Recovery of Anthracene from Anthracene–T. N. F. Complex

Chromatographic Separation.—A benzene solution of 0.6014 g. anthracene–T. N. F. complex was passed over a short column of activated alumina. The T. N. F. formed a dark ring at the top of the column which moved slowly down the column while the anthracene was readily eluted with benzene. The movement of the anthracene was followed by its fluorescence in ultraviolet light. When all the anthracene was eluted, the T. N. F. was still on the column. A quantitative recovery of anthracene was obtained by evaporation of the percolate.

Reduction with Tin and Hydrochloric Acid.—To a solution of 0.378 g. of anthracene–T. N. F. complex in 30 cc. of glacial acetic acid there was added 1 g. of tin and 5 cc. of concentrated hydrochloric acid. The mixture was refluxed twenty minutes, during which time all the tin went into solution and the mixture turned from a deep red to a very light red. The hot mixture was poured onto ice and the precipitate filtered and dried. The precipitate was dissolved in benzene, treated with norite, filtered and the filtrate concentrated. There was recovered 0.112 g. of anthracene, m. p. 213-215°.

Catalytic Reduction.—In a preliminary experiment 78.8 mg. of pure T. N. F. was reduced in ethanol solution with Adams platinum oxide catalyst at room conditions. At the end of forty-eight minutes, 9 moles of hydrogen per mole of T. N. F. was absorbed, and the compound continued to take up hydrogen slowly. An ethanol–benzene solution of 0.6128 g. of anthracene–T. N. F. complex was hydrogenated under similar conditions. At the end of 132 minutes, 8.2 moles of hydrogen per mole of compound was absorbed, at which point the reduction was interrupted. The reaction mixture was extracted with dilute hydrochloric acid and the organic layer separated, washed with water and dried. After treatment with norite, the solution gave, on concentration, 0.1590 g. of anthracene, m. p. 212-215°.

Summary

The molecular complexes between 2,4,7-trinitrofluorenone and twenty-nine aromatic polynuclear compounds are described. The hydrocarbon portion of these complexes can be readily recovered. The advantages of using the molecular complexes of 2,4,7-trinitrofluorenone for the characterization and purification of polynuclear aromatic compounds are indicated.

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[Contribution from the Departments of Chemistry of the University of Washington and of Emmanuel Missionary College]

X-Ray Crystallographic Studies of Organic Sulfonates. II. The Hemihydrates of Certain Sodium 1-Alkane-sulfonates[1]

By L. H. Jensen[1a] and E. C. Lingafelter

In the first paper of this series[1b] we reported the unit cells and space groups of the quarter-hydrates of sodium 1-octane-, 1-decane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate. We have now prepared satisfactory single crystals of the hemihydrates of sodium 1-dodecane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate. Sodium 1-octanesulfonate and 1-decanesulfonate have not formed hemihydrates under the conditions so far investigated.

Experimental

The compounds used were of the same batch as in the previous work.[1b] The crystals were grown by slow evaporation from mixtures of carbon tetrachloride and water at temperatures between *ca.* 30 and 50°. Sodium 1-dodecanesulfonate and 1-tetradecanesulfonate hemihydrates were also obtained from water alone. The crystals of all four substances are thin tabular parallel to {001} and elongated parallel to the *a* axis. The tablet is outlined by {010} and {12*l*} in most cases, rarely by {010}, {11*l*} and {12*l*} or by {010} and {11*l*}. (*l* index could not be obtained because of the extreme thinness of the crystals.)

The degree of hydration was measured by the weight loss in a vacuum drying experiment as described in the previous paper.[1b] The weight loss corresponded to the hemihydrate.

Data were obtained from oscillation and equi-inclination Weissenberg photographs using unfiltered copper radiation from a hot-cathode X-ray tube.

The constants of the monoclinic unit cells are given in Table I. In Table II the ratio a_0/b_0 is compared with the value obtained by measurement of the angle between the zone axes $\{\bar{2}10\}$ and $\{\overline{21}0\}$, using a microscope with a rotating stage.

Table I

Constants of the Unit Cell

Substance	a_0, kX.	b_0, kX.	c_0, kX.	β
$C_{12}H_{25}SO_3Na\cdot{}^1/_2H_2O$	6.86	15.40	29.40	96°30'
$C_{14}H_{29}SO_3Na\cdot{}^1/_2H_2O$	6.85	15.36	32.74	90°36'
$C_{16}H_{33}SO_3Na\cdot{}^1/_2H_2O$	6.86	15.35	36.30	94°23'
$C_{18}H_{37}SO_3Na\cdot{}^1/_2H_2O$	6.86	15.36	39.73	91°36'

Table II

Comparison of X-Ray and Goniometric Values

Substance	a_0/b_0, X-ray	a/b, goniometric
$C_{12}H_{25}SO_3Na\cdot{}^1/_2H_2O$	0.4455	0.4464
$C_{14}H_{29}SO_3Na\cdot{}^1/_2H_2O$	.4460	.4471
$C_{16}H_{33}SO_3Na\cdot{}^1/_2H_2O$	.4469	.4477
$C_{18}H_{37}SO_3Na\cdot{}^1/_2H_2O$	.4466	.4475

The densities were determined by the flotation method,[1b] using mixtures of 1,4-dioxane and car-

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[1] Presented at the Northwest Regional Meeting, Seattle, Washington, October 20, 1945.

[1a] At Emmanuel Missionary College, Berrien Springs, Michigan.

[1b] Jensen and Lingafelter, This Journal, **66**, 1946 (1944).

bon tetrachloride. The unit cell contains eight molecules of hemihydrate or four molecules of $2RSO_3Na \cdot H_2O$. The experimental and calculated densities are given in Table III.

TABLE III

DENSITIES

Substance	Obs. density, g./cc.	Calcd. density,[a] g./cc.
$C_{12}H_{25}SO_3Na \cdot {}^1/_2H_2O$	1.214	1.204
$C_{14}H_{29}SO_3Na \cdot {}^1/_2H_2O$	1.186	1.182
$C_{16}H_{33}SO_3Na \cdot {}^1/_2H_2O$	1.173	1.168
$C_{18}H_{37}SO_3Na \cdot {}^1/_2H_2O$	1.154	1.153

[a] Assuming eight molecules per unit cell.

The first and second level b axis equi-inclination Weissenberg photographs are superposable, indicating a primitive lattice, P. The $(h0l)$ festoons of the zero level photograph are absent for h odd, indicating a glide plane, a. The $(0k0)$ reflections on an a axis zero level Weissenberg photograph are absent for k odd, indicating a twofold screw axis, 2_1. The space group is thus C_{2h}^5-$P2_1/a$.

Discussion

A comparison of the c_0 values with those of the quarter-hydrates[1b] in which the long chain molecules lie parallel to the c axis, indicates that the chains in the hemihydrates must be tilted at a considerable angle from the c axis. For example, the effective length per molecule in the direction of the c-axis in sodium 1-dodecanesulfonate hemihydrate is $29.40/2 = 14.70$ kX, while for sodium 1-dodecanesulfonate quarter-hydrate it is $75.91/4 = 18.98$ kX.[2] The angle of tilt[2a] may be estimated if we assume this angle and the packing of the ends of the chains to be the same for all four hemihydrates. With these assumptions, the angle of tilt is the angle whose cosine is the ratio of the average d_{001} increment in the hemihydrates to the average c_0 increment in the quarter-hydrates. Thus $\cos(\text{tilt}) = 3.51/5.10 = 0.688$, whence the angle of tilt is *ca.* 46°30′. Using this value for the tilt, the effective cross-section of the molecule perpendicular to the chain axis may be calculated. The value obtained is 18.12 kX^2, which is slightly smaller than the value of 18.24 found for long paraffin-chain hydrocarbons[3] and considerably smaller than the cross-sections found for the corresponding sodium 1-alkanesulfonate quarter-hydrates.[1b]

While no attempt has been made as yet to establish the complete details of the structure, due to the large number of parameters involved, the general features may be inferred from the evidence as to habit, size and symmetry of the unit cell, and size and shape of the paraffin chain ions.

The habits of all alkanesulfonate crystals which have been grown in this laboratory are similar in the extreme thinness of the crystals in the c-direction. This would indicate weak crystal forces along the c axis, caused probably by a "head-to-head and tail-to-tail" arrangement, with the cations and water molecules in a layer between the heads. A similar arrangement has been suggested for the ions in the soap micelles existing in aqueous solutions at moderate to high concentrations,[4] and has been discussed by Buerger[5] for sodium palmitate and stearate. This arrangement is corroborated by the fact that c_0 is always an even multiple of the single chain length, occasionally decreased somewhat by tilt.

The cross section of a straight paraffin chain is about 4.5 by 4.0 kX. Since the unit cell is two chains long in the c-direction, the $\{001\}$ plane must contain four chains. The tilt of 46°30′ would increase the 4.5 to $4.5/0.688 = 6.5$ kX, while $(4)(4.0) = 16$ kX, thus accounting satisfactorily for the values of a_0 and b_0.

The positions of the eight paraffin chain ions may be fixed approximately if we assume that all of the sodium ions and water molecules lie in a plane parallel to the $\{001\}$ plane, with a plane of "heads" (*i.e.*, $—SO_3^-$ groups) on either side. The space group $P2_1/a$ contains a pair of glide planes $\{010\}$ with glide component $a_0/2$, separated by a distance $b_0/2$. Because of the size of the paraffin chains, no chain can lie in a glide plane. Adjacent chains in the $\{001\}$ plane will therefore be separated by $b_0/4 + a_0/2$, leading to a close packed arrangement. The presence of the 2-fold screw axis will cause all chains to be tilted in the same direction.

Summary

1. Single crystals of the hemihydrates of sodium 1-dodecane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate have been grown.
2. The substances all have the same structure. The monoclinic unit cell contains 4 molecules of $2RSO_3Na \cdot H_2O$. The space group is $C_{2h}^5(P2_1/a)$.
3. The general features of the structure are discussed.

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[2] All dimensions in the previous paper are given in kX units, rather than in Å. as labelled.

[2a] This angle is defined as the angle between the chain direction and the normal to the (001) plane.

[3] Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

[4] Harkins, Mattoon and Corrin, THIS JOURNAL, **68**, 220 (1946).

[5] Buerger, *Am. Mineral.*, **30**, 551 (1945).