TABLE VI

THIOPHOSPHORYL DIFLUOROMONOBROMIDE

Max.	Min.	s_0	c_k	s_C/s_0	s_L/s_0	s_U/s_0
	2	5.87	−23	0.908	0.959	0.939
3		7.08	39	.915	.968	.948
	3	8.21	−24	.965	.998	1.011
4		9.32	56	.984	1.014	1.032
	4	10.48	−32	.980	1.016	1.024
5		11.47	20	.971	1.016	1.016
	5	12.41	−21	.974	1.012	1.019
6		13.49	15	.971	1.005	1.015
	6	14.46	−15	.970	1.008	1.003
7		15.48	7	.959	1.003	0.994
	7	16.63	− 7	.958	1.001	.996
8		17.90	6	.959	0.999	.998
	8	19.66	− 5	.973	1.007	1.022
9		21.35	5	.956	0.999	0.994
	Average			.963	1.002	1.004
	Average deviation			.015	0.011	0.019
	P–Br, Å.			2.141	2.144	2.149
	F–Br			2.909	2.916	2.922
	S–Br			3.350	3.357	3.363
	S–F			2.794	2.826	2.761
	P–S			1.872	1.844	1.877
	P–F			1.459	1.513	1.426

In taking the averages of the s/s_0 values the last two were weighted at 1/3 and the preceding four at 2/3.

the 2.24 Å. distance calculated from the sum of the atomic radii. The P–S distance agrees with the figure obtained in $PSFBr_2$. The P–F distance agrees well with previously published results,[1] in spite of large uncertainties, and is much shorter than that calculated from the sum of the atomic radii (1.74 Å.).

TABLE VII

	$POBr_3$	$PSBr_3$	$PSFBr_2$	PSF_2Br
P–S, Å.	...	1.89 ± 0.06	1.87 ± 0.05	1.87 ± 0.05
P–F	...	...	1.50 ± 0.10	1.45 ± 0.08
P–Br	2.06 ± 0.03	2.13 ± 0.03	2.18 ± 0.03	2.14 ± 0.04
P–O	1.41 ± 0.07	...	...	...
∠BrPBr	108 ± 3°	106 ± 3°	100 ± 3°	...
∠FPBr	...	...	...	106 ± 3°

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Summary

The molecular structures of four phosphoryl and thiophosphoryl bromides and fluorobromides have been investigated with the results shown in Table VII. The phosphorus–halogen distances are shorter than the corresponding sums of the single covalent atomic radii. The P–S and P–O distances are also shorter than the respective sums of double bond atomic radii. In $POBr_3$ the P–Br distance is shorter and the BrPBr angle is larger than in any other phosphorus–bromine compound.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

X-Ray Crystallographic Studies of Organic Sulfonates. I. The Quarter-hydrates of Certain Sodium 1-Alkane-sulfonates

BY L. H. JENSEN[1] AND E. C. LINGAFELTER

In connection with the study of paraffin-chain sulfonates as colloidal electrolytes, some apparent anomalies have appeared in the heats of solution. In order to explain these effects it is desirable to have some information concerning the crystal structures of the solid phases. Preliminary investigations have shown that the sodium-1-alkane-sulfonates form several hydrated phases. This paper is a report of the study of the quarter-hydrated phase of sodium 1-octane-, 1-decane-, 1-dodecane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate.

All compounds used in the course of the investigation were of the highest purity and had been prepared by previous workers in this Laboratory by the action of aqueous sodium sulfite on the corresponding alkyl halide.[2]

In all cases the crystals were grown from saturated solutions by slow evaporation of the solvent. The crystals were found to grow more rapidly and of sufficient size from mixtures of solvents of moderate dielectric strength. Most of the crystals were grown from mixtures of C. P. carbon tetrachloride and ethanol with or without small amounts of other miscible solvents. A small quantity of glycerol added to the solvent increases the thickness of the otherwise extremely thin laths. The stable solid phase formed in this manner is the quarter-hydrate in the range from a few per cent. water to at least 25% water.

The habit was found to be the same for all crystals obtained, thin tabular parallel to {001} and elongated parallel to the *a* axis. The tablet is outlined by {010} and {110} in most cases, and occasionally by {010}, {110} and {100}.

Data were obtained from Laue, rotation, oscillation and Sauter photographs. For all moving crystal photographs Cu Kα radiation was used.

The dimensions of the unit cells were deter-

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(2) Reed and Tartar, THIS JOURNAL, **57**, 570 (1935).

mined by rotation photographs about the three axes. β was calculated from c_0 and $c_0 \sin \beta = d_{001}$. β was also checked by a zero level *b* axis Sauter photograph for each of the crystals studied. Constants of the unit cells appear in Table I.

TABLE I

CONSTANTS OF THE UNIT CELL

Substance	a_0, Å.	b_0, Å.	c_0, Å.	β
$C_8H_{17}SO_3Na \cdot {}^1/_4H_2O$	16.86	10.17	55.39	101°39′
$C_{10}H_{21}SO_3Na \cdot {}^1/_4H_2O$	16.81	10.15	65.63	103°11′
$C_{12}H_{25}SO_3Na \cdot {}^1/_4H_2O$	16.77	10.12	75.91	104°48′
$C_{14}H_{29}SO_3Na \cdot {}^1/_4H_2O$	16.75	10.06	86.06	105°54′
$C_{16}H_{33}SO_3Na \cdot {}^1/_4H_2O$	16.75	10.05	96.26	106°33′
$C_{18}H_{37}SO_3Na \cdot {}^1/_4H_2O$	16.73	10.05	106.46	107°13′

Densities were determined by the flotation method, using mixtures of 1,4-dioxane and carbon tetrachloride. The water of hydration was determined from the loss in weight upon careful drying. The results of a representative experiment using the decane-sulfonate may be of interest. From a batch of crystals which had been dried in air at room temperature, a sample weighing 0.8496 g. was taken. The sample was placed in a vacuum desiccator (0.1 mm. pressure) at room temperature. After fifty hours the sample had lost 0.0162 g., but the crystals were still clear and an oscillation photograph of one crystal showed that there had been no structural change. This initial rapid loss in weight, undoubtedly due to surface desorption, fell off by one hundred and fifty hours, after a total loss of 0.0203 g., and was followed by a constant slow loss of about 0.0008 g. per one hundred hours. After an additional five hundred hours the temperature was gradually raised to 80° giving finally a constant weight of 0.8144 g. During this latter period the crystals gradually whitened and X-ray photographs showed structural changes to be taking place. The weight loss during the structural change was 0.0149 g., which corresponds to the quarter-hydrate.

Densities and number of molecules per unit cell are given in Table II. The unit cell thus contains 8 molecules of $4RSO_3Na \cdot H_2O$.

TABLE II

DENSITIES AND NUMBER OF MOLECULES PER UNIT CELL

Substance	Observed density, g./cc.	Molecules per unit cell	Calculated density,[a] g./cc.
$C_8H_{17}SO_3Na \cdot {}^1/_4H_2O$	1.23	32	1.27
$C_{10}H_{21}SO_3Na \cdot {}^1/_4H_2O$	1.19	32	1.22
$C_{12}H_{25}SO_3Na \cdot {}^1/_4H_2O$	1.17	32	1.19
$C_{14}H_{29}SO_3Na \cdot {}^1/_4H_2O$	1.14	32	1.17
$C_{16}H_{33}SO_3Na \cdot {}^1/_4H_2O$	1.13	32	1.15
$C_{18}H_{37}SO_3Na \cdot {}^1/_4H_2O$	1.12	32	1.13

[a] Assuming 32 molecules per unit cell.

Oscillation photographs of sodium 1-octanesulfonate quarter-hydrate were indexed out to $\sin \vartheta/\lambda = 0.10$, about 750 planes reflecting in this range. It was found that reflections were extinguished from planes *h0l* for *h* or *l* odd and from planes *hkl* for $k + l$ odd. On crystals of each substance studied, the *h0l* extinction was checked by inspection of a *b* axis zero level Sauter photograph and the *hkl* extinction by inspection of *c* axis oscillation photographs. From these extinctions the space group must be C_s^4 (Aa) or C_{2h}^6 (A2/a). C_{2h}^6 is more likely since it contains 8 equivalent positions, while C_s^4 has a maximum of 4.

It is interesting that the space group is the same as that found by Buerger[3] for sodium stearate hemihydrate and sodium palmitate hemihydrate.

The effective cross-sectional area of the molecules decreases uniformly from 20.99 Å.^{2} for sodium 1-octanesulfonate quarter-hydrate to 20.08 Å.^{2} for sodium 1-octadecanesulfonate quarter-hydrate, and at the same time β increases by about 6°. The cross-sectional area, as would be expected, is somewhat larger than the value of 18.28 Å.^{2} found for sodium stearate[3] and stearic acid.[4] With each increase of chain length by two carbon atoms, there is an increase of eight carbon atoms along the *c* axis. The theoretical increase in the length of the *c* axis is calculated to be 10.18 Å., using tetrahedral bond angles and a carbon atom radius of 0.771 Å., and assuming that there is no difference in packing at the ends of the molecules and that the chains lie parallel to the *c* axis. The average experimental value for this increase is 10.21 Å.

Summary

1. Single crystals of the quarter-hydrates of sodium 1-octane-, 1-decane-, 1-dodecane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate have been grown from mixed solvents.

2. The substances all have the same structure. The unit cell contains 8 molecules of $4RSO_3Na \cdot H_2O$. The space group is probably C_{2h}^6.

SEATTLE, WASHINGTON

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(3) Buerger, *Proc. Natl. Acad. Sci.*, **28**, 529 (1942).

(4) Müller, *Proc. Roy. Soc.* (London), **A114**, 542 (1927).