

Structure for Soap Micelles as Indicated by a Previously Unrecognized XRay Diffraction Band

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TABLE I. Formation of gas and nitrite on solution of barium nitrate irradiated with 1.2 Mv electrons at a rate of approximately 1.5 watts/g.

| Irrad. time, hr. | % NO ₂ ⁻ converted to NO ₂ ⁻ | Gas formed, cc/g (22° C, approx. 73 cm) | Calc. O ₂ equiv. to NO ₂ ⁻ found, cc/g (22° C, 73 cm) |
|------------------|--|---|--|
| 2.8 | 5.5 | 5.9 | 4.9 |
| 6.0 | 10.5 | 10.1 | 9.0 |
| 9.6 | 13.0 | 12.8 | 11.5 |
| 13.0 | 18.0 | 16.4 | 16.0 |
| 17.3 | 21.1 | 19.0 | 18.9 |

spread out on a pan in the open air. The crystals initially turned yellow, but on further irradiation became milky, so that the color was obscured. Samples were taken from time to time and placed in a closed tube, to which water was admitted after evacuation. The gas was not analyzed, but the volumes produced were measured, and the nitrite content of the solutions was determined. Results of the measurements are shown in Table I. Energy was not absorbed uniformly by the salt during the irradiation because of variation of thickness of the salt layer and its distribution on the pan with respect to the electron beam; the rate of energy dissipation was estimated as roughly 1.5 watts/g salt. Solutions of irradiated salt (0.01–0.07M) showed a pH of 9 to 10, and were thus more alkaline than can be accounted for by hydrolysis of nitrite.

At 25 watt-hr./g, about 21 percent of the nitrate had been converted to nitrite. The conversion rate decreased with time, suggesting that a steady state might eventually be reached after 40 percent or more conversion.

Qualitative experiments showed that gas evolution on solution was not greatly reduced by heating the irradiated salt below the melting point, but was entirely prevented by fusion of the irradiated salt. Presumably the gas came out during fusion, but no direct observation was made on this point. Irradiation lowered the melting point of the salt, presumably because of the admixture of nitrite.

Narayanswamy¹ has reported the formation of nitrite near the surface of nitrate crystals illuminated by light of wave-length 2200–2500Å. He ascribed the localization of the reaction at the surface to the escape of oxygen gas, assuming that recombination of the products should occur in the interior. In the present experiments, practically all the gas remained trapped in the crystal (as O atoms or O₂ molecules), so that thermal recombination must occur very slowly if at all. Localization of the photolysis must be ascribed to low penetration by the exciting light.

Existence of the photolysis has been ascribed¹ to dissociation of excited NO₃⁻ ions to NO₂⁻ ions and O atoms. Under electron bombardment, the same process probably occurs; in addition, many NO₃⁻ ions will be stripped of one outer electron, forming NO₃ radicals. This radical may later pick up an electron, with a probability of forming NO₂⁻ and O rather than NO₃⁻; or it may decompose thermally to NO₂ and O. The NO₂ may remain as such in the crystal, and hydrolyze on solution to HNO₂+HNO₃; or may pick up an electron to give nitrite ion. The small amounts of hydrogen gas and of alkali are ascribed to reaction with water of electrons which were trapped during

irradiation by barium ions, or at vacancies or imperfections in the crystal lattice.

The authors are pleased to acknowledge the help and counsel of Professor Milton Burton, in charge of radiation chemistry at the Metallurgical Laboratory when this work was performed, and Dr. F. J. Safford, in charge of operating the Van de Graaff generator.

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¹ Narayanswamy, Trans. Farad. Soc. 31, 1411 (1935).

Structure for Soap Micelles as Indicated by a Previously Unrecognized X-Ray Diffraction Band*

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March 10, 1947

MEASUREMENTS on a previously unrecognized x-ray diffraction band B_M suggest that in an aqueous solution the micelle of a soap, or similar colloidal electrolyte, consists of only *one* double layer of soap molecules (Fig. 1). The subscript M designates that an associated spacing d_M measures the approximate thickness of the micelle. Over a range of concentrations of a given soap d_M is apparently constant and about twice the length of the particular molecule involved (Table I).

McBain has considered that soap micelles exist in spherical highly ionic and lamellar weakly ionic forms; whereas, Hartley has considered them as spherical only. Evidence for the lamellar micelle as a stack of double layers of soap molecules, with "bound" water between the double layers, seemed to be given by the x-ray work of Hess, Kiessig, Philippoff, *et al.* (1937–1942). Similar experimental results have been discussed in two papers^{1,2} from this laboratory in which extensive references to work on micelle structure are included.

It is now found that the spacing d_M' , associated with the new diffuse band, is essentially constant for any given soap, as it should be if it represents the thickness of the double layer. The thickness increases from 36.5Å for the 8-carbon atom soap to 58.1Å for the 16-carbon atom soap (Table I). This is an increase of 21.6Å caused by the addition of 16 C-atoms to the thickness of the double

TABLE I. Spacings in aqueous soap solutions calculated from the position of the peak of the micelle thickness band B_M .

| Potassium soap | Bragg spacing ^a d_M ±1Å | 2 × length of molecule $2l$ | Modified Bragg spacing ^b d_M' ±1Å |
|------------------------------------|--|--------------------------------|--|
| Caprylate, KC ₈ | 29.7 | 30 | 36.5 |
| Caprate, KC ₉ | 31.7 | 35 | 39.0 |
| Laurate, KC ₁₂ | 35.3 | 40 | 43.4 |
| Myristate, KC ₁₄ | 40.3 | 45 | 49.5 |
| Palmitate, KC ₁₆ | 47.3 | 50 | 58.1 |
| Sodium lauryl sulfate ^c | 37.3 | 47 | 45.9 |

^a $d_M = \lambda / (2 \sin \theta)$, valid for many diffracting layers.

^b $d_M' = 1.23\lambda / (2 \sin \theta)$, valid in the limiting case for two diffracting centers (first maximum of $\sin x/x$). Note that $d_M < 2l < d_M'$ for the simple potassium soaps.

^c Kindly supplied by the Procter and Gamble Company.

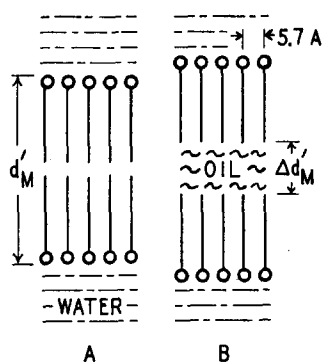


FIG. 1. Cross section of a highly idealized micelle. A. Thickness of micelle $d_M' \approx 50 \text{ \AA}$ for potassium myristate, distance between nearest hydrocarbon chains $d_S' \approx 5.7 \text{ \AA}$ (Bragg spacing $d_S = d_S'/1.23 \approx 4.6 \text{ \AA}$, molecular area $\sigma = (3)^{1/2} d_S'^2/2 \approx 27 \text{ \AA}^2$). B. Thickness of solubilized hydrocarbon layer $\Delta d_M' \approx 13 \text{ \AA}$ for benzene.

layer. The increase in double the length of the molecule is 8×2.54 , or 20.3 \AA , which is the same within the limit of error of the d_M' measurements.

The short spacing d_S , with a constant Bragg spacing of about 4.6 \AA , is essentially independent both of the length of the soap molecule and of the absence or presence of oil solubilized in the micelle. This distance corresponds to a molecular area of 27 \AA^2 in a plane perpendicular to the chains.

The lowest soap concentration at which the micelle thickness band B_M has thus far been measured is 1.3 percent by weight of potassium palmitate. The band B_I , related to the inter-micelle distance d_I , begins to be noticeable above concentrations of about 9 percent potassium laurate and about 7 percent potassium myristate. The d_I spacing, which steadily decreases with removal of water, is always larger than d_M' . The behavior of the three bands B_S , B_M , and B_I with respect to position, intensity, and width, all as a function of the particular soap and its concentration, seems to substantiate the following viewpoint. The micelle consists of one double layer of soap molecules from which the band B_M arises. As the concentration increases both the size and number of micelles probably increase. This means that the micelles are becoming closer together and a short-range order between micelles becomes more probable. This condition gives rise to the B_I band.

When a hydrocarbon is solubilized in a soap solution, the thickness d_M' of the micelle is increased an amount $\Delta d_M'$ (Fig. 1). This gives additional evidence that d_M' represents the thickness of the micelle. For example, potassium laurate solutions saturated with ethyl benzene give a $\Delta d_M'$ of about 6 \AA ; potassium myristate solutions saturated with *n*-heptane give about 11 \AA and saturated with benzene about 13 \AA . These relations will be presented in detail later.

In connection with this work the writers wish to thank Professor P. Debye for helpful advice.

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¹ W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Am. Chem. Soc.* **68**, 220 (1946).

² W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Colloid Sci.* **1**, 105 (1946).

Sound Velocity and the Temperature Change of Molecular Association in Water

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March 10, 1947

TWO empirical criteria for molecular association in liquids, proposed recently by Lagemann,¹ are based on sound velocity. Unfortunately, one of these incorrectly predicts an increase in association with increase in temperature, and the other makes no prediction.

Another quantity involving sound velocity appears better suited for providing information on temperature changes of molecular association. The molar sound velocity $R = Mv^3/d$ (where M is molecular weight, and v and d are sound velocity and density measured at the same temperature) was found by M. R. Rac² to be a temperature-independent constant for normal, non-associated liquids. But for water, and to a lesser extent such liquids as methyl alcohol and acetone, R increases considerably with temperature. It seems probable that R would remain constant even for these materials if the calculation utilized the effective M (which diminishes as association decreases) rather than the chemical-formula M . If this is true, increases in v^3/d are a direct indication of decreases in extent of association.

This is illustrated in Fig. 1, where the relative association (taken as 1.0000 at 0°C), found from the ratio of

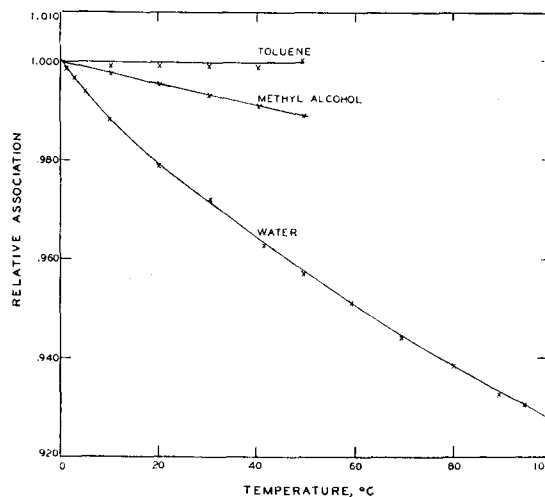


FIG. 1. Relative association of liquids as a function of temperature.

v_0^3/d_0 to v^3/d , is plotted as a function of temperature t . Water, which is highly associated, undergoes a decrease³ of about 7.2 percent in association from 0° to 100° ; while toluene, which is not associated, shows no appreciable change. Methyl alcohol occupies an intermediate position.

Correlation with the results of other methods is difficult. Over a dozen techniques have been used^{4,5} to study the association of water, but the results disagree over a range of hundreds of percent. One detailed investigation,⁶ based on Raman spectra, indicates that the association of water decreases by about 13.2 percent from 0° to 98° . However,