

Sound Velocity and the Temperature Change of Molecular Association in Water

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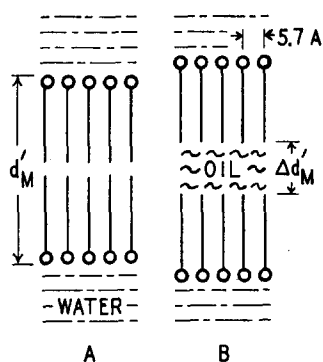


FIG. 1. Cross section of a highly idealized micelle. A. Thickness of micelle $d_M' \approx 50 \text{ \AA}$ for potassium myristate, distance between nearest hydrocarbon chains $d_S' \approx 5.7 \text{ \AA}$ (Bragg spacing $d_S = d_S'/1.23 \approx 4.6 \text{ \AA}$, molecular area $\sigma = (3)^{1/2} d_S'^2/2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

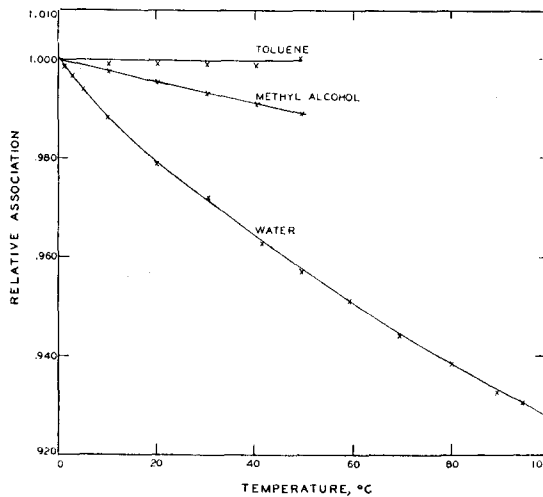


FIG. 1. Relative association of liquids as a function of temperature.

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,

molecular aggregates which are stable for only 10^{-14} second will show up in Raman scattering, but the aggregates must be stable for 10^{-6} second in order to be detected by these sound velocity measurements. The latter method would therefore be expected to yield smaller values.

It may be noted, further, that absolute values of association cannot be obtained from the ratio of observed to calculated molar sound velocities. This is true because the bond increments for calculating R already include the associating tendency due to, for example, the $-OH$ group.

¹ R. T. Lagemann, *J. Chem. Phys.* **12**, 464 (1944).

² M. R. Rao, *Ind. J. Phys.* **14**, 109 (1940).

³ The values used, for sound velocity in water, were those recently determined at one megacycle in this Laboratory by Miss Patricia E. Mortell.

⁴ N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940), p. 166.

⁵ O. Fruhwirth, *Monats. f. Chemie* **70**, 157 (1937).

⁶ I. R. Rao, *Proc. Roy. Soc. A* **145**, 489 (1934).

Non-Ionic Detergents as Association Colloids Giving Long X-Ray Spacings in Aqueous Solution

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March 4, 1947

SOAPS and other ionic detergents in solution diffract x-rays so definitely as to demonstrate the presence of lamellar micelles. These lamellar micelles expand to take in layers of hydrocarbons when the latter are solubilized in the detergent solutions. It has not been known whether such lamellar colloidal particles exist in solutions of non-

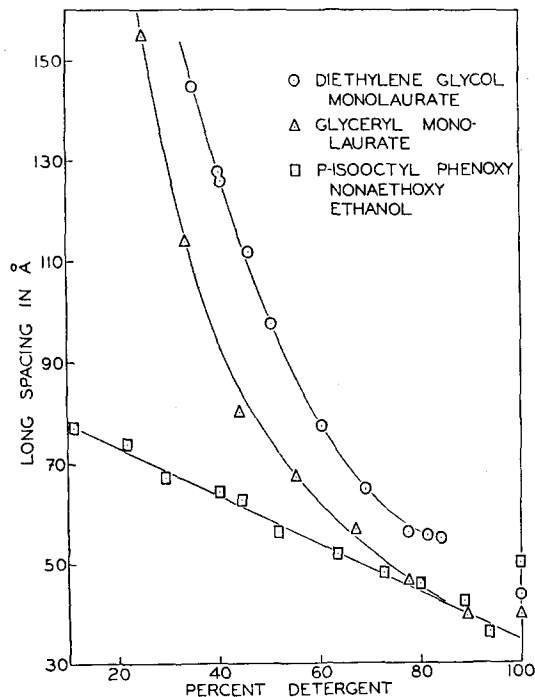


FIG. 1.

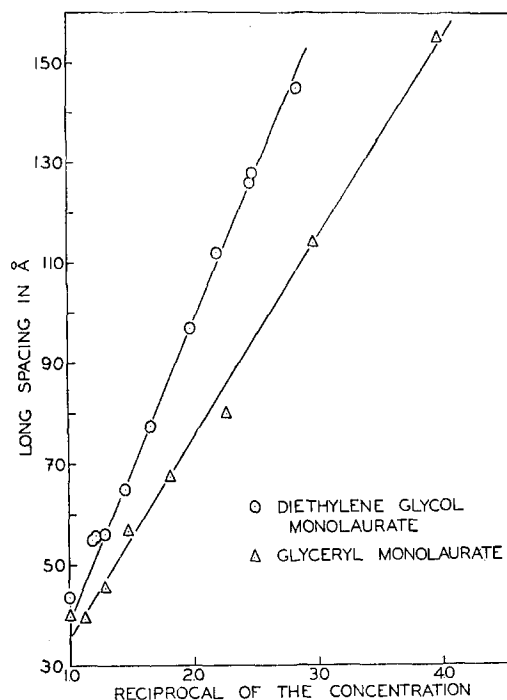


FIG. 2.

ionic detergents. It is the purpose of this note to establish that non-ionic detergents also exhibit similar long spacings on x-ray examination in aqueous solution.

The spacings observed are of the order of 40 to 150 Å and their value depends upon the concentration, as shown in the accompanying graphs.

Para-isooctyl phenoxy nonaethoxy ethanol.—This is the condensation product of *p*-isooctyl phenol with ethylene oxide. Solutions of this material in water are all isotropic solutions exhibiting anomalous viscosity.¹ They produce x-ray diffraction patterns consisting of one or two orders of a very long spacing. There is also a broad halo due to side spacings with its maximum density at 4.5 Å. The long spacing of the solutions increases almost linearly with decrease in concentration, as shown in Fig. 1. This is similar to the now well-known behavior of ionic detergents in water. The liquid material itself does not give a pattern at room temperature but, when cooled to below its melting point, it gives a long spacing of 50 Å, which agrees well with the calculated value.

Diethylene glycol monolaurate.—This surface active agent is supplied by Glyco Products Company, Inc. In aqueous systems at concentrations from about 35 percent to 85 percent, it forms two phases: one is isotropic and gives no long spacing; the other is liquid crystal and gives a long spacing which varies as the reciprocal of the concentration of the diethylene glycol monolaurate (see Fig. 2). This is decidedly in contrast with the behavior of ionic detergents. The material is not a pure chemical; the impurities are not completely known and so their effect on the long spacing has not been determined.