was determined experimentally. Within the limits of error of measurement, the heat of dilution was zero, *i.e.*, $\Delta H_{303.16} = 0.0 \pm 0.6$ cal./mole, corresponding to a dilution from 0.0543 to 0.0528 molal.

Combination of the two measured heats of solution yields $\Delta H_{303.16} = 735 \pm 15$ cal./mole for the reaction

$$Na_2SO_4\,(V) = Na_2SO_4\,(III) \qquad (3)$$

This result, in conjunction with the heat content values of Table II, leads to $\Delta H_{298.16} = 743 \pm 20$ cal./mole and $\Delta H_{450} = 740 \pm 120$ cal./mole. From the work of Kracek and Gibson,[1] it is estimated that $\Delta F° = 0$ for this reaction at 450 ± 5°K. Hence, $\Delta S°_{450} = 1.64 \pm 0.30$, from which $\Delta S°_{298} = 1.70$ may be obtained by means of entropy increments in Table II. The latter result and Pitzer and Coulter's value for the entropy of Na_2SO_4 (V) ($S°_{298.16} = 35.73 \pm 0.10$) yield $S°_{298.16} = 37.4 \pm 0.5$ cal./deg. mole for Na_2SO_4 (III). Columns 6 and 7 of Table II were obtained by combining the values of ΔH_{450} and ΔS_{450} with the heat content and entropy increments of Na_2SO_4 (III, I, 1) above 450°K.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

X-Ray Crystallography of the Sodium *n*-Alkyl Sulfates[1]

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An X-ray crystallographic study has been made of the sodium *n*-alkyl sulfates, for comparison with previous studies of the sodium 1-alkanesulfonates. Six distinct phases are reported, one of which is very similar to the α-phase of the sulfonates. Unit cells and space groups are given for all six phases.

Introduction

As an extension of our previous studies of the sodium 1-alkane sulfonates, RSO_3Na,[3-7] we have thought it of interest to compare the sodium *n*-alkyl sulfates, RSO_4Na, which may be considered as related to the sulfonates by the replacement of one methylene group by an oxygen atom. The alkyl groups which have been included in the present study are C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{14}, C_{16}, C_{18} and C_{20}.

In the work on the sulfonates, six distinct hydrated phases and one anhydrous phase have been recognized and designated α, β, γ, δ, ε, ζ, η in the order of their discovery. Because of the extreme similarity in molecular structure between the sulfonates and the sulfates, and therefore the possibility of appearance of identical or similar crystal structures, it was decided to use the same series for the sulfate phases. Thus we shall discuss in this paper the α-phase of the sulfates, which is almost identical with the α-phase of the sulfonates[8] and the ι, κ, λ, μ and ν phases, which are different from those observed for the sulfonates.

Experimental

With the exception of the *n*-eicosyl alcohol, the normal alcohols used in this work were the purest alcohols obtainable commercially, and no further attempt was made to increase the purity except for the *n*-hexyl and *n*-heptyl alcohols. The *n*-hexyl and *n*-heptyl alcohols were fractionally distilled under vacuum using a three-foot column having an outside diameter of 18 mm. and packed with small glass helices. The alcohols were obtained from several companies, including the Eastman Kodak Co., Columbia Organic Chemicals Co., Halogen Chemicals, Inc., and the Matheson Co.

The *n*-eicosyl alcohol was made in this Laboratory from *n*-octadecyl bromide (Halogen Chemicals, Inc., Columbia, S. C.) and liquid ethylene oxide (Eastman Kodak Co. white label), using the Grignard reaction. The purity of the *n*-eicosyl alcohol (m.p. 65–65.5°) was checked by comparing the powder pattern with those of known alcohols, namely, the *n*-hexadecyl and *n*-octadecyl alcohols.

All sodium *n*-alkyl sulfates were prepared by the method of Lottermoser and Stoll[9] with the exception of the sodium *n*-hexyl sulfate and sodium *n*-eicosyl sulfate which were prepared following the procedure outlined by Dreger.[10]

The crystals were grown from mixed solvents, primarily ethanol and water, by slow evaporation of the solvent from saturated solutions at constant temperature (±1°). The best crystals were grown from solutions which contained no solvents other than ethanol and water. With the sulfonates, improved crystal formation can often be attained by the addition of such solvents as carbon tetrachloride, 1,4-dioxane and glycerol. In the case of the sodium *n*-alkyl sulfates these additions were usually more detrimental than beneficial.

The data in Table I show the most favorable conditions for growing each of the phases. It should be mentioned that the crystals of the iota and lambda phases are very unstable at room temperature and effloresce to form the more stable alpha phase almost immediately. The μ-phase is also unstable at room temperature and changes to the α-phase by absorption of water vapor. The compounds having a chain of less than eleven carbon atoms form only gels if the percentage of water is raised above 5% in ethanol–water mixtures. The crystals, with the exception of the α-phase in the region of C_{10} to C_{12} and the κ-phase for C_{18} and C_{20}, were very small and poorly formed. All the crystals are extremely thin and show a considerable tendency to bend and warp.

An anhydrous phase, which we have designated the ξ phase, is known to exist from powder patterns but single crystal growth has not been attempted up to the present time due to the elaborate precautions which must be taken to grow anhydrous crystals.

The hydrate determinations were made in the apparatus

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(2) Taken from a thesis submitted by F. F. Rawlings, Jr., in partial fulfillment of the requirements for the Ph.D. degree. Procter and Gamble Fellow, 1949–1950.

(3) L. H. Jensen and E. C. Lingafelter, THIS JOURNAL, **66**, 1946 (1944).

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(9) A. Lottermoser and F. Stoll, *Kolloid-Z.*, **63**, 49 (1933).

(10) E. E. Dreger, G. I. Keim, G. D. Miles, Leo Shedlovsky and John Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).

TABLE I

CRYSTAL GROWTH

Substance	Phase	Solvent	Temp., °C.	Approx. % H_2O
$C_6H_{13}SO_4Na$	α	Ethanol	25–26	1
	λ	Ethanol	25–26	1
	μ	Ethanol	40–41	1
$C_7H_{15}SO_4Na$	α	Ethanol	25–26	1
	λ	95% Ethanol, CCl_4	25–26	5
	μ	Ethanol	40–41	1
$C_8H_{17}SO_4Na$	α	95% Ethanol	25–30	5
	μ	Ethanol	45–50	1
$C_9H_{19}SO_4Na$	α	95% Ethanol	25–30	5
$C_{10}H_{21}SO_4Na$	α	95% Ethanol	25–30	5
	ι	H_2O, 1,4-dioxane	25–26	5
$C_{11}H_{23}SO_4Na$	α	95% Ethanol	25–30	5
	ι	95% Ethanol, H_2O	25–26	25
$C_{12}H_{25}SO_4Na$	α	95% Ethanol	25–30	5
	ι	95% Ethanol, H_2O	25–26	50
$C_{14}H_{29}SO_4Na$	α	95% Ethanol	35–36	5
$C_{16}H_{33}SO_4Na$	α	95% Ethanol	40–41	5
	κ	95% Ethanol, H_2O	30–31	15
	ν	95% Ethanol, H_2O	25–26	20
$C_{18}H_{37}SO_4Na$	α	95% Ethanol	57–58	5
	κ	95% Ethanol	35–36	5
	ν	95% Ethanol, H_2O	25–26	20
$C_{20}H_{41}SO_4Na$	κ	95% Ethanol	40–41	5
	ν	95% Ethanol, H_2O	25–26	20

described by Lingafelter, Jensen and Markham,[11] although, with the exception of the α-phase, it was not possible to make equilibrium measurements at 15 mm. pressure due to unstability of hydrates and the tendency for the alkyl sulfate to hydrolyse at elevated temperatures. Above about 50°, the Toepler pump was used and only the total amount of hydration was measured.

Density measurements were made in most cases by the flotation method using 1,4-dioxane and carbon tetrachloride.

In the case of the λ- and ι-phases, which are both monohydrate phases and decompose rapidly in air at room temperature, the problem of determining the densities was very difficult. It has been shown by Wilcox[12] for the sulfonates that the γ-phase not only decomposes in air at room temperature but also decomposes immediately in mixtures of 1,4-dioxane and carbon tetrachloride. Both the γ-phase sulfonate and the ι- and λ-phase sulfates change over to the α-phase in such solvents.

The densities of the γ-phase sulfonates were measured in a water- and sulfonate-saturated mixture of benzene and carbon tetrachloride. This modification also gave fairly constant values for the ι- and λ-sulfate crystals. As a check, the C_6 and C_7 λ-phase and the C_{11} ι-phase were run using their mother liquor as one solvent and carbon tetrachloride as the other. The C_{12} ι-phase density was measured in a mixture of pure water and water saturated with potassium iodide. Since checks were obtained it is felt that these values are fairly accurate.

X-Ray crystallographic data were obtained from rotation, equi-inclination Weissenberg, and precession photographs using Cu Kα radiation (1.5418 Å.).

Discussion

The crystals of all phases are monoclinic, thin tabular on (001), usually elongated in the *a* direction and terminated by (111) and $(1\bar{1}1)$. Occasionally crystals were found terminated by (211) and $(2\bar{1}1)$ or by (121) and $(1\bar{2}1)$. The end angles (the angle between the zone axes defined by the terminating faces and (001)) as measured with a microscope with a graduated stage are found to be very convenient for rapid identification of the phases. A comparison of the observed and calculated (from **a**$_0$ and **b**$_0$ values) end angles are given in Table II.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED END ANGLES

Unit cell parameters in ångström units.

Phase	Chain length	a$_0$	b$_0$	Terminating planes	End angle Calcd.	End angle Obsd.
α	C_{12}	16.40	10.30	(111) $(1\bar{1}1)$	115°44′	115°
ι	C_{12}	9.46	14.02	(111) $(1\bar{1}1)$	68°2′	66°
κ	C_{18}	9.44	9.15	(111) $(1\bar{1}1)$	91°48′	92°
				(211) $(2\bar{1}1)$	54°34′	54°
λ	C_6	9.46	14.10	(111) $(1\bar{1}1)$	67°44′	68°
μ	C_7	8.50	6.11	(111) $(1\bar{1}1)$	108°36′	108°
ν	C_{16}	9.86	5.25	(111) $(1\bar{1}1)$	123°56′	124°
				(121) $(1\bar{2}1)$	150°12′	146°

In Table III are listed the X-ray crystallographic results (cell elements, space groups, number of molecules) and the hydration values and densities of all of the crystals investigated.

TABLE III

CRYSTALLOGRAPHIC DATA FOR SODIUM *n*-ALKYL SULFATES

Chain length	a$_0$ (Å.)	b$_0$ (Å.)	c$_0$ (Å.)	β (°)	d_{001} (Å.)	Density, g./cm.^{3} Obsd.	Density, g./cm.^{3} Calcd.
α-phase, $RSO_4Na \cdot {}^1/_8H_2O$ (see text), z = 32—eighth hydrate, Aa or A2/a for *n* even; Ia or I2/a for *n* odd							
C_6	16.46	10.41			47.30		1.352
C_7					52.54		1.302
C_8	16.49	10.37	57.79	95°54′	57.48	1.27	1.266
C_9	16.48	10.38	62.69	94°54′	62.46	1.23	1.235
C_{10}	16.45	10.38	68.06	96°48′	67.60	1.19	1.207
C_{11}	16.42	10.36	73.08	96°00′	72.68	1.18	1.187
C_{12}	16.40	10.30	78.28	98°18′	77.46	1.17	1.179
C_{14}	16.38	10.29	88.52	100°30′	87.04	1.13	1.153
C_{16}	16.38	10.30	98.88	102°36′	96.50	1.12	1.130
C_{18}	16.37	10.37	106.48	104°36′	103.04	1.11	1.137
ι-phase, $RSO_4Na \cdot H_2O$, Pa, P2/a or P2$_1$/a, z = 10—monohydrate							
C_{11}	9.51	13.99	32.74	98°6′	32.41	1.12	1.124
C_{12}	9.46	14.02	35.74	92°12′[a]	35.71	1.08	1.073
κ-phase, $RSO_4Na \cdot {}^1/_4H_2O$, P2$_1$/a, z = 8—quarterhydrate							
C_{16}	9.49	9.21	46.98	91°33′[a]	46.96	1.14	1.119
C_{18}	9.44	9.15	49.05	94°00′	48.92	1.16	1.169
C_{20}	9.50	9.16	53.48	93°48′[a]	53.36	1.15	1.157
λ-phase, $RSO_4Na \cdot H_2O$, Aa or A2/a, z = 16—monohydrate							
C_6	9.46	14.10	38.03	103°30′	36.98	1.16	1.200
C_7	9.38	14.05	44.91	97°36′[a]	44.52	1.05	1.068
μ-phase. RSO_4Na, Aa or A2/a, z = 8—indefinite hydrate							
C_6	8.52	6.14	40.38	92°36′[a]	40.34	1.31	1.298
C_7	8.50	6.11	43.61	91°12′	43.60	1.29	1.295
C_8	8.48	6.10	47.36	93°39′[a]	47.26	1.26	1.274
ν-phase, $RSO_4Na \cdot H_2O$; C$_2$, Cm or C2/m, z = 4—monohydrate							
C_{16}	9.86	5.25	40.13	91°31′[a]	40.12	1.16	1.159
C_{18}	9.78	5.27	41.48	92°11′	41.45	1.20	1.212
C_{20}	9.82	5.25	45.35	95°24′[a]	45.15	1.18	1.193

[a] Probably the correct values for β as compared with other members of series but poor upper level pictures make it impossible to be certain.

The α-phase of the sodium *n*-alkyl sulfates is quite similar to that of the sodium 1-alkanesulfonates.[3,7] Not only do they have the same space group and degree of hydration and very similar cell dimensions, but the general distribution of intensity in corresponding diffraction patterns is very similar, particularly for the longer chains

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[11] E. C. Lingafelter, L. H. Jensen and A. E. Markham, *J. Phys. Chem.*, **57**, 428 (1953).

[12] L. A. Wilcox, Ph.D. Thesis, University of Washington, Seattle, Wash., 1951.

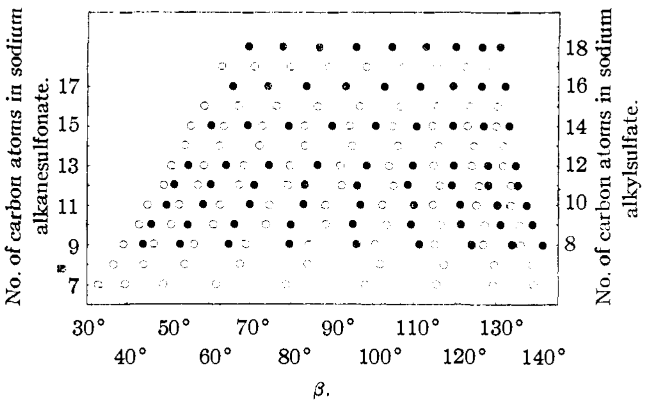

Fig. 1.—Possible values of β for sodium 1-alkanesulfonates, ○, and sodium *n*-alkyl sulfates, ●.

lengths. There are, however, some slight but definite differences.

The $\mathbf{a}_0$ and $\mathbf{b}_0$ for the sulfates are about 16.4 and 10.3 Å., respectively, while the corresponding values for the sulfonates are 16.8 and 10.1 Å.

A comparison of the possible values for β for the sulfates and sulfonates is shown in Fig. 1. The set at the extreme right for the sulfates gives A-centering for even numbers of carbon atoms and I for odd; the extreme right hand set for the sulfonates gives I for even and A for odd. In the case of the sulfonates, the values chosen were those most nearly corresponding to the probable direction of the chains. In the case of the sulfates, as shown below, the chain direction is probably not constant. We have therefore chosen the indicated values, which form the set nearest to 90° which gives Aa (or A2/a) as the space group for those having even numbers of carbon atoms and Ia (or I2/a) for those having odd numbers.

A comparison of the long spacings also shows a definite difference between the sulfates and the sulfonates. This is best illustrated by Fig. 2, in which we have plotted the deviations of the long spacings from a linear function of chain length. The linear function used is $d_{\text{least squares}} = 16.618 + 4.739N$, where N is the number of carbon atoms in the chain for the sulfonates and $N - 1$ (to account for the extra oxygen atom) is the number of carbon atoms in the chain for the sulfates. This function was derived from a least squares treatment of the long spacings of the sulfonates alone. If the long spacings of a homologous series are found to fit a linear function of the chain length, it is reasonable to assume that the chains have a constant tilt from the normal to (001), the magnitude of the tilt, τ, being given by the relation $\cos \tau =$ (slope of d_{001} *vs.* N)/5.100 (5.100 Å. is the expected increase in the direction of the chains, 4×1.275 since there are 4 chains along the *c*-axis.) The constant value of d_{001}-$d_{\text{least squares}}$ for the sulfonates thus indicates a constant tilt of $\tau = \cos^{-1}$ (4.739/5.100) = 21°40′. The long spacings of the sulfates, however, fall into three groups. For the shorter chains, 8 to 11 carbon atoms, the deviation plot shows a linear variation with a slope of 0.35. The slope of d_{001} *vs.* N would therefore have a constant slope of 4.739 + 0.35 = 5.09, indicating a tilt of $\tau = \cos^{-1}$ (5.09/5.10) = 0°. For the intermediate chains, 12 to 16 carbon atoms, the constant value of $d_{001} - d_{\text{least squares}}$ indicates a tilt of 22°, the same as for the sulfonates. Finally, the $C_{18}H_{37}SO_4Na$ has a long spacing which is about 3 Å. shorter than the predicted value, which indicates a tilt still larger than that of the sulfonates.

The data on the other phases are scanty. There can be no question as to the existence of the several phases, but in each case, only one chain length has afforded good enough crystals to unequivocally determine the space group and select the appropriate value for β. It therefore seems advisable to defer any discussion of these phases until additional data are available.

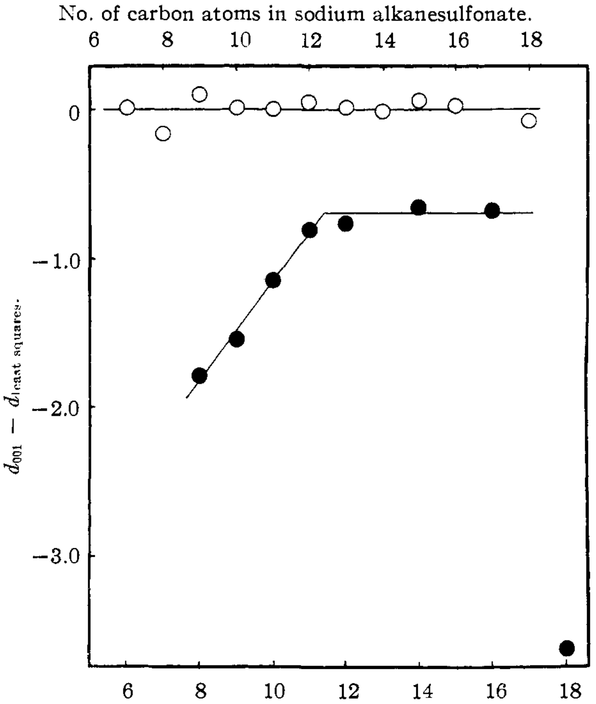

Fig. 2.—Long spacings, d_{001}, of sodium 1-alkanesulfonate, ○, and sodium alkyl sulfates, ●.

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