pounds, and hence the use of the intrinsic constant will not change the *relative* affinities of the two substances.

The first binding constant can be evaluated readily for methyl orange by substituting the known value of $K$, $4.48 \times 10^{-4}$, into (4). A value of $4.9 \times 10^4$ is obtained for $k_1$, $-5960$ calories/mole for $\Delta F_1$. For azosulfathiazole, a $k_1$ of $1.25 \times 10^5$ has been determined by methods described above. $\Delta F_1$ thus becomes $-6480$ calories/mole. The additional affinity of 520 calories which the protein has for azosulfathiazole must be attributed to the additional groups present in this molecule. Since there are many added substituents it is impossible to consider any one as most important although it seems likely that the van der Waals interaction of the added aromatic ring contributes the major portion of this extra stabilization energy. Additional investigations are in progress in which the binding of closely related analogs is being studied so that the contributions of various substituents to the binding energy may be evaluated.

**Conclusions.**—From the data and calculations presented it is obviously possible to correlate the binding of organic anions by the established principles of the law of mass action. Deviations from statistical behavior can be explained adequately in terms of electrostatic contributions and it is unnecessary to assume that the associated cations are bound simultaneously with the organic anions. The equations presented also permit the ready evaluation of equilibrium constants and free energies of binding of the first anion by the protein and consequently afford a simple quantitative method of evaluating the contributions of various structural groups to the strength of the bond.

**Acknowledgments.**—These investigations were supported in part by grants-in-aid from the Abbott Fund of Northwestern University and from the Sigma Xi Research Fund.

## Summary

Quantitative data are presented on the binding of two sulfonate anions by bovine serum albumin. The data are analyzed in terms of statistical and electrostatic factors which contribute to the strength of binding. A method of evaluating the strength of protein–anion bonds is presented.

EVANSTON, ILLINOIS RECEIVED MARCH 29, 1946

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

# Studies of Sulfonates. VIII. Some Surface and Interfacial Tension Measurements with Aqueous Solutions of Certain Alkanesulfonates

BY E. C. LINGAFELTER, O. L. WHEELER[1] AND H. V. TARTAR

The surface properties of aqueous solutions of paraffin-chain colloidal electrolytes are of both theoretical and practical interest. The change of surface tension with time including final equilibrium values at 40° has been determined in this Laboratory[1a] by the sessile bubble method for a series of solutions of varying concentrations of sodium decane, dodecane and tetradecane sulfonate, sodium laurate buffered with 0.002 $M$ sodium carbonate, and of monoethanolammonium laurate, myristate and oleate buffered with excess monoethanolamine. Long and Nutting[2] have made a similar study at 25° of sodium laurate solutions over a $p$H range of 7 to 11. Previously it has been shown[3,4] that the surface tension of solutions of sodium soaps is markedly affected by change of $p$H. Powney and Addison[4] have determined by the drop weight method the interfacial tension of solutions of alkyl sulfates (carbon chain, $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$) and of the corresponding sodium soaps at varying $p$H values against xylene. While they may have obtained reproducible results, they evidently did not obtain equilibrium values. The drop weight method does not permit the interface to age for more than a brief time, not long enough for equilibrium conditions to become established. Furthermore, these workers did not presaturate the xylene and solutions with each other; as will be shown later, this has an influence of considerable magnitude on the values obtained.

**Surface Tensions of Solutions of Dodecane Sulfonic Acid and of Magnesium Octane Sulfonate.**—The acid was prepared by the method of Zuffanti.[5]

The magnesium octane sulfonate was taken from a stock of this compound prepared by Dr. R. D. Cadle[6] in this Laboratory by precipitation with magnesium chloride from a hot solution of sodium octane sulfonate. The salt was then purified by two crystallizations from water and finally analyzed by ignition and subsequent conversion to magnesium pyrophosphate; the results were very close to the theoretical requirement.

The surface tensions of the dodecane sulfonic acid solutions were measured by the sessile

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(1) Standard Oil Company of California Fellow, 1941–1942.

(1a) Tartar, Sivertz and Reitmeier, THIS JOURNAL, **62**, 2375 (1940).

(2) Long and Nutting, *ibid.*, **63**, 84 (1941).

(3) Long, Nutting and Harkins, *ibid.*, **59**, 2197 (1937).

(4) Powney and Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937); **34**, 372 (1938); **34**, 635 (1938).

(5) Zuffanti, THIS JOURNAL, **62**, 1044 (1940).

(6) Cadle, "A Study of the Properties of Salts of Certain Higher Sulfonic Acids," Doctorate Thesis, University of Washington, Seattle, 1940.

bubble comparator procedure.[7] For the magnesium octane sulfonate solutions the pendent-drop method[8,9] was used. A departure from the conventional procedure was made in the design of the cell. It was of Pyrex glass, with body cylindrical in shape, about 5 cm. long and 4 cm. in diameter; there were two tubular openings at the top, one for connecting the syringe with the drop-forming tip and one for filling the cell with liquid for the interfacial tension measurements. Precautions identical with those required for the sessile bubble cell[7] were used in sealing on the optically plane glass windows.

The drop-forming tips ranged from 1.5 to 6.0 mm. in diameter and were ground uniformly circular in cross section. The cell was mounted in an air thermostat, with fan equipment for circulation and with temperature held constant to ±0.02° by means of a mercury toluene regulator. A variety of photographic plates and films were tried; the best results were obtained with Eastman, Panatomic X, cut film.

The experimental results from the surface tension measurements are recorded in Table I and shown graphically in Figs. 1 and 2. For comparison the curve for solutions of sodium dodecane sulfonate[1a] is included. The influence of the gegen ion is clearly manifest. In the case of the acid, the critical concentration for micelle formation (point of minimum tension) is lower than that of solutions of the sodium salt; also the minimum surface tension is higher and the increase in surface tension above the critical concentration is considerably less. The critical concentration of 0.008 *M* at 40° appears to agree with the results of the electrical conductance measurements by McBain and Betz[10] at 25°, taking into account the difference in temperature.

TABLE I

EQUILIBRIUM SURFACE TENSIONS OF SOLUTIONS OF DODECANE SULFONIC ACID AND OF MAGNESIUM OCTANE SULFONATE AT 40°

| Dodecane sulfonic acid | | Magnesium octane sulfonate | |
|---|---|---|---|
| Moles/1000 g. $H_2O$ | Surf. ten., dynes/cm. | Moles/1000 g. $H_2O$ | Surf. ten., dynes/cm. |
| 0.00300 | 37.64 | 0.0179 | 42.0 |
| .00512 | 31.73 | .0329 | 37.0 |
| .00659 | 30.31 | .0421 | 33.9 |
| .00756 | 29.76 | .0495 | 31.8 |
| .00811 | 30.38 | .0611 | 30.5 |
| .00842 | 31.30 | .0733 | 31.1 |
| .00847 | 32.87 | .0847 | 31.3 |
| .00894 | 32.15 | | |
| .00949 | 34.03 | | |
| .01279 | 36.09 | | |
| .01411 | 35.76 | | |
| .01584 | 35.58 | | |

The rate of surface aging closely paralleled that of the sodium salt; several days were required to reach equilibrium with the dilute solutions, while only a few hours were necessary above the critical concentration.

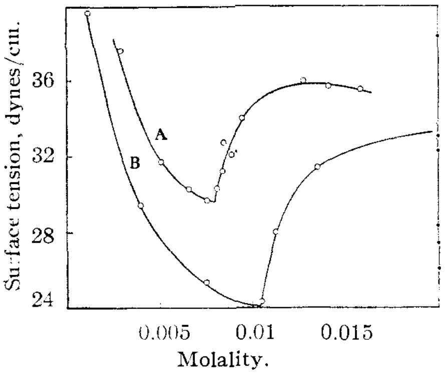

Fig. 1.—Surface tensions of solutions of dodecanesulfonic acid and of sodium dodecanesulfonate: A, acid; B, salt.

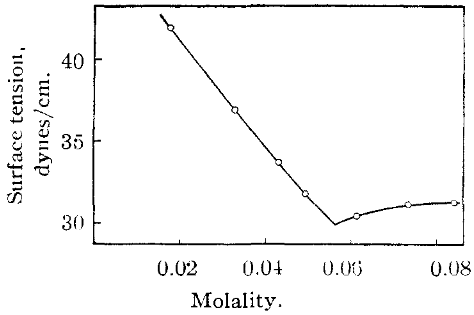

Fig. 2.—Surface tensions of solutions of magnesium octanesulfonate.

The results with magnesium sulfonate are of interest in showing the effect of a bivalent gegen ion. While change of valence in this ion is known to have considerable influence on the surface properties of solutions, very few data are given in the literature. Micelle formation definitely occurs at 0.055 *M* concentration which confirms the findings of Cadle[6] from electrical conductance measurements. Similar data for solutions of sodium octane sulfonate do not give evidence of micelle formation. It has also been shown in this Laboratory[6] that the substitution of the magnesium ion for the sodium ion in the higher members of the alkane sulfonate series lowers the critical concentration considerably.

**Interfacial Tensions of Solutions of Sodium Decane, Dodecane and Tetradecane Sulfonate against Benzene.**—Benzene of analyzed reagent quality was further purified by washings with concentrated sodium hydroxide solution and finally with water. Final purification was accomplished by fractional distillation using a column of high efficiency. The purity was checked by an accurate determination of the refractive index.

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(7) Wheeler, Tartar and Lingafelter, THIS JOURNAL, **67**, 2115 (1945).

(8) Andreas, Hauser and Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

(9) Smith and Sorg, *ibid.*, **46**, 671 (1941).

(10) McBain and Betz, THIS JOURNAL, **57**, 1905 (1935).

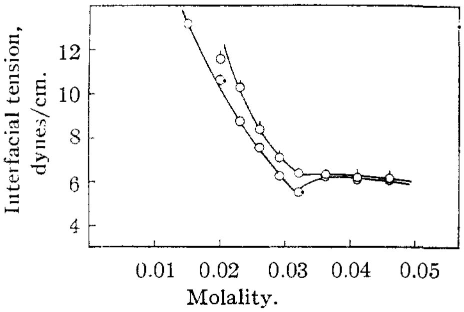

Fig. 3.—Interfacial tensions for sodium decanesulfonate: ȯ, non-equilibrium; ○, equilibrium.

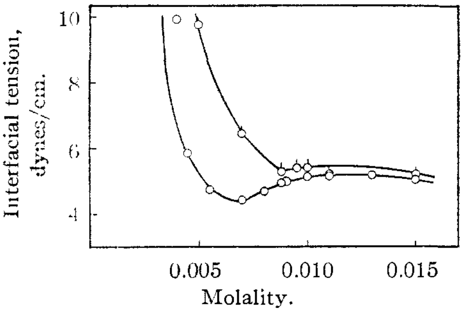

Fig. 4.—Interfacial tensions for sodium dodecanesulfonate: ȯ, non-equilibrium; ○, equilibrium.

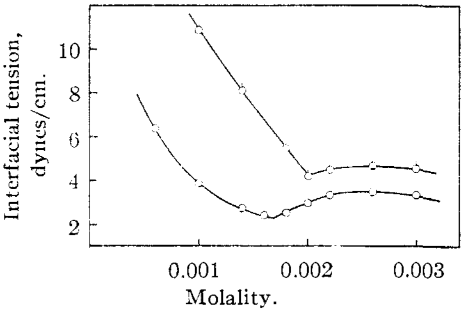

Fig. 5.—Interfacial tensions for sodium tetradecanesulfonate: ȯ, non-equilibrium; ○, equilibrium.

The sodium sulfonates were prepared by previous workers[11,12] in this Laboratory and were in a very pure state.

The measurements of interfacial tension were made by the pendent-drop method.

The aqueous solutions were prepared and each divided into two equal portions. To one half of each solution an equal volume of benzene was added, care being taken to avoid the formation of an emulsion. These were placed in tightly stoppered bottles in a thermostat and allowed to stand, with occasional rotation, for a week to permit the two liquids to become mutually saturated. The other half of each solution was kept unchanged.

Two types of measurements were made. In the first, pure benzene was placed in the cell and allowed to reach temperature equilibrium. The solution of the sulfonate was brought to temperature and a portion placed in the hypodermic syringe. The syringe was then placed in the cell and a drop of the solution formed in the benzene. It was necessary to use unusually large tips because of the small difference in density between the solution and the benzene. Photographs were made as soon as possible after the formation of the drops to obtain data furthest from the condition of mutual saturation of the liquids.

In the second procedure, the previously saturated solutions were used, thus affording a rapid approach to interfacial equilibrium. The drop was allowed to reach equilibrium before it was photographed. Aging to equilibrium took place rapidly in these systems, usually in a few minutes and never more than two hours.

The data are reported in Table II and graphed in Figs. 3, 4 and 5. The apparent critical con-

TABLE II

INTERFACIAL TENSIONS OF SOLUTIONS OF SODIUM DECANE, DODECANE AND TETRADECANE SULFONATE AGAINST BENZENE AT 40°

| Moles/1000 g. $H_2O$ | Interfacial tension, dynes/cm. Equilibrium | Non-equilibrium |
|---|---|---|
| | Sodium Decane Sulfonate | |
| 0.0150 | 13.20 | 14.70 |
| .0200 | 10.70 | 11.58 |
| .0230 | 8.80 | 10.30 |
| .0260 | 7.61 | 8.47 |
| .0290 | 6.29 | 7.16 |
| .0320 | 5.53 | 6.46 |
| .0360 | 6.36 | 6.32 |
| .0410 | 6.16 | 6.21 |
| .0460 | 6.13 | 6.20 |
| | Sodium Dodecane Sulfonate | |
| 0.00400 | 9.91 | |
| .00450 | 5.88 | |
| .00500 | | 9.75 |
| .00550 | 4.78 | |
| .00700 | 4.45 | 6.46 |
| .00800 | 4.70 | |
| .00881 | 4.96 | 5.31 |
| .00900 | 4.98 | |
| .00950 | | 5.42 |
| .01000 | 5.17 | 5.36 |
| .01100 | 5.17 | 5.15 |
| .01300 | 5.22 | |
| .01500 | 5.07 | 5.18 |
| | Sodium Tetradecane Sulfonate | |
| 0.000600 | 6.37 | |
| .001000 | 3.90 | 10.95 |
| .001400 | 2.78 | 8.12 |
| .001600 | 2.42 | |
| .001800 | 2.56 | 5.51 |
| .002000 | 2.97 | 4.24 |
| .002200 | 3.32 | 4.53 |
| .002600 | 3.50 | 4.65 |
| .003000 | 3.34 | 4.54 |

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(11) Reed and Tarter, THIS JOURNAL, **57**, 570 (1935); **58**, 322 (1936).

(12) Tartar and Wright, *ibid.*, **61**, 539 (1939).

centrations in all cases differ considerably from those found by surface tension measurements on aqueous solutions of the sulfonates.[1a] This change is considerably greater with the saturated than with the unsaturated solutions. With the latter the shift is probably caused by a partial saturation at the interface during the time that elapsed between the formation of the drop and the exposure of the photographic film.

The critical concentrations of the sulfonate solutions as shown by the equilibrium interfacial tension together with the values found by surface tension measurements on the sulfonate solutions[1a] are recorded in Table III, the percentage change in concentration being included. There is a marked relationship between this percentage and the carbon chain length of the sulfonate. The findings of Powney and Addison[4] are similar to the non-equilibrium values.

TABLE III

CHANGE OF CRITICAL CONCENTRATION UPON SATURATING AQUEOUS SOLUTIONS OF LONG-CHAIN SODIUM SULFONATES WITH BENZENE

| Length of chain | Critical concentration | | Change, % |
|---|---|---|---|
| | Surf. ten. | Interfac. ten. | |
| 10 | 0.0370 | 0.0317 | 14 |
| 12 | .0100 | .0073 | 27 |
| 14 | .0027 | .0017 | 37 |

The primary factor causing the shift in the critical concentration when the solution is saturated with benzene is not clearly understood. Most likely it is due mainly to the well-known solvent action of the micelles.[13] Many organic substances, which are normally insoluble in water, dissolve appreciably in solutions of paraffin-chain colloidal electrolytes with concentrations above the critical values; solution evidently occurs in the hydrocarbon interior of the micelle. The data presented above indicate that the benzene not only dissolves in the micelles but actually aids in their formation.

Some portion of the difference between the interfacial tension values for equilibrium and non-equilibrium conditions might possibly be due to solution of some sodium alkane sulfonate in the benzene,[14] although this would seem unlikely because of the low solubility of the sodium salt in benzene.[4] Further work is being done in an attempt to answer this question.

## Summary

1. The equilibrium surface tensions of solutions of dodecane sulfonic acid and of magnesium octane sulfonate have been determined at 40°. The data, considered with others, indicate the marked role the gegen ion plays in micelle formation.

2. Both equilibrium and non-equilibrium interfacial tensions have been measured for solutions of sodium decane, dodecane and tetradecane sulfonate against benzene. The data show that the critical concentration for micelle formation with benzene-saturated solutions is lower than that for aqueous solutions of the corresponding sulfonates not containing benzene; the decrease is a function of the carbon chain length. Benzene appears to aid in micelle formation.

SEATTLE, WASHINGTON RECEIVED[15] APRIL 9, 1946

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(13) Smith, *J. Phys. Chem.*, **36**, 1401, 1672 (1932); Lawrence, *Trans. Faraday Soc.*, **33**, 325, 815 (1937); McBain and co-workers, THIS JOURNAL, **58**, 2610 (1936); **60**, 223 (1938); **63**, 670 (1941); *Ind. Eng. Chem.*, **34**, 915 (1942); "Recent Advances in Colloid Science," Interscience Publishers, New York, N. Y., 1942, p. 99; Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie, Paris, 1936.

(14) Davis and Bartell, *J. Phys. Chem.*, **47**, 40 (1943).

(15) Original manuscript received October 8, 1943.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA AND THE DEPARTMENT OF RESEARCH IN CHEMICAL PHYSICS OF MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

# A Redetermination of the Lattice Constant of Lead

BY HAROLD P. KLUG

The lattice constants of the elements are of such fundamental importance in both theoretical and applied chemistry that it is desirable to know them with the highest precision possible. One of the problems of precise lattice constant determination is the acquisition of a sample of sufficient purity to warrant such a study. Recently a sample of lead of very exceptional purity became available, so it seemed desirable to make a redetermination of the lattice constant.[1] The results of the investigation are reported in this communication.

Spectrographic analysis indicated the sample to have a purity of $99.999^{+}$% lead. The only metallic impurity lines observed were a very weak bismuth line and a very weak copper line. The best sample of lead to have a diffraction study up to the present is apparently that used for a determination of its thermal expansion by Stokes and Wilson,[2] which they report to have a purity of 99.997%, the impurities observed being silver, copper, antimony and bismuth.

The details of the X-ray technique used in the precision lattice constant determination have been described earlier.[3] CuK radiation was used

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(1) The author wishes to express his appreciation to H. R. Harner, chief chemist, Eagle-Picher Lead Company, Joplin, Mo., for generously providing this sample.

(2) Stokes and Wilson, *Proc. Phys. Soc. London*, **53**, 658 (1941).

(3) Klug and Alexander, THIS JOURNAL, **62**, 1492 (1940).