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Structure of Micelles of Colloidal Electrolytes. III. A New Long-Spacing X-Ray Diffraction Band, and the Relations of Other Bands*

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A newly found x-ray diffraction band, obtained from aqueous solutions of soaps and detergents, gives a Bragg spacing which is independent of concentration and is close to the double-length of the molecule. This is designated as the micelle thickness or *M*-band. The already known long-spacing band, interpreted here as related to the intermicellar distance, is designated as the *I*-band. Its spacing d_I increases with decreasing soap concentration. If a hydrocarbon is solubilized in the micelles, these spacings increase by Δd_M and Δd_I . Formerly, Δd_I was supposed to give the mean thickness of the layer of oil dissolved between the ends of the hydrocarbon chains of the soap molecules as a middle layer in the micelle. However, Δd_M seems to be more directly related to this thickness. As measured by d_M , the thickness of the micelle remains constant with increasing soap concentration: e.g., the values are 40.8, 41.5, 40.7, 40.2, 39.5, 39.6, 40.2 Å for potassium myristate at 25°C at the following respective concentrations: 2.3, 4.5, 7.2, 9.8, 12.0, 13.7, and 16.5 percent. The mean "thickness" increases from 29.7 Å for potassium caprylate (C_8) to 47.3 for potassium palmitate (C_{16}). By a method explained in the text, the number of molecules in a potassium myristate micelle is calculated as 56 at 9.8 percent by use of the Bragg *I*-spacing. However, it is probable that a corrected Bragg spacing should be used. A new long-spacing band,

designated as an *X*-band, appears when an *I*-band is present and oil is solubilized in the micelles. The order of spacing is then $d_I > d_M > d_X$; e.g., in one case the values are $84 > 50 > 27$ Å.

The "cylindrical" model of the micelle preferred here differs from the lamellar and in some respects from the spherical model. It exhibits the following characteristics: (1) A micelle consists of one double-layer of soap or detergent molecules. These have their polar ends oriented outward toward the water and their non-polar ends inward toward each other. (2) The thickness of the micelle of a pure soap is essentially twice the length of the soap molecule, independent of concentration. (3) Hydrocarbons solubilize inside the micelle between the two layers of soap molecules and thus make the micelle thicker. (4) The area per soap molecule in the micelle remains practically constant, whether or not solubilized hydrocarbons are present. (5) The width or lateral dimension of the micelle and the number of soap molecules per micelle increase with increasing soap concentration and with solubilization of hydrocarbons. (6) From energy considerations the area of contact between the hydrocarbon chains of the detergent molecules and the water must be as small as is compatible with the other conditions imposed upon its structure.

I. INTRODUCTION

ACCORDING to the theory of the mechanism of emulsion polymerization developed in this laboratory,¹ the initial locus of polymerization lies in the monomer solubilized in the soap micelles, so micellar structure is important in this type of polymerization. The present paper presents a structure for the micelle and gives estimates of its size. The discovery of a new x-ray band,² which measures the thickness of the micelle, makes it necessary to reconsider the sig-

nificance of the long-spacing x-ray band investigated earlier. Solubilization data³ are also used in making certain deductions.

All previous models of micellar structure have been based on the theory of the orientation of molecules in surfaces and interfaces as developed by Harkins^{4,5} and by Langmuir,⁶ especially on the energy relations developed by the former.⁴ The following quotation⁵ is specially pertinent if it is kept in mind that the micelles constitute a new phase:

"The general law for surfaces seems to be as follows: *If we suppose the structure of the surface of a liquid to be at first the same as that of the interior of the liquid, then the actual surface is*

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¹ W. D. Harkins, *J. Am. Chem. Soc.* **69**, 1428 (1947).

² R. W. Mattoon, R. S. Stearns, and W. D. Harkins, *J. Chem. Phys.* **15**, 209 (1947).

³ R. S. Stearns, H. Oppenheimer, E. Simon, and W. D. Harkins, *J. Chem. Phys.* **15**, 496 (1947).

⁴ W. D. Harkins, F. E. Brown, and E. C. H. Davies, *J. Am. Chem. Soc.* **39**, 354 (1917).

⁵ W. D. Harkins, E. C. H. Davies, and G. L. Clark, *J. Am. Chem. Soc.* **39**, 541 (1917).

⁶ I. Langmuir, *J. Am. Chem. Soc.* **39**, 1848 (1917).

always formed by the orientation of the least active portion of the molecule toward the vapor phase, and at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt."

"At interfaces the molecules turn so that their like parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward the liquid *A* are as much like *A* as possible, and the ends toward *B* are as much like *B* as possible. So at interfaces between organic liquids and water, for example, the organic radical sets toward the organic liquid, and the polar group toward the water."

The formation of the micelle is due to the fact that there is a very high interfacial free energy between hydrocarbon and water (*ca.* 50 ergs per sq. cm) and none between hydrocarbon and hydrocarbon. Thus there is a large decrease of free energy if the hydrocarbon chains of the soap molecules leave their environment of water and aggregate to give a hydrocarbon environment. The fact that the micelles are relatively small is due to the repulsion of the polar-ionic ends of the soap molecules, which orient themselves toward the water, or the outside of the micelle, whereas the hydrocarbon chains orient toward the inside. On this basis all earlier models for the micelle and that preferred here agree as to the type of orientation involved, but disagree as to the number of kinds of micelles, their form, and their size.

Probably the oldest theory is that of McBain,⁷ who considered that there are two types of micelles, presumably in equilibrium with each other. At low concentrations he assumed a spherical ionic micelle as more prominent, but at higher concentrations, a "non-ionic" micelle. Later he considered this as weakly ionic, "lamellar," and very large, identical in structure⁸ with that proposed by a number of German investigators, who also assumed the existence of a small micelle.⁹

⁷ J. W. McBain, *Fourth Colloid Symposium Monograph* (Chemical Catalog Company, New York, 1926), p. 8; *Kolloid Zeits.* **40**, 1 (1926).

⁸ J. W. McBain, *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1942), Vol. I, pp. 122-144.

⁹ ^a K. Hess and J. Gunderman, *Ber.* **70B**, 1800 (1937); ^b W. Philippoff and K. Hess, *Ber.* **70B**, 1808 (1937); ^c K. Hess, H. Kiessig, and W. Philippoff, *Naturwiss.* **26**, 184 (1938); ^d J. Stauff, *Naturwiss.* **27**, 213 (1939); ^e H. Kiessig and W. Philippoff, *Naturwiss.* **27**, 593 (1939); ^f K. Hess, W. Philippoff, and H. Kiessig, *Kolloid Zeits.* **88**, 40 (1939);

According to Philippoff the large micelles contain about 10^7 molecules.^{9j} Hartley,¹⁰ however, considered that there is only one type of micelle, which is spherical, with a radius in a solution of a pure soap about the length of the soap molecule. He did not have the advantage of knowing the results of x-ray work, but his model agrees moderately well with the properties of soap solutions as known at that time. Its principal defect is that it does not allow the micelle of the pure soap to change in size since the radius is constant; the "cylindrical" model preferred here allows a change in size while still maintaining a constant thickness.

Krishnamurti¹¹ in early work ascribed to micelles a diffuse, long-spacing x-ray diffraction from sodium oleate solutions. Later, many x-ray and related investigations on soap solutions were carried out in Germany.⁹

On the basis of the x-ray spacings a large lamellar micelle was proposed.^{9a} This was assumed to consist of several (*ca.* 4 to 6) parallel double-layers of soap molecules, each double-layer separated from the next by a "bound" layer of water. The x-ray long-spacing, designated by us as d_I , was interpreted as measuring the identity distance from a plane in one double-layer to the corresponding plane of an adjacent one. The water layer, whose thickness was considered as d_I minus twice the length of the soap molecule, became thicker upon dilution, since d_I increased.^{9e, i} The solubilization of an oil in a given soap solution increases d_I an amount Δd_I , which was interpreted^{9e} as the thickness of the oil layer in the middle of each soap double-layer. The thickness of the water layer was assumed to remain unchanged.

The lamellar model was adopted in the first of two papers from this laboratory¹² on x-ray investigations of aqueous solutions of pure soaps. In a second paper on x-ray spacings with solu-

^a J. Stauff, *Kolloid Zeits.* **89**, 224 (1939); ^b J. Stauff, *Kolloid Zeits.* **96**, 244 (1941); ^c H. Kiessig, *Kolloid Zeits.* **96**, 252 (1941); ^d W. Philippoff, *Kolloid Zeits.* **96**, 255 (1941); ^e K. Hess, H. Kiessig, and W. Philippoff, *Fette und Seifen* **48**, 377 (1941); ^f K. Hess, *Fette und Seifen* **49**, 81 (1942); ^g H. Kiessig, *Kolloid Zeits.* **98**, 213 (1942).
¹⁰ G. S. Hartley, *Aqueous Solutions of Paraffin-Chain Salts* (Hermann et Cie, Paris, 1936).

¹¹ P. Krishnamurti, *Ind. J. Phys.* **3**, 307 (1929).

¹² W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Am. Chem. Soc.* **68**, 220 (1946), see corrections on p. 2751 in this volume.

TABLE I. X-ray bands diffracted from clear liquid aqueous solutions of colloidal electrolytes at room temperature.

Band symbol	Bragg spacing symbol	Approximate Bragg spacing, Å	Behavior	Tentative interpretation of spacing
<i>W</i>	d_W	31–3.2	a, b	From liquid water
<i>S</i>	d_S	4.5–4.6	a, c, d	Side-spacing between soap molecules in micelle
<i>M</i>	d_M Δd_M	30–60 0–15	e f	Thickness of micelle Thickness of oil solubilized in middle of micelle
<i>I</i>	d_I Δd_I	30–100 0–30	g, h i	Intermicelle spacing Increment of intermicelle spacing due to solubilized oil
<i>X</i>	d_X	25–30	b	Uncertain

^a Spacing remains constant with changing soap concentration and with simple hydrocarbons solubilized.

^b Intensity becomes weaker with increasing soap concentration.

^c Intensity becomes stronger with increasing soap concentration.

^d Intensity remains practically unchanged with simple hydrocarbons solubilized.

^e Spacing remains nearly constant with changing concentration of a given soap, is larger for longer soap molecules, and is approximately twice the length of the soap molecule; intensity becomes stronger with increasing soap concentration and with simple hydrocarbons solubilized, until this band is overshadowed by the *I*-band.

^f Spacing difference increases steadily as a hydrocarbon is solubilized in a given solution up to saturation. The behavior is very specific.

^g Spacing steadily decreases with increasing soap concentration; intensity becomes stronger with simple hydrocarbons solubilized; this band first appears at a higher soap concentration than does the *M*-band for the same soap.

^h Obtained only from solutions of high soap concentration containing much solubilized oil.

bilized hydrocarbons present,¹³ predictions of the lamellar model were tested to see if they meet the requirements of the related data.

It was assumed by both the Germans and McBain that (a) the lamellar micelle is very

large¹⁴ and (b) that the increase in spacing indicated by Δd_I because of solubilization of an oil, is the thickness of the oil layer. Now if the micelle is very large it should be possible to calculate the thickness τ of the oil layer by dividing the volume V of the oil dissolved in the micelles by the total area of the double-layers. The mean area per soap molecule is approximately 30\AA^2 . Thus

$$\tau = \frac{V}{(N/2)30(10)^{-16}} \text{cm},$$

where N is the number of soap molecules; in the double-layer it takes two molecules of soap to give an area of 30\AA^2 .

On the basis of the large lamellar model $\tau/\Delta d_I$ should be close to unity, since the double-layers are assumed to be so large as to make edge corrections insignificant.

However, the ratio found¹³ for *n*-heptane and triptane in a 25 percent solution of potassium laurate and for ethyl benzene in a 15 percent solution was, at all concentrations of the oils, very close to 0.4. This shows that either: (a) Δd_I does not give the thickness of the oil layer, or (b) the micelle is much smaller than was supposed, so the edge corrections become very large.

Actually, both of these are true.

By assuming spherical micelles, Corrin obtained better, but not perfect, agreement between τ and Δd_I .

II. GENERAL RELATIONS OF THE X-RAY DIFFRACTION BANDS

Four bands (*W*, *S*, *M*, and *I*) are obtained from clear, liquid, isotropic, aqueous solutions of pure soaps and detergents, without or with solubilized oils, at room temperature; a fifth band (*X*) has been obtained only under special conditions. Table I summarizes the order of magnitude of these spacings, the behavior of the bands, and a tentative interpretation. Figure 1 is a general diagram which represents these bands.

The fact that the short-spacing *S*-band (Fig. 2) is broad indicates a liquid type of arrangement of the soap molecules in the monolayers making up the micelles. The Debye-Keesom equation for

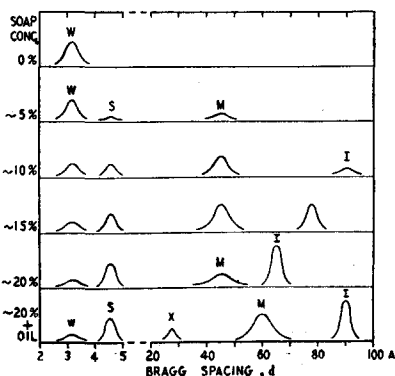


FIG. 1. General illustration of the x-ray bands diffracted from clear liquid aqueous solutions of straight long-chain colloidal electrolytes at room temperature, showing the effects of concentration and solubilized hydrocarbons. The spacings represent only the order of magnitude.

¹³ W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Colloid Sci.* 1, 105 (1946).

¹⁴ Thus in reference 8, p. 124, McBain, in a discussion of the work of Stauff (see reference 9^a, g, h) states "His 'Gross-mizellen' are identical with McBain's neutral or lamellar micelle."

diffraction from liquids

$$\lambda = 0.814(2r) \sin \theta \quad (1)$$

is derived from the first maximum of the function $(\sin sr)/sr$, where

$$s = 4\pi \sin \theta / \lambda,$$

θ is one-half the scattering angle for the maximum diffraction intensity, and r is the distance between nearest neighbors. Equation (1) combined with Bragg's equation reduces to

$$r = 1.23d_s. \quad (2)$$

For soap solutions r is about 5.5 to 5.7 Å. Assuming close-packed hexagonal arrangement, the area per soap molecule σ is

$$\sigma = (\sqrt{3}/2)r^2 = 1.31d_s^2.$$

The values of σ vary from 26.5 to 27.5 sq. Å.

III. EXPERIMENTAL

The experimental techniques have been described earlier.¹² All long-spacing x-ray photographs were taken in the vacuum small-angle diffraction camera using Ni-filtered $\text{CuK}\alpha$ radiation. An improved brass cell was used which has a capacity of 10 cc, is fitted with two pure beryllium windows 0.1 mm thick and 1 mm apart, and is sealed at the top with a large cap pressed into a rubber-gasketed groove.

The photographic films were held plane and perpendicular to the direct beam 15.00 cm from the sample. This distance was checked by the (200) diffraction from NaCl ($a = 5.628 \text{ Å}$), the (002) from graphite ($c = 6.6915 \text{ Å}$) and the (001) from lauric acid ($c \sin \beta = 27.4 \text{ Å}$).

All soaps, detergents, and oils were purified carefully. The saturated fatty acids were recrystallized repeatedly from ethyl alcohol and acetone, then hydrogenated, and finally distilled twice in a high vacuum. After neutralization the soaps were again recrystallized. All solutions, without and with solubilized oils, were made up fresh and appeared as clear as the distilled water. For solubilization, the solutions were sealed in glass ampules and shaken mechanically for several days to several weeks.

Since slits were used instead of pinholes to reduce exposure times, the films show straight bands 1.2 cm high instead of rings. Traces made on two different microphotometers showed the usual small zig-zag lines from the emulsion grain (see Fig. 7 in reference 12). A new photoelectric microphotometer was built with a narrow scanning light which covered the complete height of the bands. This averaged over a larger area and gave a very smooth trace. A rotating step-sector was used to convert densities into energies, but since the films were exposed so that the densities of the bands were on the linear part of the density-exposure calibration curve, this conversion was not used throughout.

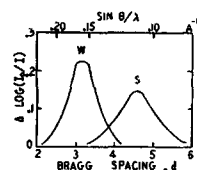


FIG. 2. The water *W*-band and the soap short-spacing *S*-band from 25.0 percent by weight aqueous potassium laurate at 25°C, resolved from the microphotometer trace.

The microphotometer traces give the complete diffraction, coherent plus incoherent, from the colloidal solutions. The shape of the whole curve is significant. To obtain *net* contributions of the bands, three different backgrounds may be applied.

1. The water background, giving the contribution from the non-micellar and the micellar soap.

2. The critical concentration background, giving the contribution from the micellar soap. However, this is not quite correct, since the concentration of non-micellar soap in equilibrium with micelles is not constant.

3. A curve drawn which fits smoothly the general trend of the trace and shows only the deviations caused by the definite bands, giving only the coherent scattering from the micelles. This is I_0 in the ordinates of the figures.

In our analysis background 3 was used. The significance of the particular background used, if any, is important.

IV. THE NEW *M*-BAND RELATED TO MICELLE THICKNESS

Since 1943, it has been noticed that the *I*-band is superimposed on what appears to be a much broader, weak background-scattering, extending from the direct beam outward and having a rather abrupt shoulder. This background pattern, which is clearly evident in an earlier photograph,^{9e} remained at soap concentrations below that at which the *I*-band disappeared but not below the critical micelle concentration. From an analysis of microphotometer traces it was suspected that this might be a real band, and a number of crucial test experiments proved its reality.

1. It was thought that the band might be due to weak $\text{CuK}\beta$ and weak continuous radiation in the incident beam. To eliminate this possibility, strictly monochromatic $\text{CuK}\alpha_1$ and α_2 only, clearly resolved in the direct beam on the films, was obtained from the (200) diffraction from a LiF crystal. However, a 65-hour exposure in the vacuum camera with two lead slits still revealed the band from a 12.2 percent potassium laurate solution.

2. When the soap solution was replaced by pure water, the band disappeared. Consequently, it is due only to the soap in solution; it was not due to any geometrical factors in the slit system or to shielding by the cell.

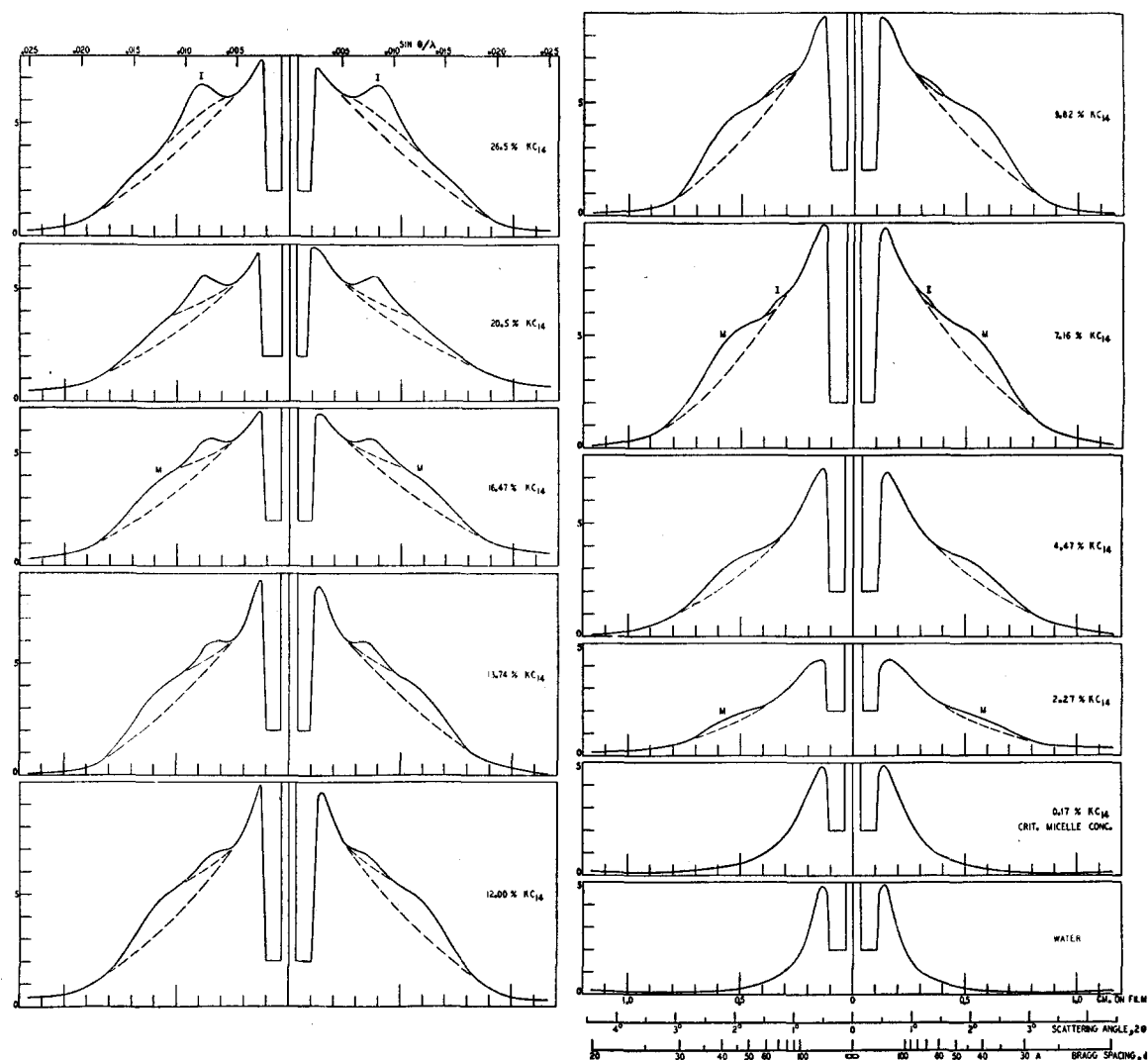


FIG. 3. Microphotometer traces of the long-spacing x-ray diffraction, taken in a vacuum camera, from aqueous solutions of potassium myristate (KC_{14}) at $25^{\circ}C$.

3. The slit system was replaced by two lead pinholes which gave a beam image on the film only 0.9-mm diameter. A 65-hour exposure of Ni-filtered CuK_{α} to the soap solution again revealed the band, so it is not due to overlapping from slits.

4. Using experimental arrangement 3, when the soap solution was replaced by pure water or by potassium laurate at its critical concentration (0.56 percent), the band disappeared. Again, it was proved to originate from the soap in solution, but only above its critical concentration.

5. Aqueous solutions of potassium laurate when aged develop visible flakes of acid-soap which contribute a very sharp, crystalline line of Bragg spacing 35.6Å to the diffraction pattern. To eliminate the presence of even sub-microscopic acid-soap particles in fresh solutions, sodium

lauryl sulfate was selected, since its solutions remain perfectly clear and have negligible hydrolysis. Experimental arrangement 3, when applied to a 15 percent sodium lauryl sulfate solution, revealed the band similar to that for 12.2 percent potassium laurate, so the band cannot be due to acid-soap. Also, solutions of potassium decyl sulfonate (with no hydrolysis) likewise show the band, and incidentally the *I*-band at high concentrations.

This band will be designated the M-band, since it measures the thickness of the micelle.

Figure 3 presents microphotometer traces of the long-spacing x-ray diffraction from aqueous solutions of potassium myristate. The ordinate is in arbitrary units of intensity as read from the

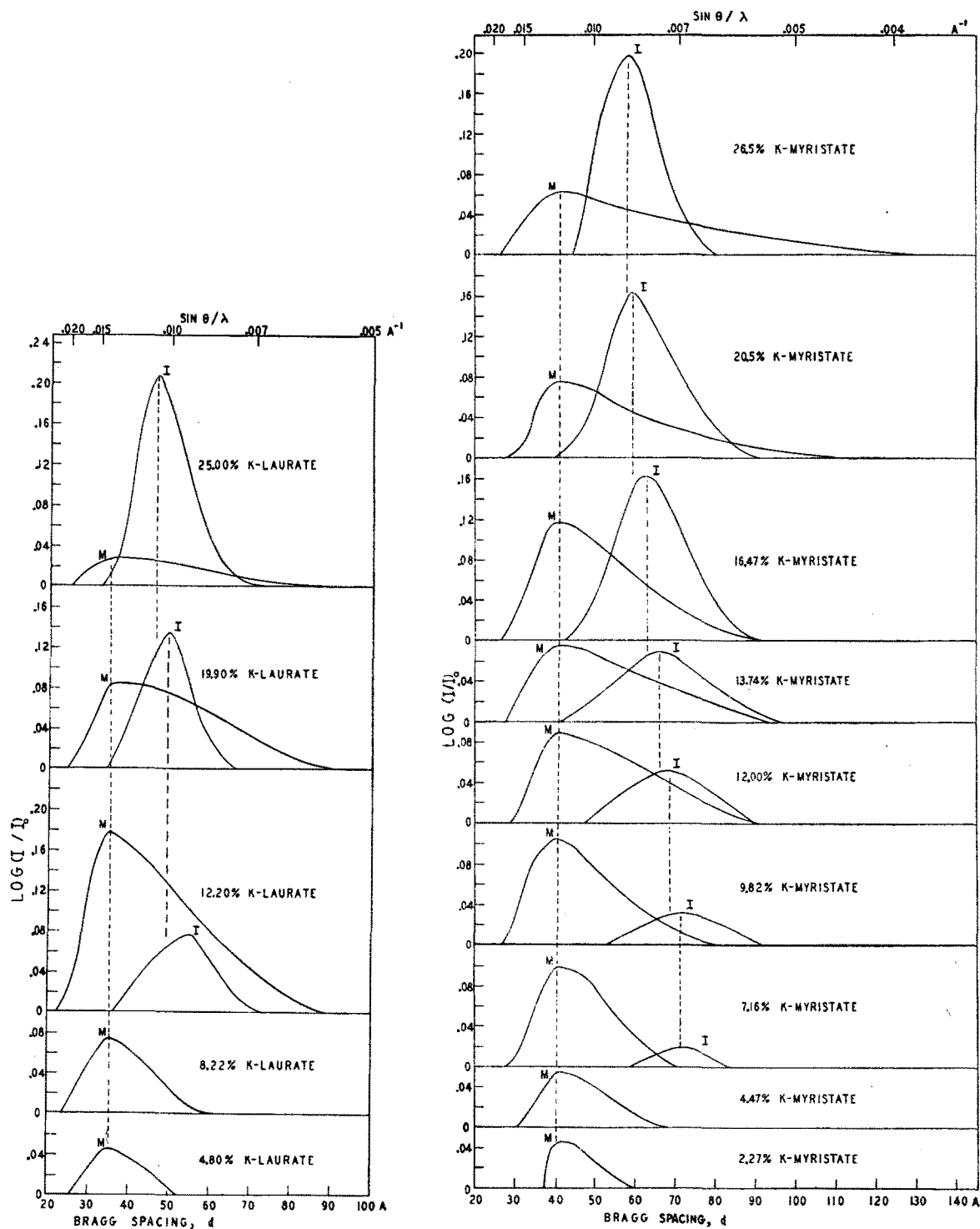


FIG. 4. Resolved *M*-band and *I*-band from aqueous solutions of potassium laurate and potassium myristate.

photoelectric microphotometer. Readings were taken every 0.013 cm across the film, and the intensity variation from the solid line shown was

never more than 0.05 of the intensity units shown. The width of the direct beam is shown by the two lines on each side of the center line and

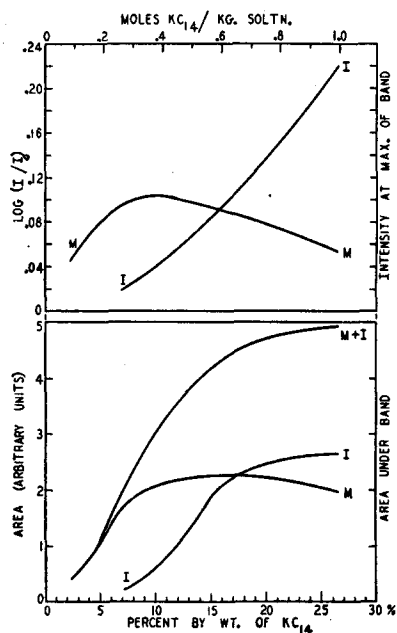


FIG. 5. Intensity at the maximum and total area under the *M*- and *I*-bands as a function of the concentration of potassium myristate (KC_{14}) in aqueous solution.

nearest it. The trace at the bottom is the scattering with water. At the critical concentration of potassium myristate (0.17 percent) no micellar *M*-band appears, even though long exposures were taken to attempt to record it. At 2.27 percent (0.08 molal) the *M*-band is evident and it becomes more pronounced at higher concentrations.

With the background drawn in, as described in Section III, the diffraction patterns can be resolved into the discrete *M*- and *I*-bands. These are shown in Fig. 4 for potassium myristate and potassium laurate. With this particular background the resolved bands come down to zero intensity. With the water or critical concentration background, they would not come down to zero.

In Fig. 5 for potassium myristate, the intensity of the *M*-band increases up to about 10 percent of this soap and then decreases, whereas that for the *I*-band steadily increases. The same general behavior holds for the areas under the bands. The concentration at which the *I*-band first appears (about 5 percent for potassium myristate, about 9 percent for potassium laurate, and about 15 percent for sodium lauryl sulfate) is considerably above the concentration at which

the *M*-band first appears. The intensities of these two bands might have been interpreted as a measure of the relative abundances of two kinds of micelles. However, a single kind of micelle may give the *M*-band and at higher concentrations, where these micelles are necessarily closer together, the *I*-band may result from a network of these micelles, giving an intermicelle spacing. At high concentrations the total diffracted intensity would then be partitioned between that from the single micelles (*M*) and that from the intermicelle arrangement (*I*). Under this supposition, with increasing concentration the *M*-spacing should remain constant whereas the *I*-spacing should decrease. This is what is observed.

TABLE II. *M*-spacings derived from the position of the peak of the *M*-band for aqueous soap solutions at 25°C.

	Percent by weight of soap	Bragg <i>M</i> -spacing $d_M \pm 1A$
Potassium caprylate	6.05	no band
KC_8	17.36	29.5 (weak diffraction)
	25.00	30.3
	29.6	30.0
	34.4	29.6
	39.9	30.7
	43.8	28.2
		Av. 29.7
Potassium caprate	7.97	30.3
KC_{10}	9.65	32.8
	10.51	31.2
	11.93	32.5
		Av. 31.7
Potassium laurate	4.80	35.5
KC_{12}	8.22	34.8
	9.10	35.0
	12.10	34.5
	12.20	35.0
	13.20	35.6
	15.00	35.2
	16.70	36.0
	19.90	35.7
		Av. 35.3
Potassium myristate	2.27	40.8
KC_{14}	4.47	41.5
	7.16	40.7
	9.82	40.2
	12.00	39.5
	13.74	39.6
	16.47	40.2
		Av. 40.3
Potassium palmitate	1.28	44.9
KC_{16}	3.44	49.1
	5.01	47.9
		Av. 47.3
Sodium lauryl sulfate	8.6	37.3
	15.0	37.1
	20.0	36.7
	25.0	38.2
		Av. 37.3

Table II presents the M -spacings for a homologous series of soaps at different concentrations.¹⁵ It is at once evident that the M -spacing is very constant for a given soap at all concentrations. The lowest concentration at which the M -band has been measured thus far is 1.28 percent potassium palmitate. A binary soap mixture should have an intermediate M -spacing.

The average M -spacing for each soap is very close to twice the length of that soap molecule as derived from crystal diffraction data or from a scale model of the molecule. Sodium lauryl sulfate falls into line also, d_M being 2.0Å longer than potassium laurate. This is reasonable, since the sulfate group is a little larger than the carboxyl group. In passing from one soap to the next longer in Table II and using two soap molecules in line to correspond to d_M , the increment should be $2 \times 2.54 = 5.08\text{Å}$. The successive increments in the average d_M are actually 2.0, 3.6, 5.0, and 7.0Å.

The question arises whether the simple Bragg spacing d_M is a measure of the actual spacing. For a spherical liquid molecule the Bragg short-spacing is increased by the factor 1.23, as shown in Eq. (2) Section II, in order to give the diameter. This results from the well-known work by Debye and also of Warren.¹⁶ However, the correction factor for micelles has not been worked out, although Debye has outlined the theoretical calculations to us. The diffraction depends, among other things, upon the total scattering from all the electrons in each molecule integrated over its length with respect to the *density* of scattering electrons distributed along the molecule. Ideally, one should have an atom of high atomic number at the polar *end* of the molecule if d_M is to give the best measure of the double-length. Because of these considerations, the simple Bragg spacings d_M and also d_I will be used until the correction factors are known.

The M -spacing is interpreted as being related to the thickness of the micelle, consisting of only *one* double-layer of soap molecules.

¹⁵ In Tables I, IIIa, and VIa, c of reference 12, the long-spacings given for solutions of sodium and potassium caprylate are now found to be those for the M -band; all other long-spacings given there still remain those for the I -band.

¹⁶ B. E. Warren, Phys. Rev. **44**, 969 (1933).

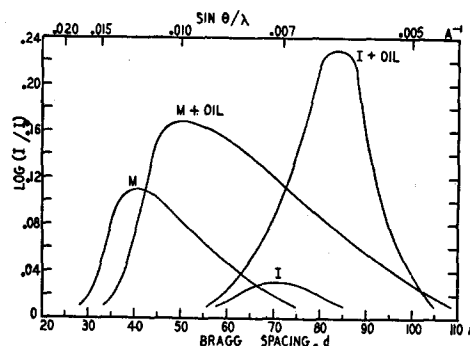


FIG. 6. Example of the increase in intensity and shift to longer spacings of the M - and I -bands from a soap solution caused by the addition of solubilized hydrocarbon. This is a 9.82 percent by weight aqueous solution of potassium myristate saturated with benzene (3.82 g benzene per 100 g soap solution).

V. EFFECT OF SOLUBILIZED OILS ON THE M -BAND

The saturation of a soap solution with a hydrocarbon oil increases both the intensity and the spacing of the M -band, an example of which is shown in Fig. 6.

Figure 7 represents the steady increase of the M -spacing up to saturation with solubilization of increasing amounts of ethyl benzene in a soap solution. With a little more hydrocarbon than the saturation value added, d_M does not increase further.

Hydrocarbons were used to *saturate* solutions of potassium laurate and potassium myristate of various concentrations. These solutions were sealed in ampules and shaken vigorously for 11 days by the use of a mechanical shaker. There

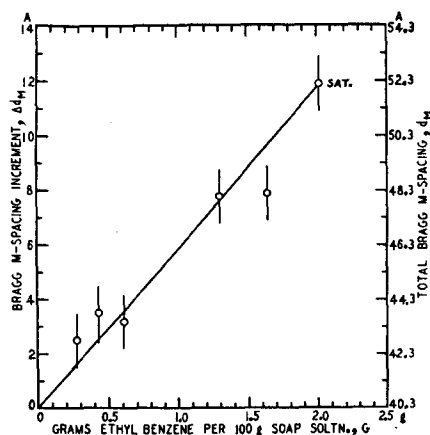


FIG. 7. Increase in the Bragg M -spacing caused by ethyl benzene when solubilized in a 7.16 percent by weight aqueous solution of potassium myristate.

TABLE III. *M*-spacings for aqueous solutions of potassium laurate (KC₁₂) and potassium myristate (KC₁₄) saturated with hydrocarbons at 25°C.

Hydrocarbon solubilized	Percent by weight of soap	Bragg <i>M</i> -spacing $d_M \pm 1\text{\AA}$	Bragg <i>M</i> -spacing increment due to hydrocarbon $\Delta d_M \text{ sat} \pm 2\text{\AA}$	Solubility, grams hydrocarbon per 100-g soap solution, G_{sat}
Ethyl benzene	7.00 KC ₁₂	40.7	5.4	1.07
	8.84	41.1	5.8	1.48
	10.09	41.5	6.2	1.77
	12.05	41.8	6.5	2.23
<i>n</i> -heptane	13.60	42.0	6.7	2.63
	4.47 KC ₁₄	50.0	9.7	0.46
	7.16	51.0	10.7	0.84
	9.82	51.2	10.9	1.24
Ethyl benzene	12.00	49.2	8.9	1.59
	13.74	48.2	7.9	1.89
	4.47 KC ₁₄	50.4	10.1	1.13
	7.16	52.2	11.9	2.02
Benzene	9.82	51.4	11.1	2.99
	12.00	48.4	8.1	4.03
	13.74	47.8	7.5	4.56
	4.47 KC ₁₄	51.2	10.9	1.57
	7.16	52.0	11.7	2.66
	9.82	49.6	9.3	3.82
	12.00	49.4	9.1	5.08
	13.74	49.0	8.7	5.96

Notes: With no solubilized hydrocarbon, $d_M = 35.3$ for KC₁₂ and $d_M = 40.3\text{\AA}$ for KC₁₄ independent of soap concentration (Table II).

At the higher soap concentrations, the values of Δd_M are less accurate because of the influence of the *I*-band (Fig. 4).

At 25°C the density of *n*-heptane is 0.679, ethyl benzene is 0.862, and benzene is 0.873 g/cc.

At 25°C the solubility in 100 grams of water for *n*-heptane is 0.005, ethyl benzene is 0.015, and benzene is 0.185 grams.

Aqueous solutions of sodium lauryl sulfate saturated with hydrocarbons give similar relations.

remained a small excess of the oil on top of the lower, clear, saturated solution which was x-rayed. Measurements on these solutions are presented in Table III. The variation of the Bragg spacing increment Δd_M for a given oil in different concentrations of a given soap is small. Of importance is the fact that the mean ethyl benzene increment for the 14 carbon atom soap is about twice that for the 12 carbon atom soap. This is in harmony with the effect of different soaps on solubilization of a given oil⁸ and agrees with other evidence in suggesting that the number of soap molecules per micelle increases as the soap molecules increase in length.

The *M*-spacing increment Δd_M is interpreted as being related to the increase in micelle thickness caused by hydrocarbon which is solubilized in the middle of the micelle.

VI. EFFECT ON THE *M*-BAND BY PENETRATION OF POLAR-NON-POLAR MOLECULES INTO THE SOAP LAYER

In contrast, when long-chain *n*-alcohols, *n*-amines, and similar polar-non-polar molecules are added to an aqueous soap or detergent solution, the *M*-spacing does not increase.¹⁷ Here it is postulated that these polar-non-polar molecules penetrate a soap monolayer in a micelle, thus not increasing the *M*-spacing thickness but making the micelle larger in lateral extension. The *S*-band short-spacing is not altered by the addition of long straight-chain molecules.

VII. A NEW UNINTERPRETED *X*-BAND

A weak, moderately broad, distinct, long-spacing band (*X*) is clearly evident in an earlier photographic reproduction.^{9e} In our work it was found when solubilized small molecules of tetrahedral symmetry¹⁸ were present. The assumed first-order spacing d_X is shorter than d_I or d_M . It has not appeared with any of the soaps used here when dissolved in water up to concentrations at which the solutions cease to be clear, and liquid, nor with dilute soap solutions containing solubilized hydrocarbons which show only the *M*-band, even after long exposures. A 17-hour exposure with 26.5 percent aqueous potassium myristate showed no *X*-band (normal exposure for the *I*-band here is 3 hours). The *X*-band appears only when the *I*-band is fairly intense and when solubilized hydrocarbons are

TABLE IV. Bragg *I*-, *M*-, and *X*-spacings (all assumed first order) from aqueous potassium myristate solutions saturated with hydrocarbons at 25°C.

	Hydrocarbon solubilized				Percent by weight of soap
	None	<i>n</i> -heptane	Ethyl benzene	Benzene	
d_I	71\text{\AA}	80	80	84	9.82
d_M	40.2	51.2	51.4	49.6	
d_X	no band	26.6	25.5	26.9	
d_I	68	74	72	77	12.00
d_M	39.5	49.2	48.4	49.4	
d_X	no band	26.4	26.0	27.1	
d_I	66	78	78	78	13.74
d_M	39.6	48.2	47.8	49.0	
d_X	no band	28.0	28.7	29.4	

The hydrocarbon solubilities for these solutions are included in Table III.

¹⁷ W. D. Harkins, R. W. Mattoon, and R. Mittelman, *J. Chem. Phys.* **15**, 763 (1947).

present. These conditions mean that the micelles are fairly close together and that they are of larger lateral extension, which is more conducive to a short-range order.

Table IV gives a collection of the I -, M -, and X -spacings for twelve solutions. It may be noted that $d_I - d_M \approx d_X$. In soap crystals odd orders are stronger than even orders. Perhaps d_X is the third order of d_I .

VIII. THE LONG-SPACING I -BAND

The well-known long-spacing band diffracted from aqueous solutions of colloidal electrolytes is called here the I -band. Some new measurements are now presented.

The microphotometer traces in Fig. 3 show the I -band. In Fig. 4 this band is resolved for various concentrations of potassium laurate and potassium myristate. The variation of the intensity and area of the I -band with the concentration of potassium myristate is shown in Fig. 5.

The German workers^{9a, i} have shown that the d_I spacing increases with dilution. A more precise description of the functional relationship between d_I and the concentration c (weight fraction of soap) is given here. Table V gives measurements from a very careful analysis of our films.

In Fig. 8 the I -spacing from Table V is plotted against c . A Cartesian plot is obviously not linear. However, a fairly linear plot is obtained by a logarithmic relationship:

$$d_I = k_1 + k_2 \log(1/c)$$

and also by a hyperbolic relationship:

$$d_I = k_3 + k_4[(1/c) - 1].$$

The expression $[(1/c) - 1]$ is identical with the grams of water per gram of soap. Both of these equations have a constant spacing (k_1 or k_3) for all soap and no water ($c = 1$). With water added (c decreasing), the spacing increases until for all water and no soap ($c = 0$) the spacing is infinite. This behavior has some physical reality, although the equations given in Fig. 8 are derived empirically.

The long-spacing from aqueous solutions of hexanolamine oleate has been reported¹⁸ as a linear function of concentration, but they con-

¹⁸ S. Ross and J. W. McBain, J. Am. Chem. Soc. **68**, 296 (1946).

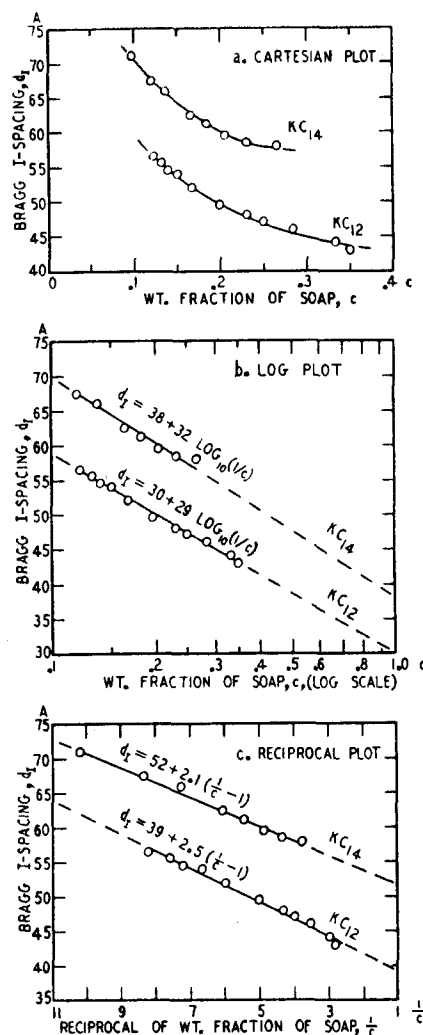


FIG. 8. The Bragg I -spacings for aqueous solutions of potassium laurate (KC_{12}) and potassium myristate (KC_{14}) plotted against the soap concentration, in a Cartesian plot, a logarithmic plot, and a reciprocal plot. The equations shown are those calculated by least squares from Table V.

sidered a first-order peak to be second order. Our measurements on the same detergent are represented better by a logarithmic function. The hyperbolic relationship has recently been applied to the spacings of non-ionic detergents.¹⁹

The I -band looks narrow on a film, but it must be remembered that the change of spacing d with scattering angle 2θ increases very rapidly at smaller angles and d approaches infinity at the direct beam.

$$\partial d / \partial \theta = -\lambda \cos \theta / (2 \sin^2 \theta).$$

¹⁹ J. W. McBain and S. S. Marsden, J. Chem. Phys. **15**, 211 (1947).

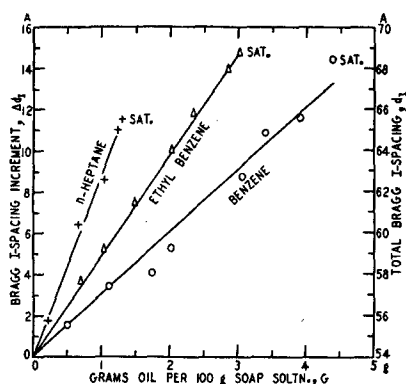


FIG. 9. Increase in the Bragg I -spacing caused by oils solubilized in a 15.0 percent by weight aqueous solution of potassium laurate. (The ethyl benzene spacings are given in Table VIII.)

The I -band plotted on a spacing basis has considerable width (Fig. 4) which may allow it to be an interparticle diffraction as from liquids.

IX. EFFECT OF SOLUBILIZED OILS ON THE I -BAND

An increase in both the intensity and the spacing of the I -band from a soap solution due only to the addition of a solubilized oil has been reported earlier.^{9e,20} In Fig. 6 the intensity of both the I -band and the M -band is increased; (a) the I -spacing and (b) the M -spacing are also increased. These increases in spacing indicate an increase in (a) the size and (b) the thickness of the micelle.

The presence of solubilized oil makes the I -band detectable at a lower soap concentration than in the absence of the oil. This is due to the related increase in thickness and size of the micelle.

With increasing solubilization of a hydrocarbon, the I -spacing increases steadily up to saturation. With a little more hydrocarbon than the saturation value added, d_I does not increase further. Figure 9 is an example of this behavior for n -heptane, ethyl benzene, and benzene. The solubilities are in this order with n -heptane the least soluble. For these three hydrocarbons, the less soluble the oil, the more rapidly the I -spacing increases. The volume of hydrocarbon is more significant than the mass in its effect on the form of the micelle. This conversion in Fig. 9 reduces the slopes but does not change the order.

²⁰ E. W. Hughes, W. M. Sawyer, and J. R. Vinograd, *J. Chem. Phys.* **13**, 131 (1945).

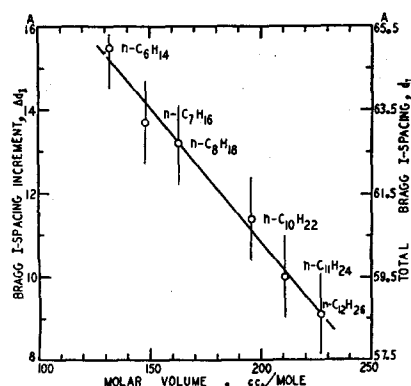


FIG. 10. The Bragg I -spacing increment for a 20.0 percent by weight aqueous solution of potassium laurate saturated with n -paraffin oils as a function of the molar volume of the oil.

In Table VI are given the I -spacings for potassium laurate solutions saturated with each of a series of different hydrocarbons.

The values of Δd_I , taken from Table VI for a 20 percent potassium laurate solution saturated with the n -paraffin oils, are plotted in Fig. 10 against the molar volume of the paraffin oil. Hughes, Sawyer, and Vinograd²⁰ report similar results for the I -band. The I -spacing increment for n -paraffin oils at saturation decreases rapidly with increasing length of the hydrocarbon chain. However, this is caused by the concomitant decrease in solubilization caused by the decrease in activity of the oil with chain length. The vapor pressure of each liquid hydrocarbon is important in solubilization.²¹

For a soap solution saturated with a given oil, the I -spacing increment is somewhat larger for a higher soap concentration (Table VI). An example of this is given in Fig. 11.

X. CALCULATION OF THE NUMBER OF SOAP MOLECULES PER MICELLE ON THE BASIS OF CERTAIN ASSUMPTIONS

Various models for the micelle have been discussed by Dervichian²² in attempting to explain the properties of soap solutions. He prefers only one kind of micelle which is small and one double-

²¹ J. W. McBain and J. J. O'Connor, *J. Am. Chem. Soc.* **62**, 2855 (1940); *ibid.*, **63**, 875 (1941).

²² D. G. Dervichian, *J. chim. phys.* **38**, 59 (1941); *Comptes Rendus* **217**, 299 (1943); *J. Chem. Phys.* **11**, 236 (1943); D. Dervichian and F. Lachamp, *Bull. Soc. Chim.* **12A**, 189 (1945).

TABLE V. I -spacings derived from the position of the peak of the I -band for aqueous soap solutions at 25°C.

	Percent by weight of soap	Bragg I -spacing $d_I \pm 1\text{\AA}$
Potassium caprate KC_{10}	22.9 28.6 38.0	43.4 41.5 39.5
Potassium laurate KC_{12}	12.20 13.20 13.90 15.00 16.70 19.90 23.10 25.00 28.4 33.3 35.0	56.5 55.6 54.5 54.0 52.0 49.5 48.0 47.1 46.0 44.1 42.9
Potassium myristate KC_{14}	9.82 12.00 13.74 16.47 18.3 20.5 23.1 26.5	71.0 67.5 66.0 62.5 61.2 59.5 58.5 58.0
Sodium lauryl sulfate	20.0 25.0 30.0	57.8 (weak diffraction) 54.1 52.9

The weight fraction of soap c is the percent $\div 100$. I -spacings for other soaps are given in an earlier paper (see reference 12).

layer thick. He proposes to interpret the long-spacing as the distance between the micelles.

In an endeavor to interpret our own experimental work, it may be assumed that the micelles are distributed in the water in a liquid arrangement, and that the Bragg spacing d_I is the distance between the center of a micelle and that of any one of its nearest neighbors. No special shape for the micelle is necessary in this "point lattice," but it seems probable that the spacing which should be applied is somewhat larger than the Bragg spacing.

The total volume V_T (micelle plus solubilized oil plus surrounding water) associated with each micelle is given by

$$V_T = (6/\pi\sqrt{2})(4/3)\pi(d_I/2)^3,$$

or

$$V_T = d_I^3/\sqrt{2}. \quad (3)$$

This comes from the geometry of close-packed spheres, which are here spheres of water enclosing the micelle, and the factor $[6/(\pi\sqrt{2})]$ accounts for the "empty spaces" among the

TABLE VI. I -spacings for aqueous solutions of potassium laurate (KC_{12}) saturated with hydrocarbons at 25°C.

Hydrocarbon solubilized	Percent ^a by weight of KC_{12}	Bragg I -spacing $d_I \pm 1\text{\AA}$	Bragg I -spacing increment due to hydrocarbon $\Delta d_{I \text{ sat}} \pm 2\text{\AA}$	Solubility, grams hydrocarbon per 100-g soap solution G_{sat}	$\Delta d_{I \text{ sat}} / G_{\text{sat}}$
None	15	54.0	0		
None	20	49.5	0		
None	25	47.1	0		
<i>n</i> -heptane	15	65.5	11.5	1.31	8.8
<i>n</i> -heptane	20	61.5	12.0	1.99	6.0
<i>n</i> -heptane	25	60.9	13.8	3.62 ^b	3.8
Triptane (2, 2, 3 trimethyl butane)	25	61.7	14.6	3.73	3.9
Benzene	15	68.5	14.5	4.38	3.3
Benzene	20	65.7	16.2	6.41	2.5
Ethyl benzene	15	68.8	14.8	3.02	4.9
Cyclohexane	20	63.0	13.5 ^c	3.20 ^c	4.2
1, 3, 5 trimethyl benzene	20	58.5	9.0 ^c	2.92 ^c	3.1
<i>n</i> -heptane	15	65.5	11.5	1.31	8.8
<i>n</i> -dodecane	15	61.5	7.5		
<i>n</i> -hexadecane	15	54.0	0		
<i>n</i> -hexane	20	65.1	15.5		
<i>n</i> -heptane	20	61.5	13.7	1.99	6.0
<i>n</i> -octane	20	60.1	13.2		
<i>n</i> -decane	20	59.2	11.4		
<i>n</i> -undecane	20	58.5	10.0		
<i>n</i> -dodecane	20	58.5	9.1		

^a 15 percent = 0.629; 20 percent = 0.839; 25 percent = 1.049 moles soap/kg. soap solution.

^b The density method¹⁸ gives 3.62; the turbidity method⁸ gives 2.67.

^c Below saturation.

Additional d_I measurements of hydrocarbons solubilized in aqueous potassium myristate solutions are included in Table IV, with the solubilities given in Table III.

spheres. The reciprocal of Eq. (3) is equivalent to

$$N_M = (\sqrt{2}/d_I^3\rho), \quad (4)$$

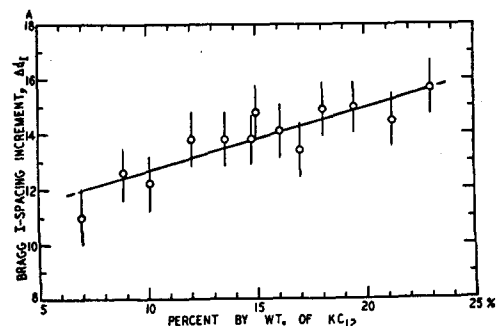


FIG. 11. Effect of soap concentration on the I -spacing increment. Each aqueous potassium laurate (KC_{12}) solution is saturated with ethyl benzene.

TABLE VII. Approximate distribution and size of micelles based on the Bragg value for d_1 .

	Potassium laurate	Sodium lauryl sulfate	Potassium myristate	Sodium oleate	Lauryl ammonium chloride
Molecular wt. m_s	238.4	288.3	266.5	304.5	221.8
Critical micelle concentration, molar	0.0235	0.0061	0.0064	0.001	0.014
Percent by weight of soap	12.2	20.0	9.8	9.4	9.7
Moles of soap per kg. of solution	0.511	0.694	0.368	0.309	0.437
Bragg I -spacing, d_1 , $\pm 1\text{\AA}$	56.5	57.8	71.0	92.3	92.8
No. micelles per gram of solution, N_M	$7.8(10)^{18}$	$7.3(10)^{18}$	$4.0(10)^{18}$	$1.8(10)^{18}$	$1.8(10)^{18}$
No. soap molecules per micelle, n_s	39	57	56	103	148
Apparent molecular weight of micelle, M	9,000	16,000	15,000	31,000	33,000
Apparent volume of micelle, V_M , \AA^3	16,000	27,000	25,000	52,000	56,000

where N_M is the number of micelles per gram of total solution and ρ is the solution density (taken as 1.00 g/cc for these dilute solutions).

Let the number of micellar soap molecules per gram of total solution be

$$N_S = c\alpha/m_s, \quad (5)$$

where c is the weight fraction of soap of molecular weight m_s and α is Avogadro's number. Strictly, c should be reduced by the amount of non-micellar soap, but since this is a relatively small quantity, and not exactly known, it is neglected.

Similarly, let the number of hydrocarbon molecules solubilized per gram of total solution be N_H , calculated from the weight fraction of hydrocarbon of molecular weight m_H . Strictly, this should be reduced by the solubility of the hydrocarbon in the non-micellar phase, but this small correction is also neglected.

The number of soap molecules n_s and hydrocarbon molecules n_H per micelle are then given by

$$n_s = N_S/N_M, \quad (6)$$

and

$$n_H = N_H/N_M.$$

The apparent molecular weight of the micelle M would be

$$M = n_s m_s + n_H m_H.$$

The apparent volume of the micelle itself V_M should be approximated by

$$V_M = V_T - (V_w/N_M), \quad (7)$$

where V_w is the volume of water per gram of total solution. Strictly, V_w should include also the volume of the non-micellar soap molecules and the volume of hydrocarbon dissolved in the non-micellar phase, but these small corrections are neglected.

In Table VII are shown several characteristics of micelles as calculated by the use of the equations given above. The values listed are for only the lowest concentration at which the I -spacing could be measured. It is not certain that calculations for higher concentrations have any validity. However, the values obtained indicate that on increasing the soap concentration, the number of micelles per gram of solution, the number of soap molecules per micelle, and the apparent volume of the micelle itself, all increase. These values are specific for each soap and each concentration.

When a certain small volume of hydrocarbon is solubilized in a given soap solution, the total volume is increased, and if the total number of micelles were to remain constant, the micelles would be separated a little farther from each other (center to center). This increase in spacing is readily calculated on a simple dilution basis. *However, the experimental d_1 spacing is increased considerably more than this.* If d_1 is interpreted as the intermicelle spacing, this would indicate a decrease in the number of micelles per unit volume, which in turn requires that each micelle contain a larger number of soap molecules. This behavior is in agreement with the solubility relations² where the rate of change $(\partial s/\partial c)_T$ of the hydrocarbon solubility s increases with increasing soap concentration c .

In Table VIII values are shown as calculated for micelles which contain solubilized ethyl benzene. These show the effects of increasing amounts of ethyl benzene solubilized in the same soap solution. The saturation of the soap solution with ethyl benzene apparently halves the number of micelles per gram of solution. This is reflected in a doubling of the number of soap molecules

TABLE VIII. Effects of increasing amounts of ethyl benzene, solubilized in a 15.0 percent aqueous potassium laurate solution, on the approximate distribution and size of micelles.

Grams ethyl benzene solubilized in 100-g soap solution only G	Bragg I -spacing $d_I \pm 1\text{\AA}$	No. micelles per gram of solution N_M	No. soap molecules per micelle n_s	No. oil molecules per micelle n_H	Apparent volume of micelle V_M
0	54.0 ($d_M = 35.3$)	9.0 (10) ¹⁸	42	0	17,000A ³
0.68	57.8	7.3	51	5	22,000
1.05	59.2	6.8	55	9	23,000
1.51	61.5	6.1	61	14	27,000
2.04	64.1	5.4	69	21	31,000
2.33	66.0	4.9	75	26	34,000
2.86	68.0	4.5	82	35	38,000
3.02 (sat.)	68.8 ($d_M = 42.4$)	4.3	85	38	40,000
<i>n</i> -lauryl alcohol 4.35 (sat.)	73.0 ($d_M = 36.0$)	3.6	99	37	51,000

The apparent average molecular weight of this micelle with no ethyl benzene is 10,000; when saturated with ethyl benzene the soap contribution is 20,000 and the ethyl benzene contribution is 4000, making a total of 24,000. These spacings are plotted in Fig. 9, and the ethyl benzene density and solubility in water are given in the notes in Table III.

per micelle. When saturated, there are apparently about half as many ethyl benzene molecules as potassium laurate molecules per micelle. The apparent volume of the micelle itself is about doubled by saturation with ethyl benzene.

The ratio of the total micelle molecular weight M converted to grams and the micelle volume V_M gives the apparent micelle density, which ranges between 0.94 and 1.02 g/cc for all entries in Tables VII and VIII. If the micelle is considered a *cylinder* of height d_M and a volume V_M , the lateral diameter would vary between 0.7 d_M and 0.8 d_M for the first three soaps in Table VII and would steadily increase from 0.7 d_M to 0.8 d_M going down in Table VIII for ethyl benzene.

With *n*-lauryl alcohol instead of ethyl benzene, the characteristics of the model are shown in the bottom line of Table VIII. The increment Δd_I is 19.0A and Δd_M is only 0.7A (see Section VI; reference 17 gives other measurements). The calculations indicate this micelle to be thinner than that with ethyl benzene, but to have a larger volume and therefore a larger lateral extension. If considered a *cylinder*, the lateral diameter would be 1.2 d_M .

The addition of simple salt to a soap solution increases the I -spacing (Table VIb of reference 12) which may be interpreted as causing the formation of larger micelles. Also, the addition of a salt increases the solubility of a hydrocarbon,³ which is presumably a consequence of an increase in size of the micelles.

Substituting Eqs. (4) and (5) in (6) and rear-

ranging gives

$$d_I^3 = (n_s m_s \sqrt{2} / \rho \alpha) (1/c),$$

which reduces to the working equation

$$d_I^3 = (2.35 n_s m_s) (1/c). \quad (8)$$

A plot of d_I^3 against $(1/c)$ from Table V yields a fairly straight line, the slope of which may be used for estimating n_s from Eq. (8). The line extrapolated to $c=1$ gives an intercept whose cube root d_I is close to d_M .

Several investigators²³⁻²⁵ have determined the rates of diffusion in soap solutions which contain micelles. From the values obtained for cetyl pyridinium chloride at concentrations from 0.002 to 0.05N Hartley calculated on the basis of a spherical micelle that the diameter of the micelle is 52A, and consists of 70 molecules of the detergent. Unfortunately, such determinations have to be made in the presence of a swamping electrolyte, and electrolytes increase the size of the micelle. However, the value obtained by Hartley is in agreement with the idea presented in this paper that the micelle is small in comparison with the size indicated by the lamellar model.

Bernal and Fankuchen²⁶ observed from solutions of tobacco mosaic virus a long-spacing x-ray diffraction. This spacing increases steadily with

²³ G. S. Hartley and D. F. Runnicles, Proc. Roy. Soc. A168, 420 (1938).

²⁴ O. Lamm, Kolloid Zeits. 98, 45 (1942).

²⁵ R. J. Vetter, J. Phys. and Colloid Chem. 51, 262 (1947).

²⁶ J. D. Bernal and I. Fankuchen, J. Gen. Physiol. 25, 111, 157 (1941).

dilution. They interpret this as the interparticle lateral spacing between the parallel virus rods. This two-dimensional relation may be analogous to a three dimensional one for micelles.

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Ultraviolet Absorption Spectrum of Toxicarol and Dehydrotoxicarol

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The ultraviolet absorption spectra of toxicarol and dehydrotoxicarol in ethyl alcohol solution were studied with a Hilger E-316 quartz spectrograph and a Hilger H-16 sector-photometer. The curve of toxicarol shows a maximum at $\lambda 2741$ with a molecular extinction coefficient 23,000. The curve drops down vertically at a wave-length $\lambda 2801$ covering an extinction range from 19,000 to 24,000. The absorption curve of dehydrotoxicarol has two maxima, one being at $\lambda 2780$ with molecular extinction coefficient 20,250, the other at $\lambda 3304$ with molecular extinction coefficient 7180. One minimum occurs at $\lambda 3114$ with coefficient at 5320.

INTRODUCTION

THE introduction of derris root extracts as insecticides¹ has excited the interest of many chemists and entomologists. They found that in the derris extracts, besides rotenone ($C_{23}H_{22}O_6$), there are other materials possessing insecticidal properties. One of these compounds, toxicarol ($C_{23}H_{22}O_6$) is a greenish yellow substance which crystallizes in the form of thin hexagonal plates and rods, has two hethoxyl groups, melts at 218° – $220^\circ C$,² and is toxic to fish.³

When toxicarol hydrate, which was obtained by the action of alcoholic alkali upon toxicarol, is boiled with alcoholic hydrochloric acid, it is readily converted to dehydrotoxicarol ($C_{23}H_{20}O_7$).

The latter crystallizes in the form of yellow rods and needles and melts at $234^\circ C$.⁴

So far, the absorption spectrophotometric study of these compounds has not yet been made. It is the interest of the present work to supply more data for the study of the molecular structure of these compounds by determining their ultraviolet absorption curves.

EXPERIMENTAL

A Hilger E-316 quartz spectrograph and a Hilger H-16 sector-photometer were used in the determination. Iron spark was used as light source. Across the 3-mm spark gap four glass tinfoil condensers of 0.12 microfarad each were connected in series, and the potential was 8000 volts. Twenty-eight strips of photograms were taken on each plate; the time of exposure was increased from 21" to 8'20". The photograph thus obtained with the sector-photometer was composed of a pair of spectrograms in close

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** In Java.

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