

The silver disulfonate was suspended in water, and the silver removed as the sulfide. The yellowish brown filtrate was evaporated down to 2000 ml., exactly neutralized with sodium hydroxide, and concentrated to incipient crystallization. The sodium salt of tetradecamethylene disulfonic acid crystallized out in the ice-box overnight. Several crops of the salt were so obtained. The crystals were purified by dissolving them in a minimum of hot water and adding twice the volume of redistilled acetone. This process of purification was repeated five times. The resulting crystals were white with a slight grayish cast and were not very soluble in water. A solution of the salt was neutral to alizarin. Like the other sodium disulfonates,¹ it showed no tendency to hydrolyze. The yield was 54% of the theoretical.

Anal. Calcd. for $\text{NaO}_3\text{S}(\text{CH}_2)_{14}\text{SO}_3\text{Na}$: C, 41.76; H, 7.01; Na, 11.43. Found: C, 41.74; H, 6.99; Na, 11.48.

The author wishes to express his thanks to Prof. H. T. Clarke of Columbia University for his kind advice and help during the course of this work; and to Mr. W. Saschek for performing the analyses.

Summary

A method for the preparation and purification of the sodium salts of the higher members of the series of the alkane- α,ω -disulfonic acids has been described. Details were given in regard to the synthesis and properties of the sodium salt of tetradecamethylene disulfonic acid.

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The Activity Coefficient of Thallous Iodate in Solutions of Alkane- α,ω -disulfonates

BY GILBERT C. H. STONE

The alkane- α,ω -dicarboxylic acids have been studied extensively by Gane and Ingold,¹ Greenspan,² and others, with the view of ascertaining the fine structure and dimensions of the aliphatic chain in such molecules. Their results, which indicate that the chain has a rigidly extended zigzag configuration, check well with X-ray data.^{3,4,5} These compounds are weak acids, not completely dissociated in aqueous solution. They do not lend themselves to studies, such as activity coefficient measurements from solubility data, which are made on the basis of theories developed on the assumption of complete dissociation. Strong dibasic acids of similar structure would be necessary. With this in mind, a series of alkane- α,ω -disulfonic acids with from one to fourteen carbons were prepared by the author.^{6,7} Titration curves of these acids indicated that they are at least as strong as sulfuric acid.

It was desired to determine the qualitative and, if possible, the quantitative effect which would be obtained by increasing the distance between the two strongly polar groups; and the saturated straight aliphatic chain seemed ideal as a separat-

ing medium, especially since its normal length and diameter are known. It was hoped that by increasing the distance of separation of these polar groups a point might be found where the molecule ceased to behave as bivalent or dibasic and perhaps functioned as two univalent ions. A study of this nature might throw some light on the structure of large-sized multicharged ions, such as the proteins, which behave as multivalent ions despite the relatively large distances which separate the charged groups.⁸

By taking advantage of the Debye-Hückel relationship

$$-\log \gamma_{\pm} = \frac{0.5056 \sqrt{\mu}}{1 + a \times 0.3286 \times 10^8 \sqrt{\mu}} \text{ at } 25^{\circ}$$

and that $\log S/S_0 = -\log \gamma_{\pm}$, solubility measurements seemed one way of attacking the problem. The "a" value gives an estimate of the average ion parameter. While the average distance of closest approach might not be expected to check with the actual size of the alkane- α,ω -disulfonate ion, as other ions are present in the solution, nevertheless, since these other ions remain the same, qualitatively and quantitatively, throughout the series of measurements, the a value should increase as the chain length increases.

In the calculations of the ionic strength

$$\mu = \frac{1}{2} \sum m_i z_i^2$$

(1) Gane and Ingold, *J. Chem. Soc.*, 1594 (1928); 2267 (1928); 1691 (1929); 1375 (1930).

(2) Greenspan, *Chem. Rev.*, **12**, 339 (1933).

(3) Bragg and Bragg, "X-Ray and Crystal Structure," G. Bell and Sons, Lockertie, Scotland, 1925, p. 294.

(4) Muller, *Proc. Roy. Soc. (London)*, **114**, 542 (1927).

(5) Caspari, *J. Chem. Soc.*, 3289 (1928).

(6) Stone, *THIS JOURNAL*, **58**, 488 (1936).

(7) Stone, *ibid.*, **62**, 571 (1940).

(8) Stone and Failey, *J. Phys. Chem.*, **37**, 935 (1933).

if the valence of the disulfonate ion is two, then for a molar solution, μ would be 3. On the other hand, if the ion were so long that it functioned as two moles of a univalent substance, μ would be 2. In other words, the tangent of the limiting law in the former case would be 0.5056, and in the latter case it would be 0.6193. With a decrease in the effective valency due to an increase in chain length, or increase in the separation of the charged groups, the tangents of the curves should be expected to increase. On the other hand, if the effective valency does not decrease and an effect is obtained due only to the increasing size of the molecule, the limiting tangent of the curve should remain the same, 0.5056, but the curves should diverge from this tangent to a greater and greater extent as the size of the ion increases.

Unfortunately, the solubility of the sodium salt of the alkane- α,ω -disulfonates reaches a maximum at the fourth or fifth carbon stage and then decreases rapidly. The salt of the fourteen carbon member of the series is just sufficiently soluble that these measurements could be made on it. To continue lengthening the chain in an attempt to achieve the above-mentioned effect seemed fruitless.

Experimental

The sodium salt of methanedisulfonic acid was prepared according to Schroeter.⁹ The salt was recrystallized

TABLE I
SOLUBILITY OF $TlIO_3$ IN THE PRESENCE OF SODIUM ALKANE α,ω -DISULFONATES

Soly. of $TlIO_3$ in water = $S_0 = 1836 \times 10^{-6}$ mole per liter at 25°

$$-\log \gamma_0 = \frac{0.5056 \sqrt{0.001836}}{1 + 3 \times 10^{-3} \times 0.3286 \times 10^8 \sqrt{0.001836}}$$

$$= 0.0208^b \quad -\log \gamma_{\pm} = 0.0208 + \log S/S_0$$

| Molarity of solvent salt | Soly. $\times 10^6$ | $-\log \gamma_{\pm}$ | $\sqrt{\mu}$ | $a, \text{\AA}$ |
|--------------------------|-----------------------------------|----------------------|--------------|-----------------|
| | ^a $NaO_3S(CH_2)SO_3Na$ | | | |
| 0.0200 | 2300 | 0.1199 | 0.249 | 2.0 |
| .0100 | 2138 | .0881 | .179 | 2.1 |
| .0050 | 2036 | .0669 | .130 | 2.0 |
| .0020 | 1937 | .0453 | .089 | 2.1 |
| .0010 | 1897 | .0362 | .070 | 1.7 |
| .0005 | 1867 | .0293 | .058 | 1.9 |

Av. 1.9

| | | | | |
|-------|------------------------|-------|------|-------|
| | $NaO_3S(CH_2)_2SO_3Na$ | | | |
| .0200 | 2220 | .1033 | .249 | 3.3 |
| .0100 | 2094 | .0779 | .179 | 3.5 |
| .0050 | 2009 | .0599 | .130 | 3.2 |
| .0020 | 1927 | .0418 | .089 | 3.6 |
| .0010 | 1887 | .0327 | .070 | (4.3) |
| .0005 | 1868 | .0283 | .058 | 2.8 |

Av. 3.3

| | | | | |
|-------|------------------------|-------|------|-------|
| | $NaO_3S(CH_2)_3SO_3Na$ | | | |
| .0200 | 2216 | .1025 | .249 | 3.4 |
| .0100 | 2094 | .0779 | .179 | 3.5 |
| .0050 | 2007 | .0595 | .130 | 3.1 |
| .0020 | 1924 | .0411 | .089 | (4.1) |
| .0010 | 1890 | .0334 | .070 | 3.5 |
| .0005 | 1868 | .0283 | .058 | (2.8) |

Av. 3.4

| | | | | |
|-------|------------------------|-------|------|-------|
| | $NaO_3S(CH_2)_4SO_3Na$ | | | |
| .0200 | 2207 | .1008 | .249 | 3.6 |
| .0100 | 2093 | .0777 | .179 | 3.5 |
| .0050 | 2003 | .0586 | .130 | 3.7 |
| .0020 | 1921 | .0405 | .089 | (4.5) |
| .0010 | 1891 | .0336 | .070 | 3.4 |
| .0005 | 1860 | .0265 | .058 | (6.0) |

Av. 3.5

| | | | | |
|-------|------------------------|-------|------|-------|
| | $NaO_3S(CH_2)_5SO_3Na$ | | | |
| .0200 | 2198 | .0990 | .249 | 3.8 |
| .0100 | 2079 | .0748 | .179 | 4.1 |
| .0050 | 1997 | .0573 | .130 | 4.2 |
| .0020 | 1915 | .0391 | .089 | (5.9) |
| .0010 | 1884 | .0320 | .070 | (5.2) |
| .0005 | 1860 | .0264 | .058 | (6.1) |

Av. 4.0

| | | | | |
|-------|------------------------|-------|------|-------|
| | $NaO_3S(CH_2)_6SO_3Na$ | | | |
| .0200 | 2196 | .0986 | .249 | 3.9 |
| .0100 | 2084 | .0759 | .179 | 3.9 |
| .0050 | 1995 | .0569 | .130 | 4.3 |
| .0020 | 1920 | .0402 | .089 | 4.8 |
| .0010 | 1890 | .0334 | .070 | (5.2) |
| .0005 | 1860 | .0264 | .058 | (6.1) |

Av. 4.2

| | | | | |
|-------|---------------------------|-------|------|-------|
| | $NaO_3S(CH_2)_{10}SO_3Na$ | | | |
| .0200 | 2176 | .0946 | .249 | 4.4 |
| .0100 | 2071 | .0731 | .179 | 4.5 |
| .0050 | 1994 | .0567 | .130 | 4.4 |
| .0020 | 1924 | .0411 | .089 | 4.1 |
| .0010 | 1885 | .0322 | .070 | 4.9 |
| .0005 | 1861 | .0267 | .058 | (5.5) |

Av. 4.5

| | | | | |
|-------|--|-------|------|-----|
| | ^a $NaO_3S(CH_2)_{14}SO_3Na$ | | | |
| .0200 | 2135 | .0875 | .249 | 5.5 |
| .0100 | 2054 | .0707 | .179 | 5.2 |
| .0050 | 1977 | .0541 | .130 | 5.7 |
| .0020 | ... | ... | ... | ... |
| .0010 | 1873 | .0307 | .070 | ... |
| .0005 | 1856 | .0267 | .058 | 5.5 |

Av. 5.5

^a In the cases of the one carbon and the fourteen carbon sodium disulfonate solutions, a different sample of the saturating salt was used. An average of 30 solubility determinations on this thallos iodate resulted in $S_0 = 1831 \times 10^{-6}$ mole per liter. ^b An a value of 3 Å. was assumed for $TlIO_3$.

several times and the analysis checked with the theoretical values.

The synthesis and purification of the other sodium salts of the alkane- α,ω -disulfonic acids, as well as their titration curves, have been described.^{6,7}

(9) Schroeter, *Ann.*, **418**, 246 (1918).

The preparation of thallos iodate and the method of analysis were those of La Mer and Goldman.¹⁰

Solutions of the sodium salts of the disulfonic acids were made up with conductivity water and of the strengths shown in Table I. These solutions were rotated with the solid thallos iodate in glass-stoppered Pyrex bottles in a water-bath for twenty-four hours at a temperature of $25.00 \pm 0.01^\circ$. The solid was allowed to settle and the supernatant solution filtered at 25.0° and then analyzed.

Discussion

From Curve I, which is a plot of the data given in Table I, it can be seen that despite the lengthening of the aliphatic chain or the greater separation of the sulfonate groups, all the curves approach the same theoretical limiting tangent of 0.5056. However, these curves deviate from the limiting tangent more and more as the chain length increases. This would indicate that the sodium salts of the alkane- α,ω -disulfonic acids behaved in solution as bivalent compounds, there being no indication in these experiments that even with a separation of fourteen carbons the two terminal negative groups ceased to have an effect upon each other.

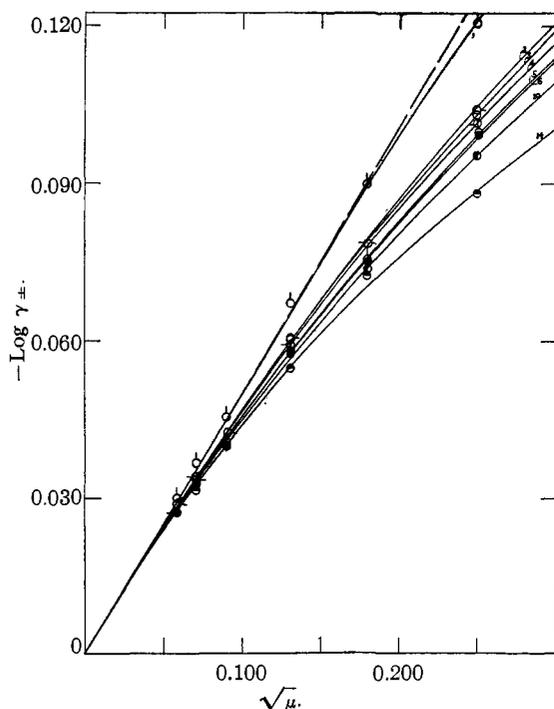


Fig. 1.—Curve 1, \circ , $\text{NaO}_3\text{S}(\text{CH}_2)\text{SO}_3\text{Na}$; Curve 2, \circ , $\text{NaO}_3\text{S}(\text{CH}_2)_2\text{SO}_3\text{Na}$; Curve 3, φ , $\text{NaO}_3\text{S}(\text{CH}_2)_3\text{SO}_3\text{Na}$; Curve 4, \square , $\text{NaO}_3\text{S}(\text{CH}_2)_4\text{SO}_3\text{Na}$; Curve 5, \ominus , $\text{NaO}_3\text{S}(\text{CH}_2)_5\text{SO}_3\text{Na}$; Curve 6, \ominus , $\text{NaO}_3\text{S}(\text{CH}_2)_6\text{SO}_3\text{Na}$; Curve 10, \bullet , $\text{NaO}_3\text{S}(\text{CH}_2)_{10}\text{SO}_3\text{Na}$; Curve 14, \bullet , $\text{NaO}_3\text{S}(\text{CH}_2)_{14}\text{SO}_3\text{Na}$.

(10) La Mer and Goldman, *THIS JOURNAL*, **51**, 2632 (1929).

The continuous deviation of the curves from the theoretical limiting tangent with increasing chain lengths may be attributed to the increasing size of the ion involved. As can be seen from the table of data, the average distance of closest approach becomes greater as the chain becomes longer. These values of a were calculated by means of the La Mer, Gronwall and Greiff extended formula of the Debye-Hückel relationship.¹¹ The calculated values of a for any one series of measurements on any one disulfonate do not vary very much. As might be expected, the values obtained for a on the most dilute solutions showed the greatest deviation from the average; in these cases the accuracy of the measurements was at its lowest.

An attempt was made to correlate the average values of a with an increase in one CH_2 group. Approximately 0.25 \AA . corresponded to the size of the methylene group. This value is far from that obtained by measurements of other kinds. However, the a values calculated on the basis of the Debye-Hückel equation do not check well with, for example, the size of the ion found by X-ray measurements. The value of a is not the absolute size of the ion, but the distance of nearest approach. Hydration, the presence of other ions, etc., will affect this value greatly.

Notwithstanding all this, the effect of separating the two charged groups of the ion is not as great as one might have expected. However, the long disulfonate ion, with a negative charge at either end, in all likelihood would bend around in the presence of an ion of opposite charge, both negative groups being attracted by the positive ion. Such a bending would greatly decrease the effective size of the disulfonate ion and account for the results obtained. This bending would not take place in the solid state nor in the case of the corresponding dicarboxylic acids, which are not greatly dissociated. Such a distortion would also explain why, even with a distance equivalent to fourteen carbon atoms between two charged groups, the bivalent disulfonate ion shows no unusual effect and behaves like a small ion of equal charge.

The author wishes to express his gratitude to Professor H. T. Clarke of Columbia University for his kind help and coöperation in the work on this problem.

(11) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **25**, 2245 (1931).

Summary

The solubility of thallos iodate was measured at 25° in aqueous solutions of the sodium salt of alkane- α,ω -disulfonic acids with from one to fourteen carbons in the separating chain. The results were considered on the basis of the Debye-Hückel equation.

All of the above-mentioned salts functioned as bivalent compounds, despite the great separation of the sulfonate groups in the case of the latter members of the series.

The values for the mean effective ionic diameters were calculated for each salt of the series of

the alkane- α,ω -disulfonates. These values increased with increasing chain length. However, this increase in effective size was equivalent to only 0.25 Å. for each additional CH₂ group in the chain.

The small increment in effective size due to the addition of a methylene group to the aliphatic chain, as well as the bivalency of the disulfonate ion, was accounted for on the assumption that the molecule bent in the presence of a positive ion, both negative groups of the disulfonate ion being attracted to the oppositely charged particle.

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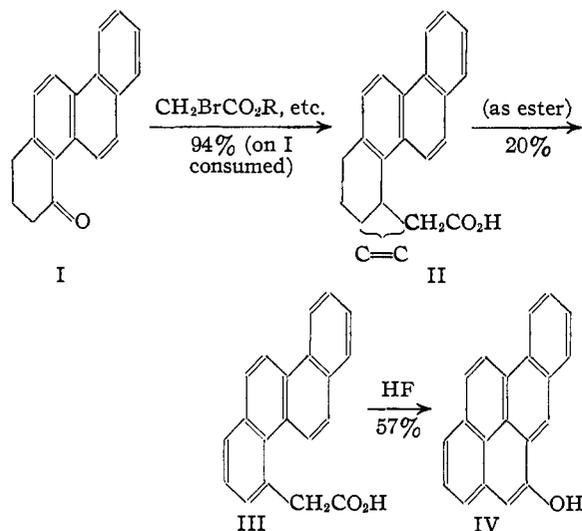
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Synthesis of 6-Hydroxy-3,4-benzpyrene and 8-Isopropyl-1,2-benzanthracene from 9,10-Dihydrophenanthrene

BY LOUIS F. FIESER AND WILLIAM S. JOHNSON

In extension of previous work¹ in which a satisfactory method was developed for obtaining 4-keto-1,2,3,4-tetrahydrochrysene (I) starting with 9,10-dihydrophenanthrene,^{1b} this ketone has been utilized for the synthesis of the hitherto undescribed 6-hydroxy-3,4-benzpyrene (IV) by the process outlined.



The Reformatsky reaction at first seemed unpromising because of the separation of an insoluble complex which stopped the reaction. While no way was found for pushing the reaction to comple-

(1) Fieser and Johnson, (a) *THIS JOURNAL*, **61**, 168 (1939); (b) *ibid.*, **61**, 1647 (1939).

tion, it proved quite satisfactory to operate under mild conditions permitting the easy recovery of the unchanged starting material in a pure form after saponification of the ester. After dehydration with formic acid, the crude acidic product, possibly consisting of a mixture of isomers, was esterified and the ester dehydrogenated with sulfur, which gave better results than palladium charcoal. The product was contaminated with a small amount of high melting material which appeared to be a hydrocarbon, but this was separated easily after saponification of the ester.

Cyclization of 4-chryseneacetic acid (III) proceeded well under the influence of anhydrous hydrogen fluoride² giving pure 6-hydroxy-3,4-benzpyrene (IV) in good yield. It seemed interesting to determine whether an intermediate ketone could be detected, for in the formation of anthrones by cyclization, the use of hydrogen fluoride provides a particularly advantageous means of isolating the material in the ketonic condition and avoiding enolization. Even with highly sensitive anthrones which have not been isolated as such, it has been possible to effect a Grignard addition by adding the reagent directly to the crude residue remaining after evaporation of the hydrogen fluoride.^{2b,3} This technique was applied in the present case and the mixture examined care-

(2) Fieser and Hershberg, (a) *ibid.*, **61**, 1272 (1939); (b) **62**, 49 (1940).

(3) Fieser and Cason, *ibid.*, **62**, 432 (1940).