The Alpha Phase of Some Sodium 1-Alkanesulfonates

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X-Ray crystallographic data for the alpha phase of some sodium 1-alkanesulfonates containing even numbers of carbon atoms (from 8 to 18) have been reported previously.[1] Alpha phase crystals for the compounds containing odd numbers of carbon atoms (from 7 to 15) have now been obtained. This paper presents the data for the odd compounds and compares them with the even compounds.

Experimental

The sodium 1-alkanesulfonates were prepared by the action of aqueous sodium sulfite on the appropriate *n*-alkyl bromides,[2] and were purified by recrystallization from 95% ethanol.

Alpha phase crystals were obtained by cooling hot saturated solutions of the sulfonates in 95% alcohol. In the case of the C_{13} and C_{15} compounds, alpha phase crystals were also obtained by slow evaporation of aqueous solutions at 30–35°, sometimes associated with beta or epsilon crystals.

The hydration of the alpha phase crystals was determined for the C_{11} and C_{13} compounds with the apparatus described by Lingafelter, Jensen and Markham.[3] The values obtained are 0.126 and 0.124 mole of water per mole sulfonate, indicating $RSO_3Na \cdot {}^1/_8H_2O$, as was found for the even compounds. In the run on the C_{11} compound, after all of the water had been removed, the sample was cooled to 95° (*i.e.*, below the transition temperature), and 0.130 mole of water per mole sulfonate was taken up, while X-ray powder patterns showed reconversion to the alpha phase.

The monoclinic crystals show the same habit as previously observed for the even compounds, thin, tabular on (001), somewhat elongated in the *a* direction, and outlined by (01*l*) and (11*l*).

The X-ray data were obtained from rotation, equi-inclination Weissenberg, and precession photographs, using CuKα radiation (λ = 1.5418 Å.). The rotation and Weissenberg cameras were calibrated with NaCl.

The dimensions of the unit cells are given in Table I in which the values for both the odd and even compounds are included for comparison. The values chosen for β are not in conformance with the convention of choosing β as near as possible to 90°, but were chosen to give a unit cell whose *c* axis is probably closest to the actual direction of the paraffin chains. The basis for this choice will be discussed below.

Table I

Unit Cell Dimensions of Alpha-$RSO_3Na \cdot {}^1/_8H_2O$

Substance	a_0, Å.	b_0, Å.	c_0, Å.	β
$C_7H_{15}SO_3Na$	16.88	10.18	55.22	115°36′
$C_8H_{17}SO_3Na$	16.89	10.19	61.19	117°21′
$C_9H_{19}SO_3Na$	16.86	10.13	65.53	115°02′
$C_{10}H_{21}SO_3Na$	16.84	10.17	71.51	116°27′
$C_{11}H_{23}SO_3Na$	16.81	10.09	75.63	114°38′
$C_{12}H_{25}SO_3Na$	16.80	10.14	81.99	116°14′
$C_{13}H_{27}SO_3Na$	16.76	10.04	86.10	114°40′
$C_{14}H_{29}SO_3Na$	16.78	10.08	92.26	115°59′
$C_{15}H_{31}SO_3Na$	16.77	10.07	96.33	114°21′
$C_{16}H_{33}SO_3Na$	16.78	10.07	102.51	115°34′
$C_{18}H_{37}SO_3Na$	16.76	10.07	112.78	115°23′

Densities were determined by the flotation method using 1,4-dioxane and carbon tetrachloride. The unit cells contain 32 molecules of $RSO_3Na \cdot {}^1/_8H_2O$, with calculated and observed densities agreeing in all cases to better than 0.9%.

With the unit cells chosen as indicated in Table I, the extinctions of *hkl* for *k* + *l* odd and *h*0*l* for *h* (or *l*) odd indicate the space groups Aa (C_s^4) or A2/a (C_{2h}^6) for the odd compounds, while Ia(C_s^4) or I2/a(C_{2h}^6) is indicated for the even compounds by the extinctions of *hkl* for *h* + *k* + *l* odd and *h*0*l* for *h* (or *l*) odd.

Discussion

The angle of tilt of the chain direction from the normal to the (001) plane can be estimated from the ratio of the increase in d_{001} (Δd), between homologs to the expected increase in chain length. A comparison of d_{001} values from reported paraffin-chain compounds in which the tilt is zero gives an average value for the increase in chain length of 1.275 Å. per carbon atom. Since Δd is constant throughout the homologous series, with no significant difference between the odds and the evens, the average Δd has been calculated by a least squares treatment, assuming d_{001} to be a linear function of the number of carbon atoms. This gave Δd = 4.739 Å. Thus the tilt is 21° 40′ (*i.e.*, $\cos^{-1}[4.739/(4)(1.275)]$).

Since this calculation indicates a constant tilt of 21° 40′ it seems reasonable to choose the values of β given in Table I, since none of the other possible choices give values of (β − 90°) which are as constant through the series or as near to 21° 40′. The difference between 21° 40′ (the angle of tilt of the chains) and 25° 34′ (the average value of β − 90°) is readily explained by the assumption that, although the several chains in a given crystal are parallel, successive chains in the *c*-direction are not co-linear, there being a shift in the *a* direction between successive chains to permit efficient packing of the chain-ends.

This explanation is corroborated by the fact that β − 90° is approaching the value of the tilt as the chain length increases, due to the fact that the effect of the shift in the *a*-direction has a smaller effect on β, the greater the length of the unit cell in the *c*-direction.

The relation between tilt, β, and the shift at the chain ends can be treated quantitatively as follows. Let τ = actual tilt of chains; Δa = shift at the chain ends (total effect per unit cell). Then

$$d_{001} \tan\left(\beta - \frac{\pi}{2}\right) = d_{001} \tan \tau + \Delta a$$

$$\Delta a = d_{001}\left[\tan\left(\beta - \frac{\pi}{2}\right) - \tan \tau\right]$$

Using this equation, values of Δa for the several members of the series have been calculated for various assumptions of τ until a value of τ was found which gave a constant Δa for all members. This calculation gave a constant $\Delta a \cong 2.86$ Å. for τ = 22° 45′ for the odds and $\Delta a \cong 4.96$ Å. for τ = 23° for the evens. These two values of the tilt are certainly equal within the accuracy of the calculation and the difference of ~1° between this value and the tilt calculated from Δd_{001} is probably less than experimental uncertainties.

Thus it appears that the odd and even members of the homologous series of sodium 1-alkanesulfonates have the same tilt, ~22°, the only difference in their structures being in the displacement between successive layers of the structure.

The great similarity of the structures of the odd

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(1) L. H. Jensen and E. C. Lingafelter, This Journal, **66**, 1946 (1944). In this article the alpha phase was erroneously reported to be $RSO_3Na \cdot {}^1/_4H_2O$ instead of $RSO_3Na \cdot {}^1/_8H_2O$. *Cf.* ref. 3 below.

(2) R. M. Reed and H. V. Tartar, This Journai, **57**, 570 (1935).

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

and even compounds is also evident from a comparison of the distribution of diffraction intensity in reciprocal space, all members of the series showing regions of relatively high intensity in the same positions.

The effective cross-sections of the paraffin chains normal to their chain direction, calculated from $1/8a_0b_0 \cos \tau$, have an average value of 19.6 Å.[2], and show a slight decrease with increasing chain length.

The average molar volume increment is found to be 29.6 $cm.^3/CH_2/mole$.

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Densities and Thermal Expansion Coefficients of Several Organofluoro Compounds

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The densities of several liquid organofluoro compounds were determined (see Table I) in an attempt to find some liquid having an exceptionally high thermal expansion coefficient for an industrial application. The expansion coefficient, α, is defined as $(d_1 - d_2)/d_2(T_2 - T_1)$ where d_1 is the density at the lower temperature, T_1 and d_2 the density at T_2. Published density measurements[1] on perfluoro-*n*-heptane and perfluoro-1,3,5-trimethylcyclohexane indicate that large values of α might be expected for fluorine compounds.

TABLE I

DENSITIES AND THERMAL EXPANSION COEFFICIENTS OF ORGANOFLUORO COMPOUNDS AT VARIOUS TEMPERATURES

Temp., °C.	Ethyl difluoroacetate	Ethyl trifluoroacetate	Benzotrifluoride	1,1,1-Trifluoro-2,3,3-trichloropropene	1,1-Difluoro-3,3-dichloropropene-2	*p*-Flurotoluene	*p*-Fluorobromobenzene	α-Fluoronaphthalene	α-Fluoroanisole
	Density, g./ml.								
30.00	1.1600	1.1670	1.1762	1.5940	1.4401	0.9869	1.5859	1.1256	1.1054
40.00	1.1446	1.1466	1.1621	1.5753	1.4248	.9763	1.5710	1.1168	1.0948
50.00	1.1287	1.1260	1.1478	1.5549	1.4069				
60.00	1.1125		1.1353	1.5336	1.3881	.9548	1.5413	1.0995	1.0734
70.00	1.0958		1.1184	1.5117	1.3692				
80.00	1.0790		1.1033	1.4905	1.3503	.9329	1.5114	1.0821	1.0514
100.00						.9102	1.4803	1.0649	1.0297
120.00							1.4490	1.0464	1.0061
140.00							1.4167	1.0284	0.9824
160.00								1.0091	
Temp. range, °C.	Thermal expansion coefficient, $\alpha \times 10^5$								
30– 40	135	178	121	119	108	108	94	79	97
40– 50	141	183	124	131	127				
50– 60	145		129	139	135				
40– 60						113	96	78	100
60– 70	152		133	145	138				
70– 80	157		137	142	140				
60– 80						118	99	80	104
80–100						125	105	81	106
100–120							108	88	117
120–140							114	88	121
140–160								96	

All of the liquids used were purified by distillation. Calibrated, Sprengel type, Pyrex glass pycnometers having ground glass caps and an approximate capacity of 11 ml. were used. Agitation of the thermostatic fluid, 18 liters of mineral oil, was accomplished by two turbine pumps which brought the oil from the bottom of the lagged metal vessel to the surface. A De Khotinsky thermoregulator which activated a Fisher–Surfass electronic relay afforded temperature control of ±0.02°. The temperatures were measured using National Bureau of Standards thermometers. The average value of two density measurements was taken. From the precision of the temperature control, the accuracy of the weighing (±0.1 mg.) and the agreement obtained for duplicate samples, it is estimated that the coefficients are accurate to ±1% for a 10° range.

A comparison of the expansion coefficients of the fluorinated compounds (Table I) with values calculated from density measurements[2] on the corresponding unfluorinated compounds reveals, in general, that the coefficients are greater for the fluorinated compounds. For example, α-fluoroanisole has a coefficient 2% greater than anisole over the same temperature range. For α-fluoronaphthalene the coefficient is 3% greater than for naphthalene; *p*-fluorobromobenzene, 2% greater than bromobenzene and benzotrifluoride, 12% greater than toluene. Toluene and *p*-fluorotoluene have nearly identical coefficients.

Ethyl acetate has a high expansion coefficient, typical of esters. Ethyl difluoroacetate has an even higher coefficient and ethyl trifluoroacetate has a coefficient that is 31% greater than that of the

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[1] A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 375 (1947).

[2] "Annual Tables of Physical Constants," Sec. 301 (C), American Committee of Annual Tables, National Research Council, Princeton, New Jersey (1941).