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The ε Phase of Some Sodium 1-Alkanesulfonates*

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Six different hydrated phases of the sodium 1-alkanesulfonates have now been identified. The ϵ phase, which contains $\frac{1}{4}$ mole of water per mole of sodium alkanesulfonate, is triclinic. The unit cell contains 8 molecules. The long chains are tilted at an angle of $\sim 41\frac{1}{2}$° from the normal to (001).

The sodium salts of the 1-alkanesulfonic acids, like the ordinary sodium soaps (Gardiner, Buerger & Smith, 1945), crystallize in a number of different phases (Jensen & Lingafelter, 1944, 1946), differing in structure and in water content. We have succeeded in growing single crystals of six such phases. This paper deals with that phase which we have called the ϵ phase. We have obtained single crystals of sodium 1-dodecane-, 1-tetradecane-, 1-hexadecane-, and 1-octadecane-sulfonates in this phase by crystallization from solutions in carbon tetrachloride–ethanol–water or 1,4-dioxane–ethanol–water at *c.* 30° C. The triclinic crystals are extremely small, very thin tabular parallel to (001) and outlined by $(10l)$ and $(01l)$ or very occasionally by $(10l)$, $(01l)$, and $(1\bar{1}l)$. The l index is difficult to obtain because of the extreme thinness of the crystals.

The extent of hydration of the ϵ phase was determined by an apparatus described elsewhere.‡ As reported there, this phase is the $\frac{1}{4}$ hydrate. The first phase investigated, the α phase, was originally reported to be the $\frac{1}{4}$ hydrate (Jensen & Lingafelter, 1944). It now seems definite that the α and ϵ phases are not isohydrous, the α phase being a $\frac{1}{8}$ hydrate.

X-ray diffraction data were obtained from oscillation and Weissenberg photographs using copper radiation. The constants of the triclinic unit cells are given in Table 1. These are in all cases the reduced primitive cells. In the cases of C_{12}, C_{14} and C_{16}, it was possible to choose the sense of a, b and c so that all angles are obtuse. This was not possible for C_{18} so that Buerger's Rule 3 (Buerger, 1942, p. 366) cannot be applied. There are three possible choices according as α, β or γ is taken to be acute. We have chosen the angle nearest to 90° to be acute.

Densities were determined by the flotation method, using 1,4-dioxane and carbon tetrachloride, and are recorded in Table 2. The unit cell contains eight molecules of $R\mathrm{SO_3Na}.\frac{1}{4}\mathrm{H_2O}$.

Table 2. *Densities*

Substance	Experimental (g.cm.$^{-3}$)	Calculated* (g.cm.$^{-3}$)
$C_{12}H_{25}SO_3Na.\frac{1}{4}H_2O$	1·218	1·210
$C_{14}H_{29}SO_3Na.\frac{1}{4}H_2O$	1·183	1·174
$C_{16}H_{33}SO_3Na.\frac{1}{4}H_2O$	1·166	1·166
$C_{18}H_{37}SO_3Na.\frac{1}{4}H_2O$	1·154	1·139

* Assuming $z=8$.

From the magnitudes of the unit-cell dimensions and their variation with the length of the paraffin chain, as well as from the habit, it is apparent that the long-chain molecules lie parallel to each other with the ionic heads all lying in (001) planes. The angle between the chain axis and the normal to this plane may be estimated from the variation of d_{001} with chain length (if we assume that the tilt does not vary with chain length).

$$\cos\tau = \Delta d_{001}/2{\cdot}55\Delta n,$$

where Δd_{001} is the difference in d_{001} for a pair of homologues differing in chain length by Δn carbon atoms. Thus we obtain from a comparison of C_{12} and C_{14}, $\tau=40$°; from C_{14} and C_{16}, $\tau=44\frac{1}{2}$°; and from C_{16} and C_{18}, $\tau=40$°. This variation is probably not significant and we may use $\tau=41\frac{1}{2}$° as an average value of the tilt. This angle may be compared with the values obtained for some of the other phases of the sodium 1-alkanesulfonates:

$$\alpha,\ 10\text{–}20°;\quad \beta,\ 45°;\quad \gamma,\ 40°;\quad \delta,\ \sim 53°.$$

A 'physical' unit cell can be chosen by assigning

Table 1. *Constants for conventional unit cell*, $\epsilon\, R\mathrm{SO_3Na}.\frac{1}{4}\mathrm{H_2O}$

Substance	a_0 (A.)	b_0 (A.)	c_0 (A.)	α	β	γ
$C_{12}H_{25}SO_3Na.\frac{1}{4}H_2O$	9·90	10·76	30·76	93° 20′	93° 45′	111° 6′
$C_{14}H_{29}SO_3Na.\frac{1}{4}H_2O$	9·92	10·76	34·89	95° 26′	94° 19′	110° 28′
$C_{16}H_{33}SO_3Na.\frac{1}{4}H_2O$	9·92	10·77	38·21	91° 0′	92° 3′	111° 32′
$C_{18}H_{37}SO_3Na.\frac{1}{4}H_2O$	9·93	10·82	42·14	93° 5′	89° 21′	111° 23′

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indices of 200 and 020 respectively to the middle of three intense spots which appear on the second festoon of zero-level b- and a-axis Weissenberg photographs. Constants for such a cell appear in Table 3. The fact that the tilt of this c axis from the normal to the ab plane is the same as the tilt of the chains calculated from Δd_{001} indicates that the chains probably lie along the c axis.

Table 3. *Constants for physical unit cell,* $\epsilon\, R\mathrm{SO_3Na}.\tfrac{1}{4}\mathrm{H_2O}$

Substance	a_0 (A.)	b_0 (A.)	c_0 (A.)	α	β	γ	τ_c*
$C_{12}H_{25}SO_3Na.\tfrac{1}{4}H_2O$	9·90	10·76	40·63	113° 14′	110° 29′	111° 6′	41° 46′
$C_{14}H_{29}SO_3Na.\tfrac{1}{4}H_2O$	9·92	10·76	45·87	113° 37′	110° 29′	110° 28′	41° 17′
$C_{16}H_{33}SO_3Na.\tfrac{1}{4}H_2O$	9·92	10·77	50·57	114° 27′	108° 46′	111° 32′	41° 0′
$C_{18}H_{37}SO_3Na.\tfrac{1}{4}H_2O$	9·93	10·82	56·05	114° 38′	108° 59′	111° 23′	41° 25′

* Tilt of c axis from normal to ab plane.
Calculation of tilt from Δd_{001} and Δ theoretical chain-length change: average $\tau = 41°\ 27'$.

Using the angle of tilt as $41\tfrac{1}{2}°$, we may calculate the effective cross-section of the molecules normal to the chain axis, $\sigma = \tfrac{1}{4} a_0 b_0 \sin\gamma \cos\tau$. Thus we obtain 18·6 A.². This value may be compared with those obtained for some other substances: α sodium 1-alkanesulfonates, 20–21; β sodium 1-alkanesulfonates, 18·1; γ sodium 1-alkanesulfonates, 23·0; δ sodium 1-alkanesulfonates, 22·4; C_nH_{2n+2}, 18·2; α sodium soaps, 18·2; α acid soaps, 18·4; β acid soaps, 19·0; A potassium caprate, 18·5 A.².

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The Probability Distribution of X-ray Intensities. III. Effects of Symmetry Elements on Zones and Rows

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A symmetry element that causes equivalent atoms to coincide in groups of n in a plane (or line) projection produces a zone (or row) of reflexions whose average intensity is $n\Sigma$, where Σ is the sum of the squares of the scattering factors of the atoms in the unit cell. The average for the general reflexions is Σ; the difference between the zone (or row) average and the general average may be useful in the purely X-ray determination of space groups. The effects of simple symmetry elements on the probability distribution of the intensities are summarized in two tables.

1. Introduction

The first statistical treatment of the intensity of X-ray reflexions showed that the average intensity of the general (hkl) reflexions is given by

$$\langle I \rangle = \sum_{j=1}^{N} f_j^2 \equiv \Sigma, \qquad (1)$$

where f_j is the scattering factor of the jth atom and the sum is over all atoms in the cell (Wilson, 1942; Harker, 1948; Hughes, 1949). More refined consideration, based on the central limit theorem, showed that the probability of the hkl reflexion from a non-centrosymmetric crystal having an intensity I is given by the acentric* (A) distribution function

$$_{1}P(I) = S^{-1} \exp\{-I/S\}, \qquad (2)$$

where S is a distribution parameter, and by the centric* (C) distribution function

$$_{\bar{1}}P(I) = (2\pi S I)^{-\frac{1}{2}} \exp\{-I/2S\}, \qquad (3)$$

if the crystal is centrosymmetric (Wilson, 1949). The centric distribution was discovered empirically by Hughes (1949), and both distributions have been verified

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* These convenient adjectives were suggested by Rogers (1949).