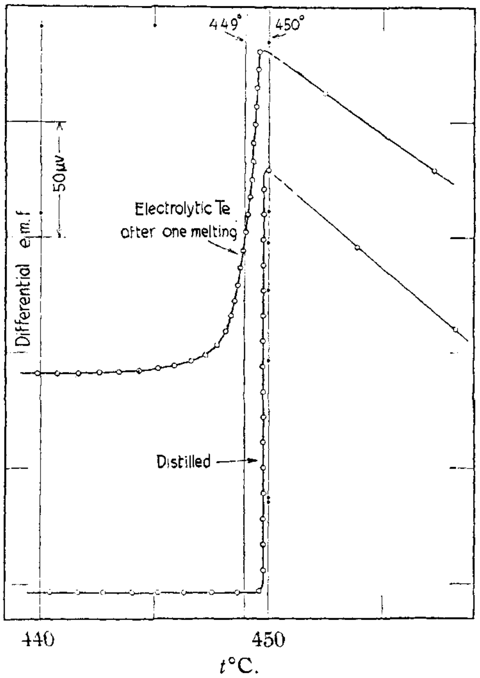

Fig. 1.—Typical differential heating curve characteristics of melting electrolytic tellurium before and after distillation in Pyrex glass.

the boiling point of sulfur. From these they derive a correction of 40 microvolts at 450°C., and state the melting point of tellurium to be 452°C. Now, their sulfur point seems obviously unreliable. If we neglect it, we may derive a correction of approximately 15 microvolts from their other two points, which would make their value 449.5°C., within 0.3°C. of the value determined in this work.

It is often mentioned that tellurium melted in a glass vessel causes a shattering of the glass on freezing, owing to an apparent expansion. This does not happen with pure tellurium, in our experience. Impure metal often carries considerable quantities of oxide as impurity, and we believe the shattering to be due to a reaction of the impurities with the glass and subsequent adhesion of the ingot to the glass, rather than to some peculiarity of tellurium itself. In our distillation experiments we have observed a shattering even with vitreous silica.

Acknowledgment.—We are indebted to S. Skowronski and the International Smelting and Refining Company for supplying some of the electrolytic tellurium used in this work.

Summary

The melting point of tellurium purified by vacuum distillation in Pyrex glass, and tested to be free of selenium, was determined to be 449.8° ± 0.2°C.

Washington, D. C. Received May 7, 1941

[Contribution from the Research Laboratory of the Radio Corporation of America and the Department of Chemistry, Stanford University]

An Electron Microscope Study of Curd Fibers of Sodium Laurate

By L. Marton, J. W. McBain and R. D. Vold

The electron microscope has been used to photograph curd fibers of sodium laurate with direct magnification up to 19,000 diameters. The image so obtained is sufficiently sharp to relate the physical and mechanical properties of soap curd more closely to its ultimate fine structure. The results afford a striking confirmation of previous conclusions based on less direct evidence, and add greatly to the detail with which the general picture can now be presented.

Experimental

The sodium laurate used in this work has already been described.[1] Samples were prepared for the electron microscope by dipping a 400-mesh screen into a 5.6 wt. % solution of this soap in water, which contained 0.02 wt. % excess sodium hydroxide to prevent hydrolysis. The screen was immediately dried in vacuum and introduced into the object chamber of the electron microscope.[2] The whole process of fiber formation occurs in this instance in only a few minutes so there is little opportunity for the formation of regular, highly oriented structure of macroscopic size. As the fibers are formed on cooling and desiccation, they shrink and pull apart along their length. Almost all the "free" ends of fibers occur in pairs and were originally joined together.

From the many photographs taken, Plates 1, 2 and 3 showing curd fibers of sodium laurate at a direct magnification of 11,000 to 18,000 diameters, were selected.

Discussion

The most obvious conclusion from the photographs is that the sodium laurate curd consists of

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(1) R. D. Vold and M. J. Vold, This Journal, **61**, 37 (1939).

(2) L. Marton, *Phys. Rev.*, **58**, 57 (1940); *J. Bact.*, **41**, 397 (1941).

Fig. 1.

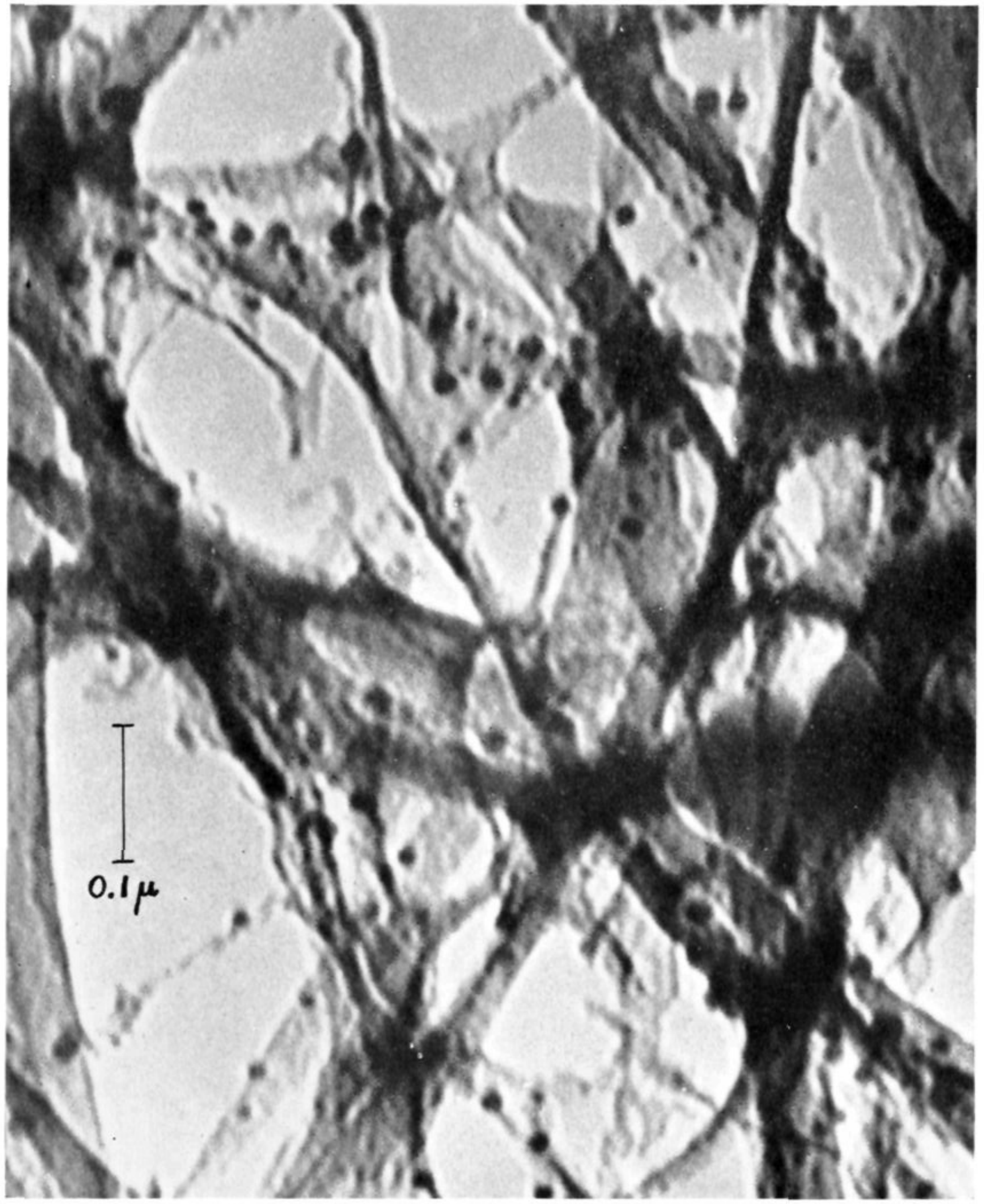

Fig. 3.

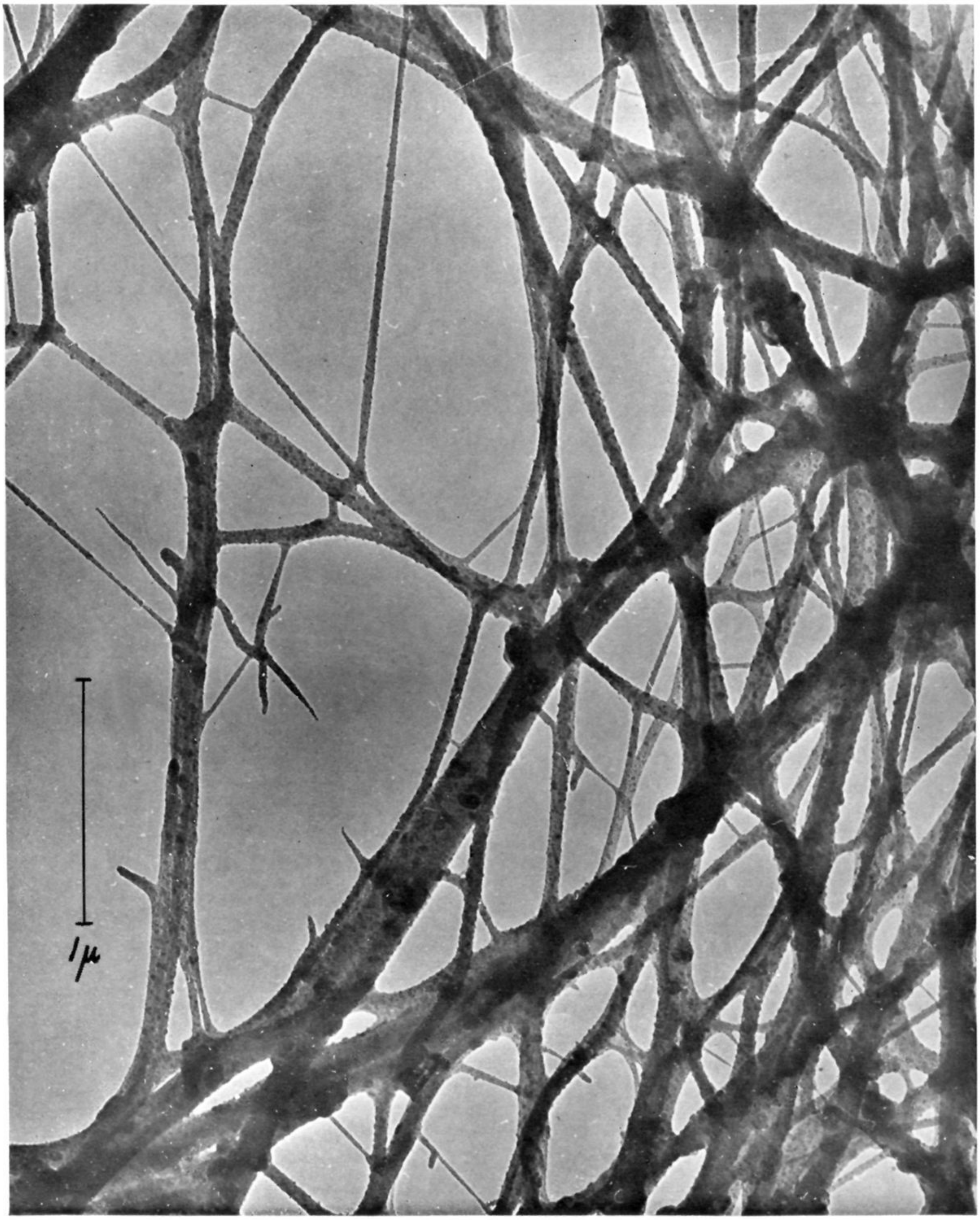

Fig. 2.

an interlocked mesh of fibers. In order that the carboxylate groups and methylene groups, respectively, may be adjacent to one another in the manner found by X-rays for the monoclinic crystals, it is only to be expected that the fibers should be much wider than they are thick. Direct confirmation of the ribbon-like nature of the fibers can be seen in Plate 1 at point A, where a ribbon-like fiber is twisted between its two points of attachment to other fibers.

It is interesting to compare the sizes of these fibers with the diameters to be expected if they are made up of bundles of the ultimate fibers whose structure has been determined by X-ray diffraction. In fibers of sodium palmitate,[3] prepared by stretching a thread-like drop of solution across a hole in a card, cooling and dehydrating, the lattice unit consists of two molecules placed end to end, and these units are oriented perpendicularly to the long axis of the fiber. Single fibers of sodium laurate would then be 37 Å. in width.[4] The extent to which the cross-sections of fibers visible with the electron microscope are even multiples of 37 Å. was investigated by making 335 measurements of the widths of fibers appearing on Plate 3. A microcomparator with a magnification of 39 diameters was used, the measurements being made to an accuracy of about 10 Å. The criterion for the determination of width of the fibers was the distance between places with the greatest gradient in intensity distribution.[5]

Since the absolute error increases with width of fiber, so that for high multiples a mere scattering of results must appear, we may confine our examination chiefly to the narrowest fibers. No fibers were found with widths less than 40 Å. If there are any smaller ones, they are below the resolving power of the instrument. For those up to 180 Å. there is one result each at 40, 50, 60, 70, 110 and 140; there are nine at 80, and four at 90; three at 120 and six at 130; two at 150, nineteen at 170 and four at 180. This clearly shows three peaks; namely, at 83, 127 and 172. These are respectively equal to approximately two, three and four times 42 Å. We should expect a fifth multiple at about 210, but the peak comes at 220 with fifteen examples. The next peaks come at 285 and 350, with much more uniform scattering beyond. The sixth multiple is represented by a blurred peak collected at 240, 250 and 260.

The unit thus appears to be about 42 ± 10 Å. rather than the 37 Å. which would correspond to the length of the double molecules. Quite possibly this difference is real and attributable to hydration which is known to occur and to expand the space lattice of micelles in solution.[6] The curd fibers which at first appear opaque become translucent after several photographs have been made. Even when they are completely dehydrated under such circumstances, they need not necessarily shrink to the exact width of perfect crystals.

The concept of the soap curd derived from the electron microscope is in accord with previous deductions based on microscopic and ultramicroscopic curd fibers. Photographs of macroscopic curd fibers, which may grow to an inch or more in length, have been published by Vold and Ferguson.[7] Such fibrous bundles have a high luster and even when grown very slowly in a closed vessel from liquid crystalline soap at 90° are obviously composed of finer fibers. The appearance at intermediate magnifications[8] (60 to 120 diameters) is very similar. Photographs with the ultramicroscope at high magnifications[9] show them as a felt of very long fine fibers separating from solution. These again appear to be made up of still finer fibers.

The criss-cross brush heap structure of such curd provides numerous small interstices which may enmesh large amounts of water so that the whole, even when containing only 12.5% soap, is a fairly rigid solid. In many cases the soap is not uniformly distributed along the length of the fiber, although the size and shape of the bead-like units of some fibers cannot be inferred from the ultramicroscope itself.

That the finest fibers of a soap curd must actually approach molecular dimensions also had been inferred from the tremendous surface available in sodium palmitate curd for the sorption of

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[3] P. A. Thiessen and R. Spychalski, *Z. physik. Chem.*, **A156**, 442 (1931).

[4] 36.7 Å. results from values for *c* spacings of rhombic crystals of sodium stearate and sodium palmitate determined by P. A. Thiessen and J. Stauff, *Z. physik. Chem.*, **A176**, 397 (1936). Values from 36.7 to 38.3 can be calculated from atomic radii (Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 1939).

[5] *Cf.* B. v. Borries and E. Ruska, *Naturwissenschaften*, **27**, 281 (1939).

[6] K. Hess and J. Gundermann, *Ber.*, **70**, 1800 (1937); J. Stauff, *Kolloid-Z.*, **89**, 224 (1939); W. Philipoff and H. Kiessig, *Naturwissenschaften*, **35**, 593 (1939).

[7] R. D. Vold and R. H. Ferguson, THIS JOURNAL, **60**, 2066 (1938).

[8] K. Maclennan, *J. Soc. Chem. Ind.*, **42**, 393T (1923).

[9] R. Zsigmondy and W. Bachmann, *Kolloid-Z.*, **11**, 152 (1912); W. F. Darke, J. W. McBain and C. S. Salmon, *Proc. Roy. Soc.*, **A98**, 395 (1921).

methylene blue.[10] That there must be numerous interstices of small effective diameter was also known from the fact that water enmeshed in the curd has a much lower thermodynamic activity than can be accounted for on the basis of dissolved soap.[11] The rate of expulsion of solution in a centrifugal field under known pressure is also in agreement, predicting a mean diameter of about 10,000 Å. for the capillary spaces.[12]

The present electron microscope pictures show at a glance the exact fine structure of the curd. The fibers of sodium laurate are seen to be not only closely interwoven but to be actually grown together at angles ranging from 15 to 90°, perhaps with preferred angles of 30, 45 and 60°. This doubtless contributes greatly to the mechanical strength of a solid cake. Moreover, the spaces within the angle between all such branches are obviously to be correlated with the capillary spaces of variable diameter which were assumed to account for the variation of the activity of water in hydrated soap curd.[11]

The fibers might grow together, retaining rows of parallel double molecules at right angles to each branch, either in the same or two different planes. In the former case consideration of the monoclinic angle or of the angle of tilting corresponding to the interlocking of zigzag chains of carbon atoms[13] would give preferred angles of branching. Likewise such growth would account for the many instances in which both branches are of the same diameter or one is twice the other. The resolving power of the electron microscope is not yet sufficiently great to distinguish between genuine twinning and disorderly grouping of molecules at the junction.

One of the most characteristic features of these photographs is the non-uniformity of the fibers and the presence of a large number of roughly circular blacker patches. At very high magnifications even the homogeneous body of the fiber has a mottled appearance. If this appearance is actually inherent in the soap fiber, rather than being an artifact, it may signify that there is another structural unit within the fiber in addition to the essentially infinite row of parallel double molecules perpendicular to the fiber axis. Such a micellar grouping might be related to the mosaic structure of the surface of crystals.[14]

The black spots are clearly regions of higher concentration as shown by the increased darkening whenever the electron beam passes through two superposed fibers. That they are actually soap rather than some random impurity is suggested by their multiplicity, relative regularity of arrangement, and their smooth outline. In fact, sodium laurate appears to be concentrated in part in granules of 100–200 Å. diameter along the surface of otherwise uniform fibers (*cf.* the ultramicroscopic appearance[9]).

This great irregularity may be caused by the rapid dehydration during the exposure in the electron microscope. The flat surface of a ribbon-like fiber which is essentially hydrocarbon in nature must be fairly hydrophobic, so that even the soap solution would tend to collect in minute drops rather than spreading evenly. The evaporation of these drops might produce amorphous lumps which would be incorporated into more highly oriented structures only very slowly.

Possibly these granules may be related to aggregates pre-existing in the soap solution. Detergent solutions are known to contain two kinds of micelles,[15] one of which, the "neutral" or lamellar micelle, has a structure resembling that of the dry fibers.[6] The structure of the ionic micelle is not known with certainty, although it has been presumed to be essentially spherical.[16] The fibers might be formed by oriented aggregation of lamellar micelles, less elongated and less regular aggregates being deposited as small lumps around ionic micelles serving as nuclei. This alternative is supported by the further fact that the electrical conductivity of curd[17] necessitates the presence of charged particles on the surface of the fibers.

Summary

Electron microscope photographs of a curd of sodium laurate show that it consists of a mass of fibers which are thin ribbons whose widths tend to be integral multiples of approximately twice the length of the sodium laurate molecules. The fibers branch to form a felt, which accounts for the rigidity of the curd. The fiber junctions also

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[10] J. W. McBain, J. M. McDowell and M. E. Worden, This Journal, **61**, 2540 (1939).

[11] J. W. McBain, M. J. Vold and S. A. Johnston, *ibid.*, **63**, 1000 (1941).

[12] J. W. McBain and T. F. Ford, *ibid.*, **62**, 866 (1940).

[13] C. G. Lyons and E. K. Rideal, *Proc. Roy. Soc.* (London), **A124**, 333 (1929).

[14] A. Smekal, *Z. angew. Chem.*, **42**, 489 (1929); *Z. Physik*, **55**, 289 (1929); F. Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 253 (1929).

[15] J. W. McBain, *Nature*, **145**, 702 (1940).

[16] J. W. McBain and C. S. Salmon, This Journal, **42**, 427 (1920).

[17] M. E. L. McBain, *Trans. Faraday Soc.*, **164**, 153 (1935).

give rise to many capillary spaces of variable diameter in which water can be retained, even at very low relative humidity. Some of the sodium laurate apparently is not a part of the fibrous structure but is present as granules 100–200 Å. in diameter irregularly spaced along the fiber.

RESEARCH LABORATORY
RADIO CORPORATION OF AMERICA
CAMDEN, N. J., AND
DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED FEBRUARY 24, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Acid Hydrolysis of Methyl Acetate in Dioxane–Water Mixtures

BY HERBERT S. HARNED AND ARTHUR M. ROSS, JR.[1]

The exhaustive study of the properties of hydrochloric acid in dioxane–water mixtures, made in this Laboratory,[2] has invited further research upon the catalytic activity of this acid in these media. For this purpose, the acid-catalyzed hydrolysis of a simple ester (methyl acetate) has been selected. Dioxane is apparently an inert solvent, and is, at the same time, completely miscible with water. The use of dioxane–water mixtures as media, therefore, gives a wide variation in water concentration as well as drastic changes in dielectric constant, ranging from 80 in water to 2 in pure dioxane.

In addition to the velocity measurements, the activity coefficient of the ester was determined by measurement of its vapor pressure over these mixtures at 25°. These data, together with the known vapor pressures of water in dioxane–water mixtures, and the properties of hydrochloric acid are sufficient to calculate all factors of the Brönsted[3] equation for reaction velocities with the obvious and necessary exception of the activity coefficient of the "fugitive" complex. This material will form a comprehensive body of evidence upon which certain aspects of the theory may be discussed.

Reaction Velocity Measurements.—The velocity measurements were made by the usual method of titration with standard sodium hydroxide solution. A special reaction vessel designed to secure a minimum exposure of the reaction solution to the atmosphere at the time of sampling was employed. All chemicals were carefully purified.

In order to express the results on different concentration scales, density measurements were required. These were executed in 30-cc. density bottles at the completion of a run. Several experiments showed that the density change during reaction was entirely negligible. This was proved by placing the initial reaction mixture in a 200-cc. bulb surmounted by a 2-mm. capillary. Once thermal equilibrium had been attained, no motion of the meniscus in the capillary could be observed.

The hydrolysis is of the first order with respect to ester in aqueous solutions. Our results show that it remains of first order throughout the range of dioxane strengths. The calculation of the velocity constant from the buret readings was made by the method of Guggenheim[4] which avoids the use of an infinity reading. Two sets of readings were taken such that each member of the second set is made at a fixed and constant time interval after each corresponding member of the first set. Using the first order velocity equations, we obtain

$$\ln (R_{t+T} - R_t) = \ln \Delta R = -k_t + \text{constant} \quad (1)$$

where T is the constant time interval, R_{t+T} and R_t are the buret readings at the times indicated and k is the velocity constant. By plotting ln ΔR against t, k may be obtained.

In practice these readings were made in two groups of seven to eight, about an hour elapsing between successive readings within a set. The first set was made well before, the second well after, the "half-life" of the reaction. At 25° this meant a difference of a full day for the 0.1 M mixtures, and overnight for the 0.2 M mixtures. About half these intervals were required for the same acid strengths at 35°.

A detailed discussion of errors seems unnecessary. The measurements in water were found to be reproducible to within less than 1% and

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[1] This communication contains part of the material of a dissertation presented by Arthur M. Ross, Jr., to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1939.

[2] Harned, Morrison, Walker, Donelson and Calmon, THIS JOURNAL, **61**, 49 (1939). This communication contains a bibliography of the other contributions to this subject.

[3] *Z. physik. Chem.*, **102**, 169 (1922); *Chem. Rev.*, **5**, 231 (1928).

[4] Guggenheim, *Phil. Mag.*, [7], **2**, 538 (1926).