chains were assumed to be at the expected positions and held fixed in the last cycles of refinement together with isotropic thermal factors deduced from the carrier atoms. The 001 reflection was excluded in the last stages of refinement because it was judged to be severely influenced by extinction or absorption. The atomic scattering factors of the S atoms were corrected for anomalous dispersion. In the final refinement cycle $(\Delta/\sigma)_{\text{max}}$ was 0.1 and 0.3 for positional and thermal parameters respectively of the methyl groups. The minimum and maximum heights in the final Fourier difference synthesis were -0.4 and 0.6 e \AA^{-3} respectively. The final R and wR were 0.11 and 0.14 respectively and $S = 0.9$. Poor quality of all the crystals used for intensity-data collection together with their quick and complete X-ray decay prevented the attainment of better agreement indices. The scattering

Table 1. Final fractional coordinates and B_{eq} values of the non-H atoms with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j b_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
S(1)	0.2694 (1)	-0.0149 (2)	0.1089 (<1)	3.1 (1)
O(1)	0.2836 (4)	0.1182 (8)	0.1558 (1)	3.7 (2)
O(2)	0.3749 (7)	-0.1722 (13)	0.1127 (2)	9.6 (4)
O(3)	0.2688 (5)	0.1571 (8)	0.0714 (1)	4.7 (2)
O(4)	0.1464 (6)	-0.1299 (12)	0.1097 (2)	8.5 (4)
C(1)	0.1810 (6)	0.2783 (11)	0.1640 (2)	3.8 (3)
C(2)	0.2162 (6)	0.4092 (12)	0.2062 (2)	4.1 (3)
C(3)	0.1068 (6)	0.5639 (12)	0.2197 (2)	4.2 (3)
C(4)	0.1387 (7)	0.7089 (13)	0.2611 (2)	4.9 (3)
C(5)	0.0285 (7)	0.8573 (13)	0.2754 (2)	4.8 (3)
C(6)	0.0597 (7)	1.0039 (14)	0.3171 (3)	5.4 (4)
C(7)	-0.0513 (8)	1.1498 (14)	0.3316 (2)	5.3 (4)
C(8)	-0.0203 (8)	1.2938 (15)	0.3735 (3)	6.0 (4)
C(9)	-0.1317 (8)	1.4369 (15)	0.3882 (3)	6.1 (4)
C(10)	-0.1042 (10)	1.5821 (17)	0.4299 (3)	7.2 (5)
C(11)	-0.2157 (11)	1.7211 (22)	0.4439 (4)	9.0 (7)
C(12)	-0.1948 (14)	1.8643 (25)	0.4850 (4)	10.9 (8)
S(2)	0.7554 (1)	0.2232 (2)	0.0285 (<1)	2.2 (<1)
O(21)	0.7630 (3)	0.2959 (6)	0.0811 (1)	2.8 (2)
O(22)	0.8701 (3)	0.0855 (6)	0.0228 (1)	2.8 (2)
O(23)	0.6380 (3)	0.0866 (6)	0.0223 (1)	2.9 (2)
O(24)	0.7523 (3)	0.4515 (6)	0.0039 (1)	2.8 (2)
C(21)	0.7633 (7)	0.1047 (11)	0.1170 (2)	4.4 (3)
C(22)	0.7817 (7)	0.2237 (14)	0.1631 (2)	4.9 (3)
C(23)	0.6732 (7)	0.3870 (13)	0.1735 (2)	4.8 (3)
C(24)	0.6978 (7)	0.5132 (14)	0.2183 (2)	4.9 (3)
C(25)	0.5892 (8)	0.6729 (15)	0.2301 (3)	5.4 (4)
C(26)	0.6199 (8)	0.8109 (15)	0.2734 (3)	5.4 (4)
C(27)	0.5111 (7)	0.9666 (16)	0.2858 (3)	5.7 (4)
C(28)	0.5415 (8)	1.1067 (16)	0.3287 (3)	5.9 (4)
C(29)	0.4316 (8)	1.2575 (17)	0.3423 (3)	6.4 (4)
C(30)	0.4606 (9)	1.3981 (18)	0.3849 (3)	6.9 (5)
C(31)	0.3505 (12)	1.5425 (23)	0.3988 (4)	9.3 (7)
C(32)	0.3722 (15)	1.6835 (28)	0.4396 (5)	11.8 (10)
Na(1)	0.0877 (2)	0.2540 (4)	0.0196 (1)	3.3 (1)
Na(2)	0.4203 (2)	0.2562 (3)	0.0173 (1)	2.9 (1)
O(31)	0.0028 (4)	0.5767 (7)	0.0573 (1)	3.5 (2)
O(41)	0.5146 (3)	0.5732 (7)	0.0563 (1)	3.4 (2)

factors were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on the HP 1000/F minicomputer (Cerrini & Spagna, 1977) of the CNR Research Area. The final atomic parameters are reported in Table 1.*

Discussion. Hereinafter t-SDS and g-SDS will be used to refer to the two independent anions numbered from O(1) to C(12) and from O(21) to C(32) respectively as indicated in Fig. 1, where bond lengths and angles have been reported.

The S—O(ester) bond length of each independent sulfate group is significantly longer than the other three S—O bond lengths; furthermore all the O—S—O valence angles of each polar head are significantly larger than those including the ester O atoms. As already pointed out for a monoclinic SDS phase (Coiro, Mazza & Pochetti, 1986), both these geometrical features may be caused by the negative charge shared among the three

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43561 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

non-ester O atoms of each sulfate group. The high thermal motion (see Table 1) of the end of the hydrocarbon chains is probably responsible for the apparent shortening of the two terminal C—C bonds and for the increase in the relative valence angles of both the hydrocarbon tails. The average C—C bond lengths and C—C—C valence angles are 1.506 (11) Å, 114.9 (7)° and 1.512 (12) Å, 114.6 (7)° for the t- and g-SDS anions, respectively.

The relevant torsion angles of the two anions, with the signs according to the convention of Klyne & Prelog (1960), are reported in Table 2. While the conformation of the hydrocarbon chain of the t-SDS anion is completely *trans*, that of the g-SDS anion differs markedly in the O(21)—C(21)—C(22)—C(23) torsion angle which is 64.6 (7)°.

Table 2. *Relevant torsion angles (°) for the two independent anions with e.s.d.'s in parentheses*

O(2)—S(1)—O(1)—C(1)	-174.5 (5)	O(22)—S(21)—O(21)—C(21)	-62.6 (4)
O(3)—S(1)—O(1)—C(1)	62.8 (5)	O(23)—S(21)—O(21)—C(21)	57.8 (4)
O(4)—S(1)—O(1)—C(1)	-54.7 (5)	O(24)—S(21)—O(21)—C(21)	177.9 (4)
S(1)—O(1)—C(1)—C(2)	-173.3 (4)	S(21)—O(21)—C(21)—C(22)	175.6 (4)
O(1)—C(1)—C(2)—C(3)	-174.3 (5)	O(21)—C(21)—C(22)—C(23)	64.6 (7)

A view of the crystal packing on the *ac* plane is shown in Fig. 2. Each asymmetric unit constitutes half the cell content and is composed of two SDS and two water molecules. The hydrocarbon chains of the two independent SDS anions run almost parallel to each other and the angle between the lines joining the extreme non-methylic C atoms of each chain is 0.7 (2)°. The t- and g-SDS hydrocarbon chains are consequently equally inclined on the *ab* plane with an angle of 39.6 (2)° in both cases, as well as on the *ac* plane with angles of 40.1 (2) and 39.6 (2)° respectively. The molecules arrange themselves in a lamellar structure with alternately polar and apolar slabs which extend on the *ab* plane.

Adjacent polar heads lying in a monolayer are displaced from the *ab* plane in a zigzag fashion along the *a* direction. The water molecules are far from the *ab* plane, do not screen the Coulombic interactions between sodium and sulfate ions and form hydrogen bonds among sulfate groups belonging to the same monolayer. A similar zigzag arrangement of the polar heads has been found in the monoclinic SDS phase with a 1:8 water:SDS ratio (Sundell, 1977), whereas in the other monoclinic SDS phase (Coiro *et al.*, 1986), which

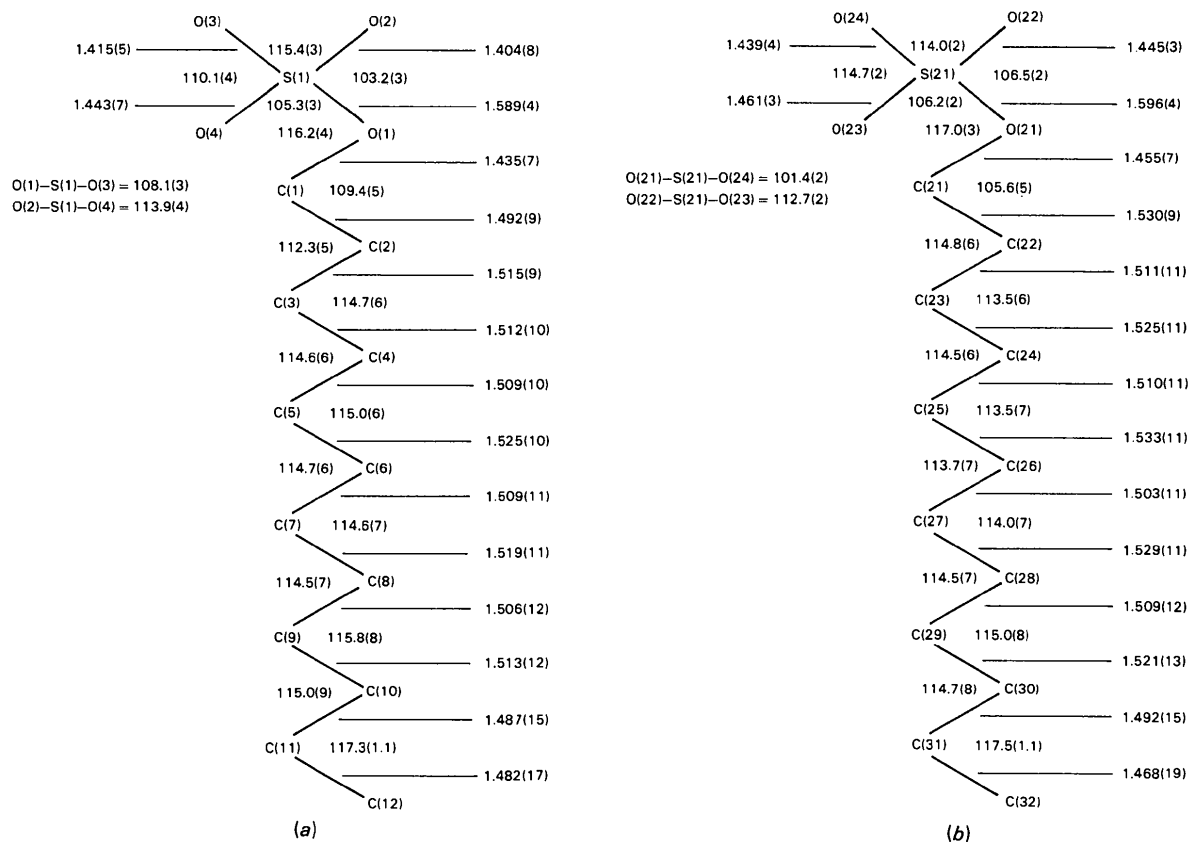


Fig. 1. Atomic numbering, valence bond lengths (Å) and angles (°) found for the two independent SDS anions, (a) t-SDS, (b) g-SDS. E.s.d.'s are given in parentheses.

has a higher water:SDS ratio (1:2), the polar heads are all equally displaced from the *ab* plane. Moreover, in the last phase the water molecules lie in the middle of the polar slab, screen the ion-ion interactions and form hydrogen bonds between sulfate groups belonging to facing monolayers.

In the present phase the interactions among the sodium ions and the O atoms both of the polar heads and of the water molecules are shown in Fig. 3. Each Na(1) and Na(2) ion forms six contacts, ranging from 2.372 (4) to 2.499 (4) Å and from 2.339 (4) to 2.460 (4) Å, respectively, with four O atoms of four different polar heads and with the O atoms of two symmetrically related water molecules. The distance between the two sodium ions is 3.472 (3) Å. The angles O...Na...O around each sodium ion are reported in Table 3 where it can be noted that they conform fairly well to two octahedral distorted arrangements having the atoms O(3) and O(24ⁱⁱⁱ) in common.

From Fig. 3 a pseudo-mirror plane perpendicular to the line joining the two sodium ions and nearly perpendicular to the *a* axis is apparent.

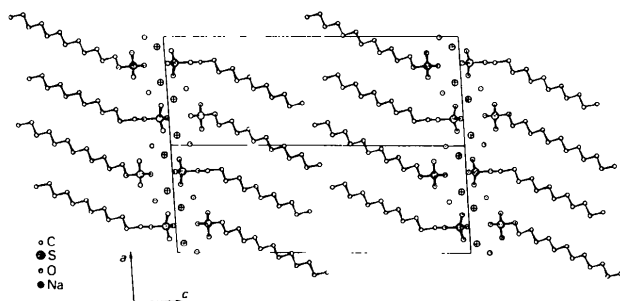


Fig. 2. A view of the crystal packing projected on the *ac* plane.

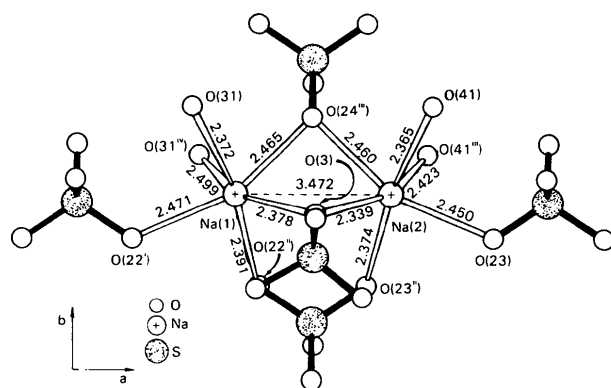


Fig. 3. The coordination formed from the two independent sodium ions with the surrounding O atoms. Empty and filled bonds represent Na...O interactions (Å) and S-O bonds (Å) respectively. E.s.d.'s are in the range 0.005–0.006 Å and 0.003 Å for the Na...Na contact. The symmetry code is the same as that shown in Table 3.

Table 3. The O...Na...O angles (°) occurring around the two sodium ions

E.s.d.'s are in the range 0.2–0.3°.

O(31)...Na(1)...O(3)	99.5	O(41)...Na(2)...O(3)	97.0
O(31)...Na(1)...O(24 ⁱⁱⁱ)	82.8	O(41)...Na(2)...O(23)	85.2
O(31)...Na(1)...O(31 ⁱⁱⁱ)	90.8	O(41)...Na(2)...O(41 ⁱⁱⁱ)	90.7
O(31)...Na(1)...O(22 ⁱ)	85.7	O(41)...Na(2)...O(24 ⁱⁱⁱ)	83.1
O(22 ⁱⁱ)...Na(1)...O(3)	90.1	O(23 ⁱⁱ)...Na(2)...O(3)	89.0
O(22 ⁱⁱ)...Na(1)...O(24 ⁱⁱⁱ)	105.3	O(23 ⁱⁱ)...Na(2)...O(23)	85.1
O(22 ⁱⁱ)...Na(1)...O(31 ⁱⁱⁱ)	83.7	O(23 ⁱⁱ)...Na(2)...O(41 ⁱⁱⁱ)	87.2
O(22 ⁱⁱ)...Na(1)...O(22 ⁱ)	83.8	O(23 ⁱⁱ)...Na(2)...O(24 ⁱⁱⁱ)	105.8
O(3)...Na(1)...O(24 ⁱⁱⁱ)	76.9	O(3)...Na(2)...O(23)	122.8
O(24 ⁱⁱⁱ)...Na(1)...O(31 ⁱⁱⁱ)	76.2	O(23)...Na(2)...O(41 ⁱⁱⁱ)	83.0
O(31 ⁱⁱⁱ)...Na(1)...O(22 ⁱ)	82.2	O(41 ⁱⁱⁱ)...Na(2)...O(24 ⁱⁱⁱ)	78.1
O(22 ⁱⁱ)...Na(1)...O(3)	126.7	O(24 ⁱⁱⁱ)...Na(2)...O(3)	77.7
O(31)...Na(1)...O(22 ⁱ)	168.7	O(41)...Na(2)...O(23 ⁱⁱ)	170.2
O(22 ⁱⁱ)...Na(1)...O(24 ⁱⁱⁱ)	155.3	O(23)...Na(2)...O(24 ⁱⁱⁱ)	157.5
O(3)...Na(1)...O(31 ⁱⁱⁱ)	149.6	O(3)...Na(2)...O(41 ⁱⁱⁱ)	153.5

Symmetry code: (i) $x-1, y, z$; (ii) $1-x, -y, -z$; (iii) $1-x, 1-y, -z$; (iv) $-x, 1-y, -z$.

The contacts that the O atoms of the two water molecules form with the surrounding atoms of the polar slab are shown in Fig. 4. No H atom was identified in the Fourier difference map. However, as far as the position of the water H atoms is concerned, the following considerations can be made in view of the geometry of the interactions among the water and surrounding O atoms. The contacts O(31)...O(4ⁱⁱ) and O(41)...O(2ⁱⁱ) of 2.712 (8) and 2.717 (8) Å, respectively, indicate hydrogen-bond formation involving one H of each water molecule. Since the lone pairs of the water O atoms are likely to be oriented toward the positively charged sodium ions, as indicated by the angles O(4ⁱⁱ)...O(31)...Na(1), O(4ⁱⁱ)...O(31)...Na(1), O(2ⁱⁱ)...O(41)...Na(2) and O(2ⁱⁱ)...O(41)...Na(2^{iv}) of 124.2 (1), 116.6 (1), 120.4 (1) and 121.2 (1)°, respectively (see Table 4), the other H of each water molecule should be directed in between O(21) and O(24) on one side, and in between O(21ⁱⁱⁱ) and O(24ⁱⁱⁱ) on the other side, probably forming bidentate hydrogen bonds.

In Fig. 5 the sodium ions, the sulfate groups and the water molecules belonging to a monolayer are projected on the *ab* plane: each polar head is surrounded by six polar heads arranged in a very distorted hexagonal way, at variance with the monoclinic phase with a water:SDS ratio of 1:2.

Much weaker van der Waals interactions are present in the apolar region. Although the hydrocarbon chains are strongly tilted on the *ab* as well as on the *ac* plane in order to give a better packing they do not give rise to energetically favourable intermolecular contacts. As expected the atomic thermal factors increase along each chain from the polar head to the terminal methyl group, indicating a decrease in the interaction energy along this direction. The shortest intermolecular contact among the methyl groups within the tail-to-tail region is 3.973 (18) Å occurring between C(12) and C(32) at $-x, 4-y, 1-z$.

Considering the average area per polar head, the lamellar thickness and the chain tilting for the three

SDS crystal phases differing in water content the following remarks can be made. In the 1:8 water:SDS ratio monoclinic phase (Sundell, 1977) where the water content is the smallest and only one of the four independent sulfate groups takes part in hydrogen bonding, the average area per polar head is 20.9 \AA^2 , the lamellar thickness (corresponding to half the length of the long axis, since the unit cell contains two double layers) is 38.8 \AA , and the hydrocarbon chains are almost perpendicular to the polar plane (79°) and lie approximately in the ac plane with angles varying between 4 and 7° .

As can be seen from the other monoclinic phase with a 1:2 water:SDS ratio (Coiro *et al.*, 1986), increasing the water content causes an increase in the average area per polar head to 25.8 \AA^2 and a shrinking of the lamellar thickness to 30.8 \AA corresponding to the long crystal axis. This shrinking mostly takes place by a tilting of the hydrocarbon chain on the polar plane (46°) since the tilting on the ac plane (15°) is limited.

The higher water content present in the triclinic phase increases the average area per polar head to 29.5 \AA^2 and causes a further shrinking of the lamellar thickness to 28.9 \AA , which takes place by tilting the chains on the ab (40°) and ac (40°) planes.

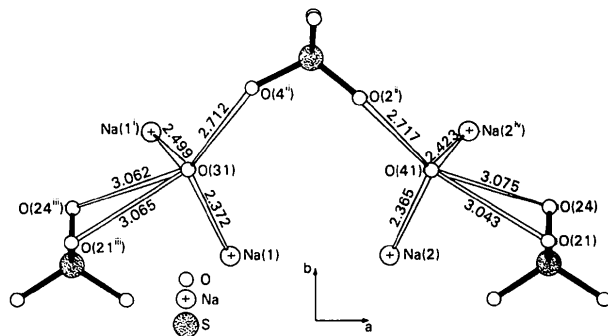


Fig. 4. The shortest interactions (\AA) that the two independent water molecules form in the crystal. Empty and filled bonds represent intermolecular interactions and S—O bonds respectively. E.s.d.'s are in the range 0.004 – 0.008 \AA . The symmetry code is the same as that shown in Table 4.

Table 4. The non-valence bond angles ($^\circ$) occurring around each water molecule

E.s.d.'s are in the range 0.2 – 0.3° .

Na(1')...O(31)...Na(1')	89.2	Na(2)...O(41)...Na(2 ^h)	89.3
Na(1')...O(31)...O(4 ^h)	124.2	Na(2')...O(41)...O(2 ^h)	120.4
Na(1')...O(31)...O(4 ^h)	116.6	Na(2 ^h)...O(41)...O(2 ^h)	121.2
Na(1')...O(31)...O(21 ^{III})	91.6	Na(2')...O(41)...O(21)	92.5
Na(1')...O(31)...O(24 ^{III})	83.5	Na(2')...O(41)...O(24)	83.9
Na(1')...O(31)...O(21 ^{III})	95.7	Na(2 ^h)...O(41)...O(21)	95.8
Na(1')...O(31)...O(24 ^{III})	51.4	Na(2 ^h)...O(41)...O(24)	51.5
O(4 ^h)...O(31)...O(21 ^{III})	129.6	O(2 ^h)...O(41)...O(21)	128.0
O(4 ^h)...O(31)...O(24 ^{III})	151.6	O(2 ^h)...O(41)...O(24)	155.5

Symmetry code: (i) $-x, 1-y, -z$; (ii) $x, 1+y, z$; (iii) $x-1, y, z$; (iv) $1-x, 1-y, -z$.

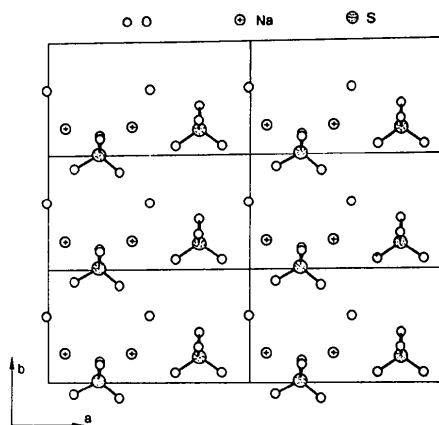


Fig. 5. A projection on the ab plane of the sulfate groups and sodium ions which lie on the same side of a polar region. Isolated open circles represent water molecules.

Therefore from these structural investigations it seems that the higher the water content, the larger the average area per polar head and the smaller the lamellar thickness. Furthermore, the shrinking of the lamellar thickness does not take place by interdigitation of the chains (Vincent & Skoulios, 1966) but occurs by increasing the chain tilting on the ab and ac plane.

This work has been financially supported by the Progetto Finalizzato 'Chimica fine e secondaria' of the Consiglio Nazionale delle Ricerche. We thank Professor E. Giglio for reading the manuscript and for helpful discussions. Drawings were made by Mr M. Viola.

References

- CERRINI, S. & SPAGNA, R. (1977). Abstr. 4th Eur. Crystallogr. Meet., Oxford, Vol. A, pp. 7–8.
- COIRO, V. M., MAZZA, F. & POCHEZZI, G. (1986). *Acta Cryst.* **C42**, 991–995.
- CONTE, C., DI BLASI, R., GIGLIO, E., PARRETTA, A. & PAVEL, N. V. (1984). *J. Phys. Chem.* **88**, 5720–5724.
- DILL, K. A., KOPPEL, D. E., CANTOR, R. S., DILL, J. D., BENEDEDOUCH, D. & CHEN, S. (1984). *Nature (London)*, **309**, 42–45.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–528.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MENGER, F. M. & DOLL, D. W. (1984). *J. Am. Chem. Soc.* **106**, 1109–1113.
- MUKERJEE, P. & MYSELS, K. J. (1971). *Critical Micell Concentrations of Aqueous Surfactant Systems*. US Superintendent of Documents, Washington, DC.
- SUNDELL, S. (1977). *Acta Chem. Scand. Ser. A*, **31**, 799–807.
- VINCENT, J. M. & SKOULIOS, A. (1966). *Acta Cryst.* **20**, 432–440.