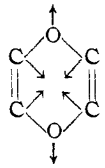
vibration, which is represented below, would be totally symmetrical for the molecule of dioxadiene.



The band separation occurring near 750 cm.$^{-1}$ in the different systems may represent a combination of the vibrations described above, although it is reasonable to expect a ring vibration similar to the "breathing" vibration prominent in the benzene spectrum. Bands are present in all systems which probably represent two quanta of the 550 cm.$^{-1}$ vibration. The next prominent band is found separated by about 1150 cm.$^{-1}$ from the band assigned as 0–0 band in the allowed transitions and is thought to be due to a symmetrical ring vibration. There are a number of bands in the region 1200–1600 cm.$^{-1}$ but only one of these, 1460 cm.$^{-1}$ in the second system, is of outstanding intensity. An intense band is present in each system near 1700 cm.$^{-1}$ Its prominence suggests a fundamental vibration but the value seems surprisingly high for an excited state frequency. The bands are so placed that they could represent a combination of the 1150 and 550 cm.$^{-1}$ frequencies if the potential energy curves happened to be in a position to favor this transition.

The other bands are of lower intensity and can be accounted for as combinations or overtones and the C–H stretching vibration. There seems to be very little change in fundamental frequencies in the different band systems; differences of 20 cm.$^{-1}$ are not believed to be significant in general although the error of measurement differs in different regions of the spectrum. The small changes in frequency and short progressions indicate that the structure of the ring is not greatly changed by the electronic excitations.

The conclusions above must necessarily be of a tentative nature. A study of the Raman spectra of dioxadiene would be valuable as a test of the assignments since totally symmetrical vibrations of the normal molecule would appear as polarized lines and those of the B_g classes as depolarized lines. They would not be found in the infrared spectra. The Raman spectrum of 1,4-cyclohexadiene was measured by Kohlrausch and Seka[13] who observed frequencies of 400, 706, 987, 1196, 1676 and 3032 cm.$^{-1}$, together with others attributed to 1,3-cyclohexadiene which was present as impurity.

Acknowledgment.—The authors wish to make grateful acknowledgment to Dr. Emma P. Carr and Dr. Mary L. Sherrill for their interest and assistance throughout the work, and to Dr. R. S. Mulliken for helpful suggestions.

Summary

The ultraviolet absorption spectra of dioxene and dioxadiene have been measured up to wave numbers of 62,000 cm.$^{-1}$ Five separate band systems have been observed for dioxadiene and vibrational separations measured. Possible interpretations of the data are given on the basis of the symmetry of the molecule.

[13] K. W. Kohlrausch and R. Seka, *Ber.*, **68**, 528 (1935).

SOUTH HADLEY, MASS. RECEIVED AUGUST 27, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Structure of Soap Micelles Indicated by X-Rays and the Theory of Molecular Orientation. I. Aqueous Solutions[1]

BY WILLIAM D. HARKINS, RICHARD W. MATTOON AND MYRON L. CORRIN

I. General Structure of Soap Micelles.—Soap solutions and those of many other detergents exhibit an extremely interesting structure, which is revealed by a combination of X-ray data with the theory of orientation of molecules in surfaces. The manifold uses of soap in life and industry are dependent in part upon this structure and in part upon the behavior of the molecules whose structure is responsible for that of the soap solutions. In the present work the principal attention has been focused upon the soaps themselves, that is, upon the alkali salts of the *n*-long paraffin chain (fatty) acids.

On account of the extreme insolubility of long paraffin chains in water, it is to be expected that the alkali salts of the high fatty acids should not exhibit a large molecular solubility, although the presence of the highly polar —COO^-A^+ groups should increase the solubility greatly above that of the acids, which are much more soluble than the paraffins of equal chain length. However, it is found that at room temperature potassium laurate (12 carbon atoms) gives a clear solution at concentrations somewhat above 35%, and potassium myristate (14 carbon atoms) above 26%. These extremely high values may be taken to indicate that solid soap may reduce its free energy by going into solution in some other form than that of single molecules. It is found that in general most of the soap dissolved is present as

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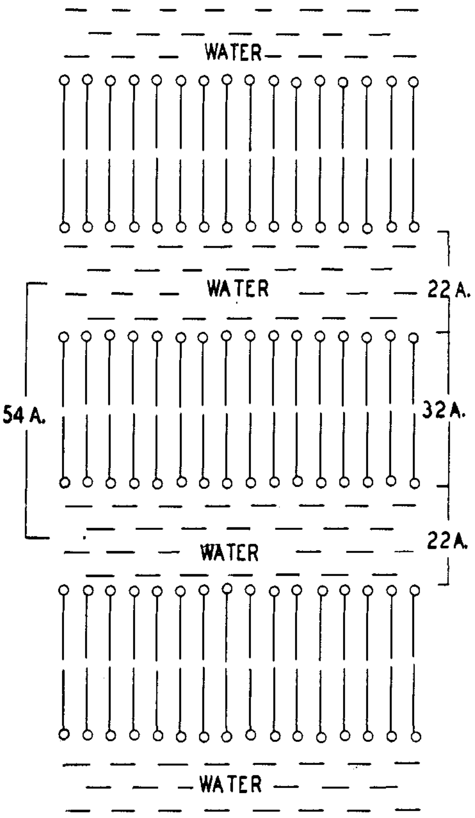
[1] The work reported in this paper was done in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

aggregates, each of which contains a large number of molecules. McBain[2] designated these aggregates as micelles, and this term has been used by Hartley[3] and many others.[4] However, these two investigators have not been in full agreement as to the structure of the aggregates. Hartley believed that all soap micelles are spherical, while McBain advanced the idea much earlier that they exhibit several different forms, the smallest, spherical, and the largest, flat plates. The latter considers that the spherical micelles are highly ionic and the plate-like only slightly ionic.

At the time when the present work was begun, a theory of the general type of structure of soap micelles had already been developed by a number of workers.[5–13] While their general picture of the structure of these micelles seems to be correct, since it is in accord with what has been learned of the structure of soap films, as interpreted by the orientation theory, the X-ray spacings found by them did not lead to any general relationships, since their experimental values of the spacings exhibited numerous discrepancies.

It was shown earlier by Fischer and Harkins[14] that the adsorbed film between a hydrocarbon oil and a sodium oleate solution at 0.1 *M* concentration is *monomolecular,* with the $\text{—COO}^-\text{Na}^+$ group oriented toward the water, and the hydrocarbon or oil group toward the oil. At 0.1 *M*, the area occupied in the film was about 30 sq. Å. per sodium oleate molecule. The area occupied by soap molecules which do not contain a double bond is smaller.

Soap molecules are highly adsorbed at the surface of an aqueous solution of a soap, or at the interface between the solution and a hydrocarbon oil. The adsorption takes place because it is accompanied by a decrease in free energy of the system. This decrease would also occur if we could have initially a soap solution of not too small a concentration without micelles. The molecules would then begin to "associate" themselves into double layers, with the polar groups toward the water and the oil groups toward each other. In these layers sodium oleate molecules also occupy an area of about 27 sq. Å., as shown by X-rays, but this value was obtained in a solution of a much more concentrated soap than 0.1 *M*. Except in dilute soap solutions, the *lateral* spacing of the molecule in adsorbed films or micelles is determined largely by the dimensions of the molecules. The general structure which our work indicates for the cross section of a micelle of potassium laurate in its 15.0% solution (0.74 mole to 1000 g. of water with a mole ratio of 0.0133 for soap/water) is pictured schematically in Fig. 1.



Cross section of soap micelles in 15% potassium laurate.

Fig. 1.—Highly idealized representation of the structure of a part of a soap micelle in a 15% potassium laurate solution. Each double layer of soap has in the direction of the short spacing, parallel to the layer, the structure of a liquid and not the regular structure shown for convenience.

The *only* parts of this structure which result from the X-ray measurements, the details of which are given later, is the distance of 54.0 Å., designated as the long, or layer spacing and the distance 4.4 Å. for the Bragg short spacing. Since the double length of the potassium laurate molecule is calculated to be 32 Å., the excess over this to give the total 54.0 Å. is assumed to be due to the presence in the "sandwich" of a layer of water 22.0 Å. in thickness.

While the general structure of a micelle, as represented here, does not differ from that favored by Hess and others (refs. 5–9), they obtained no general relation between layer thickness and the

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(2) J. W. McBain, *Trans. Faraday Soc.*, **9**, 99 (1913).

(3) G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie, Paris, 1936.

(4) A. Reychler, *Kolloid Z.*, **12**, 277 (1913).

(5) R. Krishnamurti, *Indian J. Phys.*, **3**, 307 (1929).

(6) (a) K. Hess and J. Gunderman, *Ber.*, **70**, 1800 (1937); (b) W. Philippoff and K. Hess, *ibid.*, **70**, 1808 (1937).

(7) K. Hess, H. Kiessig and W. Philippoff, *Naturwissenschaften*, **26**, 184 (1938).

(8) K. Hess, W. Philippoff and H. Kiessig, *Kolloid Z.*, **88**, 40 (1939).

(9) (a) J. Stauff, *ibid.*, **89**, 224 (1939); (b) J. Stauff, *Naturwissenschaften*, **27**, 213 (1939).

(10) (a) H. Kiessig and W. Philippoff, *ibid.*, **27**, 593 (1939); (b) H. Kiessig, *Kolloid Z.*, **96**, 252 (1941).

(11) W. Philippoff, *ibid.*, **96**, 255 (1941).

(12) H. Kiessig, *ibid.*, **98**, 213 (1942).

(13) K. Hess, *Fette u. Seifen*, **49**, 81 (1942).

(14) E. K. Fischer and W. D. Harkins, *J. Phys. Chem.*, **36**, 98 1932).

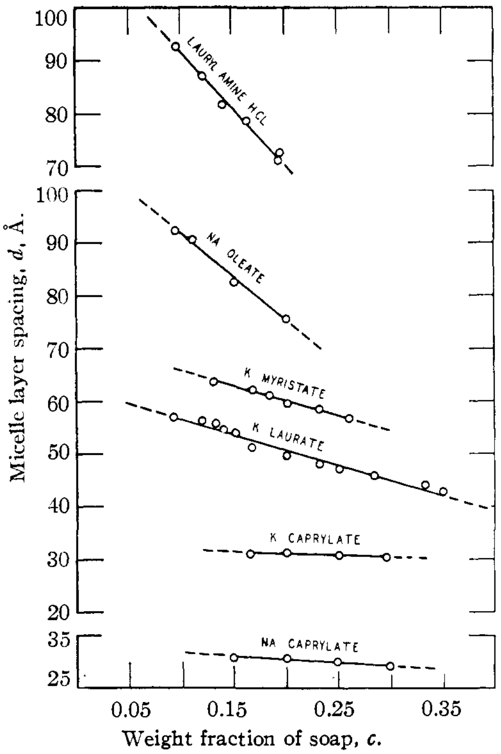


Fig. 2a.—Micelle layer spacing of soaps in Å. *vs.* $\log_{10}$ of the weight fraction of soap.

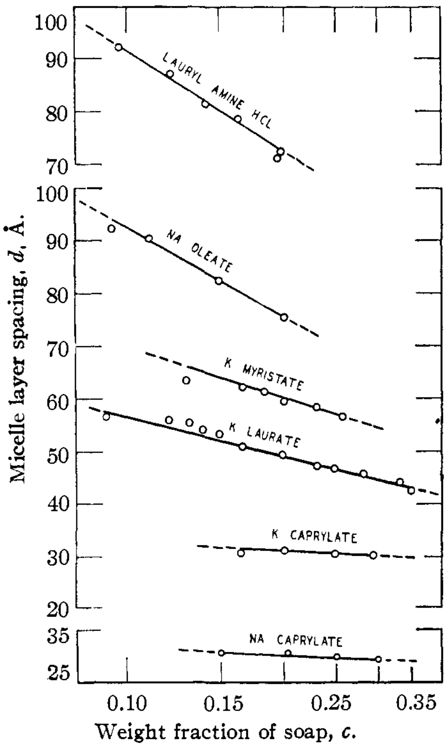


Fig. 2b.—Micelle layer spacing as a linear function of the weight fraction.

amounts of soap and water present. However, there is excellent agreement between some of their results[8] and those presented here.

The X-ray photographs of the soap solutions were taken in a cell 1 mm. thick, provided with windows 0.1 mm. in thickness, while in a vacuum camera. The film distance was 15 cm. but 36.5 can be used (see Section VII).

II. Change in the Total and Water Spacings of Soap Micelles as a Function of Concentration.—An important discovery which resulted from the determination of the long, or layer, X-ray spacings (d) of soap micelles is that the spacing increases with decreasing concentration (Table I and Figs. 2a and 2b), according to a definite law which for the soaps of the n-long paraffin chain molecules may be expressed in terms of the length (l) of the molecule

$$d = 2l + k \log (l/c) \tag{1}$$

in which k is a constant and c is the weight of soap per gram of solution, or $S/(S + W)$, in which S

Table IA

Long or Layer (d_l) and Short (Bragg) (d_s) X-Ray Spacings of Micelles in Soap Solutions at Room Temperature

c = soap/(soap + water) by wt.; *none* indicates no lines on film.

$c \times 100$ $\pm 0.1\%$	d_l ± 1.0, Å.	d_s ± 0.1, Å.
NaC$_8$, Sodium Caprylate		
15.0	30.8	None[a]
20.1	30.7	
25.0	30.0	
30.0	29.2	4.5
~43[b]		
~49[c]		
KC$_8$, Potassium Caprylate		
16.5	31.0	None[d]
20.0	31.2	
25.0	30.8	
29.6	30.4	None[a]
~45[e]		
~47[f]		
KC$_{12}$, Potassium Laurate		
4.8	None[g]	None[h]
9.1	57.0	4.6
12.1	56.3	
13.2	55.6	
13.9	54.5	
15.0	54.0 ± 0.6[i]	4.7
16.6	51.9	
16.7	50.6	4.5
19.9	49.6	
23.1	48.0	4.6
25.00	47.1 ± 0.5[j]	4.6
28.2	46.2	
28.6	45.8	4.5
33.3	44.1	4.6
35.0	42.9	4.5
41.1[c]	37.1	4.4
KC$_{14}$, Potassium Myristate		
9.1		None[k]
13.0	63.8	4.6
16.7	62.4	
18.3	61.2	4.5
20.0	59.6	
23.1	58.5	
25.9	56.7	4.5
33.3[c]		4.4
KC$_{16}$, Potassium Palmitate		
4.8		4.1
9.1		4.1
16.7[m]		4.1
20.0[m]		4.1
NaC$_{18}^{=}$, Sodium Oleate		
9.1		4.6
9.3	92.3	4.5
9.4	92.3	
11.0	90.5	
13.0		4.6
15.0	82.5	4.5
16.7		4.5
20.0[n]	75.6	4.6
C$_{12}$, Laurylamine Hydrochloride		
9.7	92.8	None[d]
12.2	87.4	4.6
14.1	81.8	4.5
16.4	78.8	4.5
19.4	71.3	4.4
19.6[b]	72.7	4.5

[a] Six hours on medium speed film. [b] Clear viscous liquid. [c] Clear gel. [d] Three hours on medium speed film. [e] Viscous liquid. [f] Slightly cloudy gel. [g] Ten hours on fast film. [h] Ten hours on medium speed film. [i] Average of 10 separate solutions. [j] Average of 5 separate solutions. [k] Twenty-five hours on fast film. [m] White gel. [n] Clear pale yellow viscous liquid.

and W are the weights of soap and water, respectively. When expressed in this form, the last term gives an apparent thickness of the water layer, which is thus indicated as a logarithmic function of the soap concentration.

However, the constants given in Table IB below for the different soaps are those calculated directly from the experimental values of Table IA, or

$$d = k_1 + k_2 \log (l/c) \qquad (2)$$

TABLE II

VALUES OF THE CONSTANTS IN THE EQUATIONS FOR THE LAYER SPACINGS OF SOAP MICELLES AT 25°

$$d_l = k_1 + k_2 \log_{10} (l/c)$$

a. Constants in the Logarithmic Equation

Carbon atoms	Soap	k_1[b]	k_2
8	Potassium caprylate[a]	27.9	4.7
8	Sodium caprylate	24.7	8.6
12	Potassium laurate	32.4	24.3
14	Potassium myristate	38.8	30.4
18	Sodium oleate	37.0	55.3
12	Laurylamine hydrochloride	27.2	64.8

[a] The values for the caprylates are the least accurate. [b] k_1, which for the n-long chain paraffin soaps is not very different from 2 l, and also k_2 increase with the length of the molecules (with chain length).

The X-ray measurements of the layer spacings have not been made below 9% nor above 35.0% (except for one soap 55%) soap although short spacings have been measured at 4.5%. Thus, the range of concentrations is sufficiently small to make it possible to represent the layer spacings in another way, that is, as a linear function of the weight fraction of soap (c) or

$$d_l = b - ac \qquad (3)$$

The layer for spacing hexanolamine oleate solutions follows the logarithmic relation between 15 and 55%, but exhibits a wide departure from the linear relation. However, it is not certain that no phase changes occur in this interval. The solution which contains 55% of this soap was provided through the kindness of Professor J. W. McBain.

b. Constants in the Linear Equation

Carbon atoms	Soap	b	a
8	Sodium caprylate	32.5	10.2
8	Potassium caprylate	32.4	6.9
12	Potassium laurate	62.2	58.0
14	Potassium myristate	71.5	56.7
18	Sodium oleate	107.7	162.0
12	Laurylamine hydrochloride	113.0	211.4

The constants of the equations (Table II) have been determined from a very large number of measurements of the long micelle layer spacings. Each experimental point in Figs. 2a and 2b represents the average of several measurements, often as many as 5 to 10, obtained by the use of different samples of soaps prepared from purified acids.

The layer spacings for n-long paraffin chain soaps are given for soaps with 8, 12 and 14 carbon atoms in the chain. The constant, k_1, is nearly twice the length of the soap molecule and thus increases, as is obvious, very nearly as the length

TABLE IIIa

LONG OR LAYER SPACINGS OF SOAP MICELLES AT VARIOUS CONCENTRATIONS AS INTERPOLATED FROM THE EQUATION $d = k_1 + k_2$ LOG $(1/c)$ (WITH EXTRAPOLATED VALUES AT 5 AND 3% IN PARENTHESES)

	Number of carbon atoms					
	8	8	12	14	18	12
% Concn. (c × 100)	Sodium caprylate	Potassium caprylate	Potassium laurate	Potassium myristate	Sodium oleate	Lauryl amine hydrochloride
Micelle Layer Spacing in Å.						
35	28.6	30.0	43.5	(52.7)	62.2	56.7
30	29.2	30.4	45.1	54.7	65.9	61.1
25	29.9	30.7	47.0	57.1	70.3	66.2
20	30.7	31.2	49.4	60.0	75.6	72.5
15	31.8	31.8	52.4	63.8	82.6	80.6
10	33.3	32.6	56.7	69.2	92.3	92.0
5	[a]	[a]	(64.0)	(78.4)	(108.9)	(111.5)
3	[a]	[a]	(69.4)	(85.1)	(121.2)	(125.9)
2 × Length of Molecule in Å.						
	22.1	22.1[b]	32.4	37.5		
Apparent Water Layer Thickness in Å.						
35	6.5	7.9	11.1	15.2		
30	7.1	8.3	12.7	17.2		
25	7.8	8.6	14.6	19.6		
20	8.6	9.1	17.0	22.5		
15	9.7	9.7	20.0	26.3		
10	11.2	10.5	24.3	31.7		
5	[a]	[a]	(31.6)	(40.9)		
3	[a]	[a]	(37.0)	(47.6)		

[a] Below the micelle critical concentration. [b] Supposedly very slightly longer than for sodium soap, but difference unknown.

TABLE IIIb

DATA OF HESS, KIESSIG AND PHILIPPOFF[8]

	Number of carbon atoms							
% Concn. (c × 100)	5-Sodium valerate	6-Sodium capronate	7-Sodium heptylate	8-Sodium caprylate	9-Sodium nonylate	10-Sodium caprinate	12-Potas. laurate	18-Sodium oleate
Micelle Layer Spacing in Å.								
29.5	17.6							
33.5		22.4						
29.4			24.6					
28.5				30.0 (29.4[a])				
26.5					31.6			
27.4						37.7		
33.4							43.5 (44.0[a])	
16.85								80
2 × Length of Molecule in Å.								
	14.7	17.1	19.6	22.1	24.7	27.2	32.2	
Water Layer Thickness in Å.								
29.5	2.9							
33.5		5.3						
29.4			5.0					
28.5				7.9 (7.3[a])				
26.5					6.9			
27.4						10.5		
33.4							11.3 (11.8[a])	

[a] Our own data given for comparison.

of the soap molecule, while k_2, the slope of the straight line, also increases rapidly. Sodium oleate ($k_2 = 55.3$) and laurylamine hydrochloride ($k = 64.8$) exhibit the largest slopes.

The constants for the linear equations were determined in the same way, but they do not exhibit any obvious relation to the sizes of the soap molecules. The logarithmic equations seem to be more adapted to treatment of the data thus far obtained.

The micelle layer spacings and the apparent water layer thicknesses are given in Table IIIa, in which extrapolated values are given in parentheses. Table IIIb gives data for other soaps with hydrocarbon chains as short as 5 carbon atoms. The values for the thickness of the water layer do not agree with those of Hess, Kiessig and Philippoff, since $d_w = d_1 - 2\,l$, while they use d minus the spacing in the solid.

Bound and Free Water.—Normally the long spacing in soap solutions is considered a function of the soap concentration, *i. e.*, the relation between the weight of soap and the total weight of soap plus water. It has, however, been demonstrated that in soap solutions exhibiting the ability to diffract X-rays a water layer occurs between double layers of soap molecules. In a sense the water contained in this layer is an integral part of the soap micelle rather than a solvent. The true soap concentration is then given by the weight of soap and the weight of free water which is equal to the total weight of water minus that bound in the micelles.

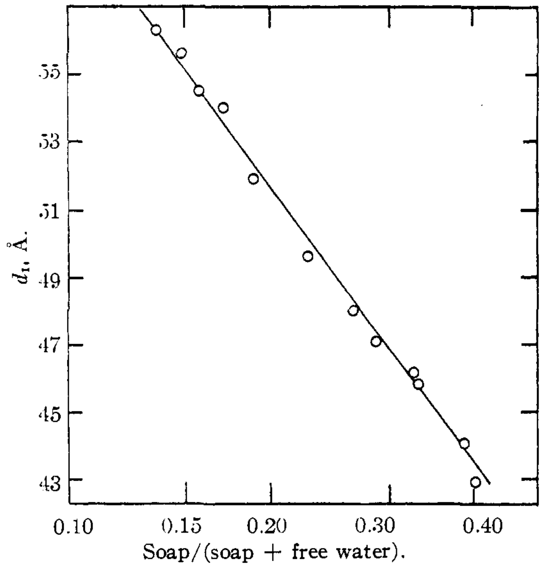


Fig. 3.—Apparent long X-ray spacings for potassium laurate as a function of the concentration of the soap in "free water."

The weight or, more exactly, the volume of bound water may be calculated from the weight of soap per unit weight of solution, from the thickness of the water layer which is considered as the difference between the long spacing and the double length of the soap molecules, and from the cross-sectional area of the soap molecule. The general expression for bound water in unit mass of solution is given by

$$\text{HOH (bound)} = \frac{c}{2M} N\sigma d_{\text{HOH}}$$

where c is the weight of soap per unit weight of solution, M the molecular weight of soap, N Avogadro's number, σ the cross-sectional area of the soap molecule and d the thickness of the water layer. The free water may then be calculated by difference, and the concentration of soap in this free water then determined. Table IV gives the results of such a treatment for potassium laurate solutions.

Table IV

Long X-Ray Spacings for Potassium Laurate as Related to Free Water

Soap / Soap + total HOH	d_1	d_{HOH}	HOH (bound)	Soap / Soap + free HOH
0.121	56.3	24.3	0.104	0.135
.132	55.6	23.6	.103	.147
.139	54.5	22.5	.111	.156
.150	54.0	22.0	.117	.170
.166	51.9	19.9	.117	.188
.199	49.6	17.6	.124	.227
.231	48.0	16.0	.131	.266
.250	47.1	15.1	.134	.289
.282	46.2	14.2	.142	.329
.286	45.8	13.8	.140	.333
.333	44.1	12.1	.143	.389
.350	42.9	10.9	.135	.405

The X-ray spacing is a logarithmic function of the corrected soap concentration as shown in Fig. 3. No corresponding direct linear relation is possible within the limits of experimental error.

Both the logarithmic and linear relations between the synthetic soap concentration and the long spacing lead to the conclusion that the amount (weight or volume) of bound water passes through a maximum. In the linear expression

$$\text{HOH (bound)} = \frac{c}{2M} N\sigma(k_1 - k_2c - 2l)$$

where l is the length of the soap molecule. For potassium laurate, assuming a linear relationship, this reduces to

$$\begin{aligned}\text{HOH (bound)} &= K(62.2 - 58.0c - 32.0)c\\ &= K(30.2c - 58.0c^2)\end{aligned}$$

and for a maximum in bound water

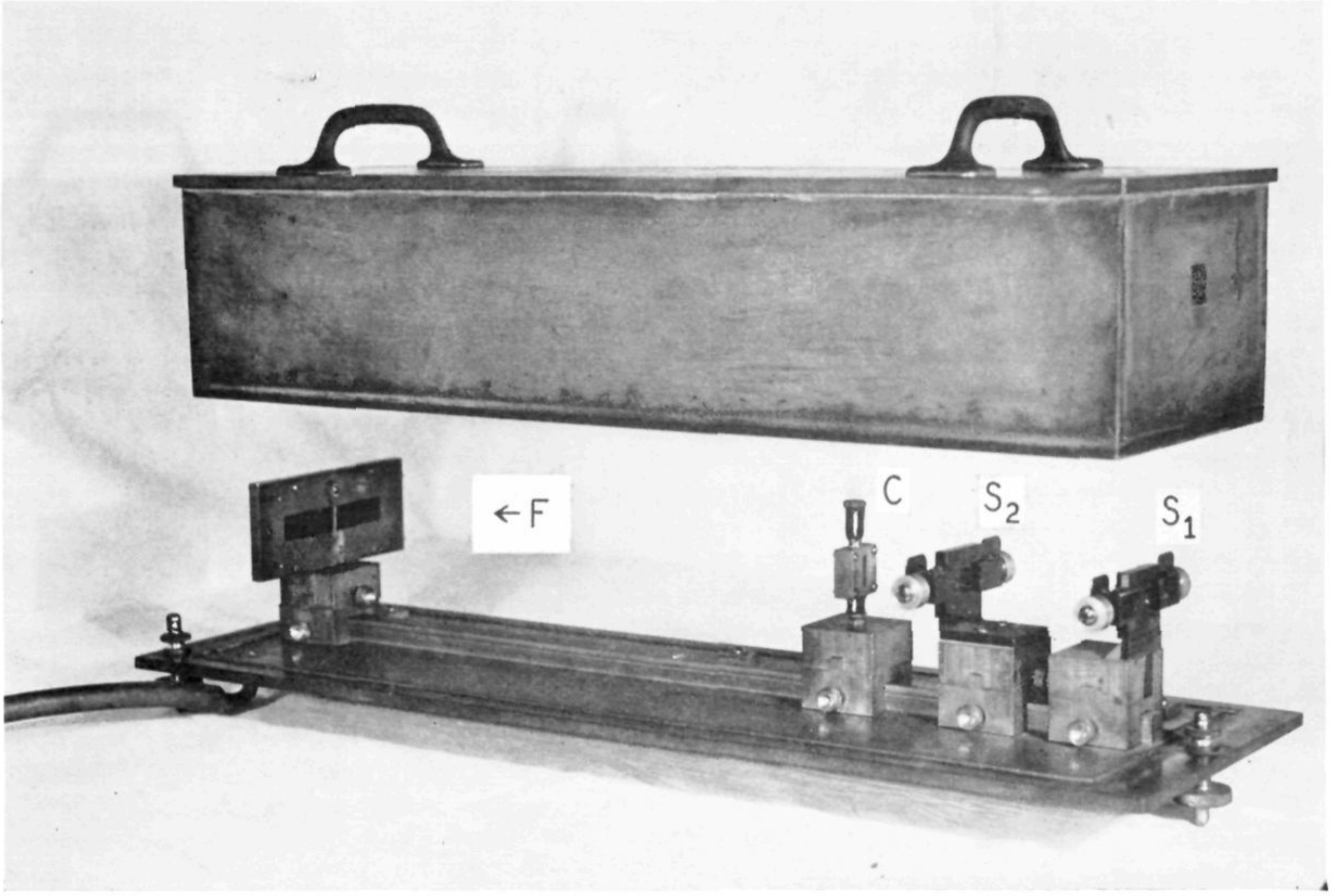
$$\begin{aligned}-116.0c + 30.2 &= 0\\ c &= 0.260\end{aligned}$$

Assuming a logarithmic relation

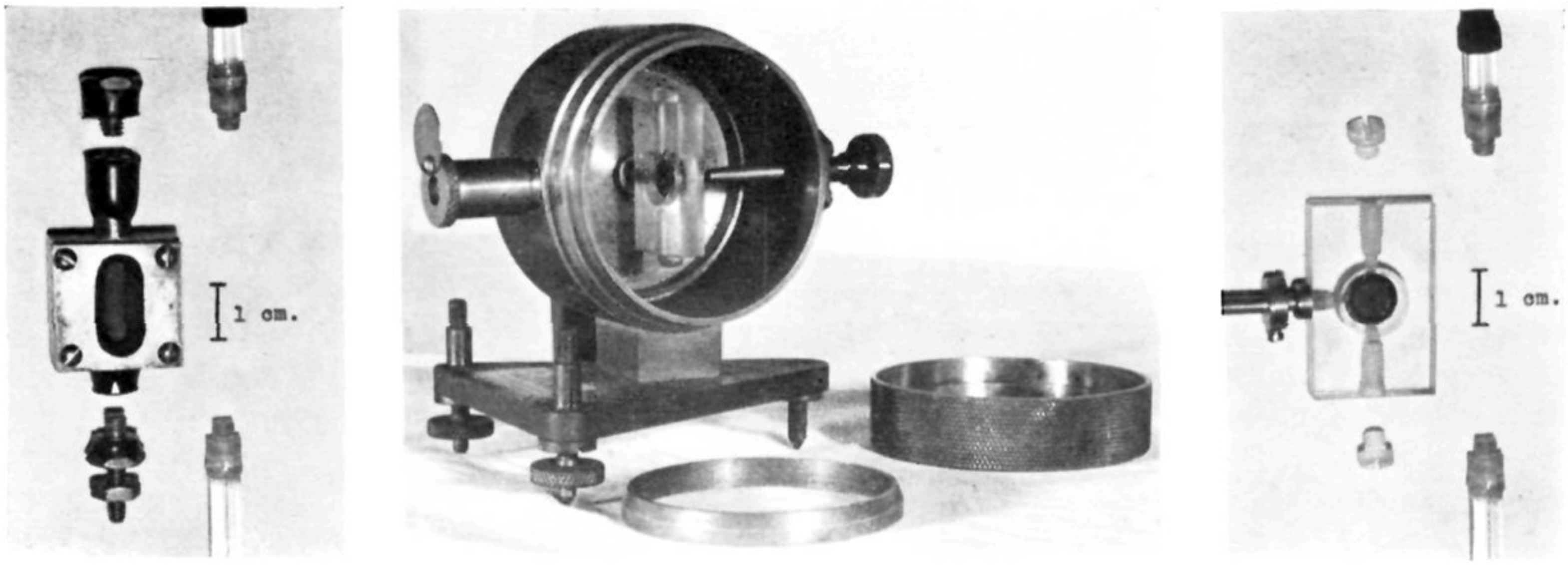
$$\begin{aligned}\text{HOH (bound)} &= K(32.4 - 24.3 \log c - 32.0)c\\ &= k_3c \log c = k_4c \ln c\end{aligned}$$

and for a maximum

$$\begin{aligned}\ln c + 1 &= 0\\ c &= 0.368\end{aligned}$$

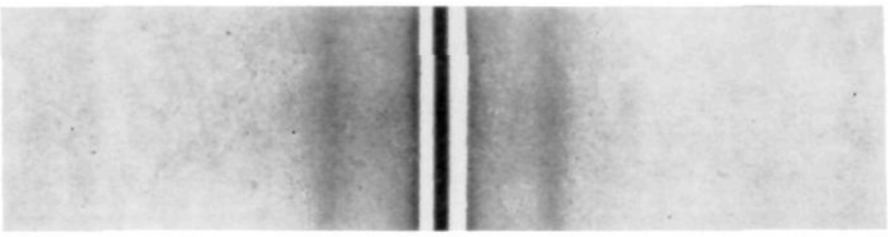


Long spacing vacuum camera.

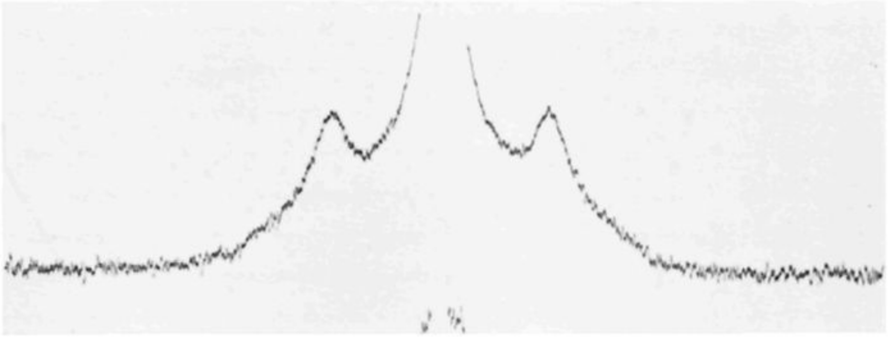


Long spacing cell. Short spacing camera. Short spacing cell.

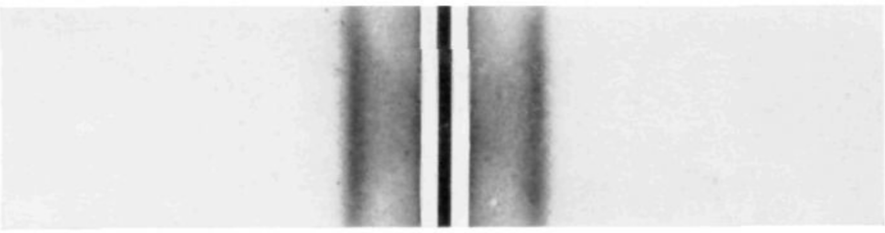
Fig. 6.—(Top) Vacuum camera for long or layer spacing. S_2 and S_1, first and second slits (see window in vacuum box above S_1; this is covered with a beryllium sheet 0.1 mm. thick); C, cell; F, X-ray film. (Middle) Short spacing camera with cell. (Lower left) Long spacing cell 1 mm. thick of brass or plastic, with beryllium windows 0.1 mm. thick. Plugs below and above keep cell vacuum tight. In new design cell has cylindrical reservoirs on right and left. Tubes on right used for filling cell. (Lower right) Cell for short spacing.



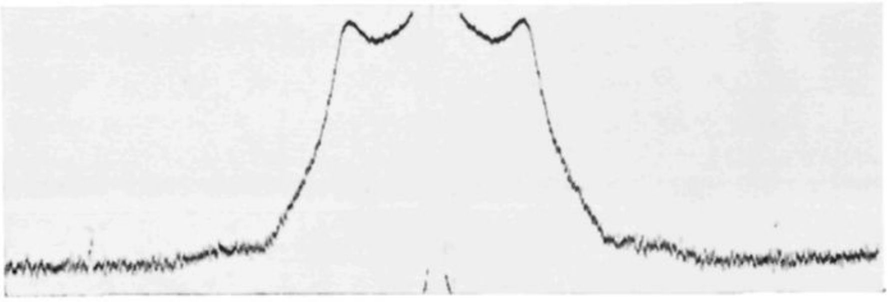
Film 509; 25.00% KC_{12}, $d = 47.1 \pm 0.5$ Å.



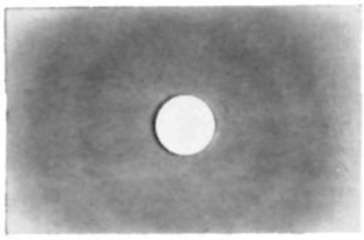
Film 509.



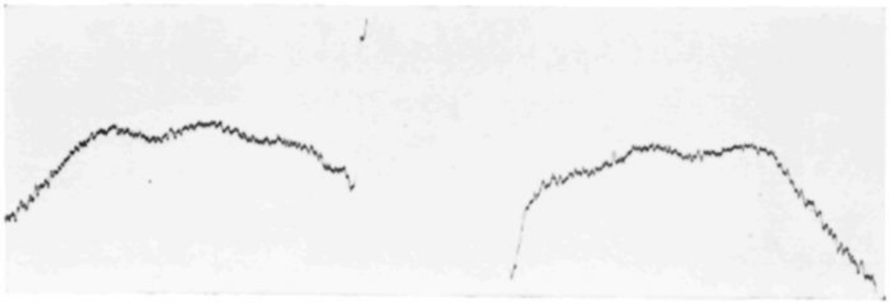
Film 521; 3.56 g. of *n*-heptane in 100 g. of 25.00% KC_{12}; $d = 60.8 \pm 0.8$ Å.



Film 521.



Film 520; 25.00% KC_{12}, $d = 4.5 \pm 0.1$ Å.; $\sigma = 26.4 \pm 1$ sq. Å.[2]



Film 520.

Fig. 7.—Films, beginning at the top: (1) Lines left and right give long or layer spacing of soap micelles in a 25.0% potassium laurate solution. Long spacing = 47.1 ± 0.5 Å. as obtained from 2. From the diffuseness of the lines the thickness of the micelles, presumably 4 or slightly more double lines thick, could be calculated. This calculation is made inaccurate by the fact that even in the direction of the long spacing the micelle is not a true crystal. (2) Photometer tracing of above. (3) Same as 1, except contains 3.56 g. of *n*-heptane per 100 g. of soap solution. Long spacing = 60.8 ± 0.8 Å. as obtained from 4. X-Ray lines are made sharper and more intense by presence of oil. (4) Photometer tracing of 3. (5) Outer X-ray ring gives water spacing and inner ring short Bragg spacing of soap molecules. Short spacing = 4.5 ± 0.1 Å. Molecular area for close packing = 26.4 ± 1 sq. Å. Diffuseness of X-ray lines indicates that the water and also the soap in the direction of the short spacing are in the liquid state.

From the experimental results the bound water does not pass through a maximum at a soap concentration of 0.260. A concentration of 0.368 was not attained in the experiments, but the variation in bound water between concentrations of 0.282 and 0.350 is quite small, which suggests that the rate of change of bound water with respect to soap concentration is approaching zero. From this point of view the logarithmic relationship seems more satisfactory than the linear.

The spacings for potassium laurate as calculated on the basis of the free water are given in Fig. 3 (Table IV). The relation in this figure is far from linear if the axes are: x = wt. of soap/(wt. of free water + soap), y = long spacing; and is only made linear on the basis of the logarithmic plot. On this basis and because k_1 is nearly twice the length of the molecule if an n-long paraffin chain soap is involved, the semi-logarithmic plot (Fig. 2a) is favored over the linear plot (Fig. 2b).

III. Area per Molecule (σ) and Short Spacing (d_s) in Soap Layers.—The double layers of soap molecules are arranged with their hydrocarbon ends oriented toward each other, thus constituting a hydrocarbon layer. The layers of soap molecules exhibit a liquid type of structure as indicated by the diffuseness of the ring which represents them.

The X-ray values are obtained at such high concentrations that the packing of the soap molecules varies only very slightly within the experimental range. Where the short range order (there is no long range order) is perfect (actually there is the disorder of a liquid), the pattern may be represented as close-packed hexagonal: *i. e.*, a single molecular chain surrounded by six others. Within the limits of this short range order, soap molecules with from 8 to 14 carbon atoms in the chain exhibit a molecular area of 26 sq. Å., while a tightly packed monolayer of stearic acid on water occupies a *mean* area of 20 sq. Å. The 26 sq. Å. given above is smaller than the mean area, since it is correct only where there is close packing.

The short spacing of the micelles is obtained, as indicated below, by the diameter of the inner of two X-ray diffraction rings. It is this diameter which remains practically unchanged, but the intensity decreases as the chain becomes shorter or the solution becomes more dilute.

The inner of the two rings occurs at the same position for different soap solutions and corresponds to a Bragg spacing (d_s) of about 4.4 Å. Since the position of this ring appears to be independent of the length of the molecules, it seems to be associated with the lateral separation of the molecular chains. This conclusion seems justifiable, but it is not correct (as has been done by some investigators) to identify the observed value of the Bragg spacing with the shortest distance between two molecular chains.

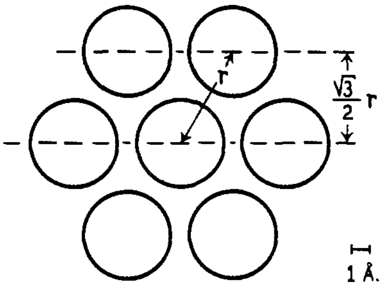


Fig. 4.—Short spacing: relationship of the chain-to-chain spacing, r, to the Bragg spacing, d_s, ($r = 1.23\ d_s$). Actually the chains are arranged irregularly, since the width of the X-ray lines indicates that in this plane the structure is that of a liquid.

The short spacing, d_s, is the spacing in Ångström units calculated by Bragg's equation directly from the diffraction ring. The chain-to-chain spacing, r, is the spacing in Ångström units from one chain to the next nearest chain. The arrangement of chains in a single layer is that of a liquid system, but for the calculation of the chain-to-chain distance may be assumed as hexagonal (Fig. 4). The first maximum of the function $\frac{\sin x}{x}$ occurs for $x = 7.725$ radians. The relation of r and d_s is

$$r = \frac{7.725 d_s}{2\pi} \text{ or } r = 1.23 d_s \text{ (= commonly 5.6 Å.)}$$

The area per molecular chain, σ, in square Ångström units, is calculated from

$$\sigma = \frac{\sqrt{3} r^2}{2} \text{ or } \sigma = 1.31\ d_s^2$$

IV. Decrease of Free and Total Energy in the Change from Molecular to Micellar Soap.—Single soap molecules in aqueous solution exhibit two types of molecular interfaces with the water: (1) a polar–polar interface between the polar part of the soap ion or molecule and the water, and (2) a non-polar–polar interface between the hydrocarbon chain and the water. The latter is the locus of a moderately large interfacial energy per unit area. On account of this, the hydrocarbon chains, except for the effect of thermal flagellation, fold back on themselves to give as little area as possible. When thus folded, the hydrocarbon chain of potassium palmitate may be assumed to exhibit an interfacial area of the order of 350 sq. Å. = 350×10^{-16} sq. cm. or 2×10^{10} sq. cm. per mole.

At 25° the interfacial free energy is 54.5 erg cm.$^{-2}$ and the total energy about 77 erg cm.$^{-2}$. In the micelles the hydrocarbon chains are adjacent to each other, so any interfacial energy with water should disappear.

If the principle of independent surface action is applied, the following relations are obtained: a decrease of 1.1×10^{12} erg mole^{-1} or 26,280 cal. mole^{-1} in the free energy and 1.5×10^{12} erg mole^{-1} or 35,800 cal. mole ($= E$) in the total energy would occur in a change of the paraffin chains from single molecules to micelles. According to the Boltzmann equation

$$P = Ae^{E/RT}$$

where A is a constant involving the *a priori* probabilities of the two states. This would give an enormous probability in favor of micelles of a palmitate soap rather than single molecules, unless A is excessively small.

Undoubtedly, it is this decrease in energy which causes the aggregation of micelles.

There are other factors which reduce the probability, such as the work done in overcoming repulsion between the ions. This factor is reduced by the effect of the gegenions. Also, according to Williams[15] the dielectric constant is smaller in the neighborhood of charged ions, and this factor causes an increase in electrical energy.

With unit value of A, the probability that a molecule of a palmitate soap would be in the micelle rather than a single molecule in water would be 2×10^{26}, if the probability depended upon the hydrocarbon chains alone. Obviously, this is very greatly reduced by the ionic and other electrical and dipole effects of the $—COO^-A^+$ part of the soap. However, it is the lowering of energy in the removal of the hydrocarbon chains from contact with the water that causes the micelles to form.

V. Mixtures of Pure Soaps (Potassium Laurate and Potassium Myristate).—The X-ray diffraction photograph of an aqueous solution which contains a mixture of potassium laurate and potassium myristate does not show two distinct maxima characteristic of each pure soap, but rather only one maximum intermediate between them. In this work the total number of soap molecules per gram of mixed solution was kept constant by mixing the equimolal solutions, 16.7% potassium laurate and 18.3% potassium myristate in the proportions 3:1, 2:2 and 1:3. The layer spacings and chain spacings are shown in Table V. Figure 5 shows a linear relationship between the layer spacing and the ratio of the two kinds of soap molecules with the total number of soap molecules per gram of mixed solution kept constant. In each micelle there seem to be present both kinds of soap molecules in the given ratio.

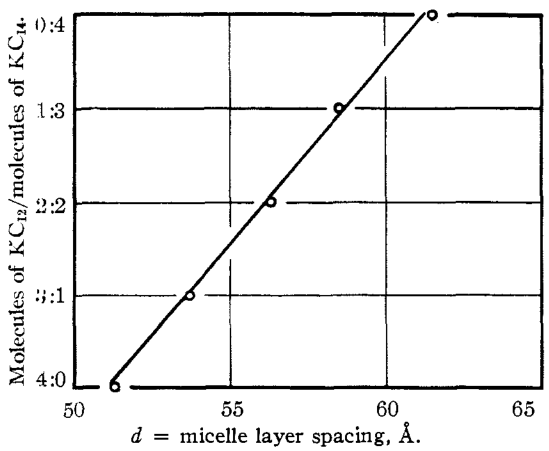


Fig. 5.—Linear variation of the layer spacing in a binary mixture as a function of the relative number of molecules.

TABLE V

MIXTURES OF POTASSIUM LAURATE AND POTASSIUM MYRISTATE

KC_{12}:KC_{14}[a]	Layer spacing ±1 Å.	Short spacing ±0.1 Å.	Chain-chain spacing ±0.1 Å.	Molecular chain area ±1 sq. Å.
[b]4:0	51.3	4.6	5.7	28
3:1	53.7			
2:2	56.3	4.5	5.5	26
1:3	58.5			
[c]0:4	61.5	4.5	5.5	26

[a] Ratio of number of KC_{12} molecules to KC_{14} molecules. The total number of soap molecules per gram of mixed solution was kept constant. [b] 16.7% KC_{12} solution. [c] 18.3% KC_{14} solution.

VI. Effect of Salts on the Micelle Layer Spacings.—The addition of potassium or sodium chloride to a soap solution has been found to produce marked effects upon the long micelle spacing and the intensity of the X-ray pattern. These effects are represented in Table VIa and b and summarized in Tables VIc. The amount of salt added is expressed as moles of salt per 1000 g. of soap plus water. The effects are as follows:

1. The addition of either potassium or sodium chloride increases the long spacing and therefore, presumably, the water spacing, since the short spacing is not materially affected.
2. The addition of sodium chloride produces a slight cloudiness or a small amount of a white precipitate, while with potassium chloride this does not occur.
3. The addition of sodium chloride gives a stronger, and potassium chloride a weaker, diffraction intensity.
4. Sodium chloride added in larger amounts causes a gel to form.

Thus it seems probable that the potassium salt makes the micelles smaller while the sodium salt makes them larger.

VII. Apparatus and Experimental Procedure.—A full wave rectified potential of 31 kilovolts is applied to the copper target of a G. E. X-ray tube operated at 23 ma. tube current. The CuKα line (1.539 Å.) is filtered through an electroplated pure nickel filter 0.015 mm. thick.

The long spacing vacuum X-ray camera is shown in Fig. 6. The filtered X-ray beam passes through a window of pure beryllium 0.004″ thick cemented on the camera cover and then through two lead slits, S_1 and S_2, each 0.16 mm. wide and 9 cm. apart. The X-rays then pass through the cell, C, holding the soap solution and finally register on the photographic film, F. The adjustable slits, cell, and film holder are each mounted on brass blocks (Fig. 6) each of which can be moved laterally and longitudinally

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(15) J. W. Williams, *Chem. Rev.*, **8**, 303 (1931).

TABLE VI

EFFECT OF ADDITION OF SALTS TO AQUEOUS SOAP SOLUTIONS

a. Effect of Addition of Sodium Chloride or Potassium Chloride to Sodium or Potassium Caprylate Solutions (NaC$_8$ or KC$_8$).

Moles soap per kg. pure soap solution	% Soap	Moles salt per kg. pure soap solution	% Salt	Comments on solution	d_l Long spacing, Å.	d_s Short spacing, Å.
NaC$_8$						
0.903	15.0	0	0	Clear	30.8 ± 1.5[a]	None[b]
		0.428 NaCl	2.5	Cloudy	31.9 ± 1.5[a]	None[c]
		0.856 NaCl	5.0	Some white ppt.	33.0 ± 1.5	
		0.712 NaCl	10.0	Some white ppt.	35.6 ± 2.5	
1.806	30.0	0	0	Clear	29.2 ± 1.0	4.5
		4.28 NaCl	2.5	Some white ppt.		4.6
0.903	15.0	0	0	Clear	30.8 ± 1.5[a]	None[b]
		0.428 KCl	3.19	Clear	30.8 ± 1.5	
		0.856 KCl	6.38	Clear	33.0 ± 1.5	
		1.712 KCl	12.76	Clear	36.9 ± 3.0[d]	
KC$_8$						
0.903	16.46	0	0	Clear	31.0 ± 1.5	None[b]
		1.712 NaCl	10.0	Cloudy	35.6 ± 2.5	
		1.712 KCl	12.76	Clear	None[e]	

b. Effect of Addition of Potassium Chloride to Potassium Laurate Solutions (KC$_{12}$)

KC$_{12}$						
0.700	16.7	0	0		50.6 ± 1.0	4.5
		0.208 KCl	1.554		52.4 ± 3.0[d]	
		0.559 KCl	4.160	Clear liq.	57.7 ± 4.0[d]	
		0.832 KCl	6.216	Clear gel	None[f]	
0.969	23.1	0	0		48.0 ± 1.0	
		0.769 KCl	5.74		57.6 ± 1.0[d]	
1.200	28.6	0	0		45.8 ± 1.0	
		0.357 KCl	2.66		51.1 ± 1.5[d]	

c. Comparative Summary of Long Spacings and Estimated Relative Intensities

						Relative intensity
NaC$_8$						
0.903	(15.0)	0	(0)	Clear	30.8 ± 1.5	3
		1.712 NaCl	(10.0)	Some white ppt.	35.6 ± 2.5	5
		1.712 KCl	(12.76)	Clear	36.9 ± 3	1
KC$_8$						
0.903	(16.46)	0	(0)	Clear	31.0 ± 1.5	3
		1.712 NaCl	(10.0)	Cloudy	35.6 ± 2.5	2
		1.712 KCl	(12.76)	Clear	None[e]	0

[a] Weak, broad. [b] Three hours on medium speed film. [c] Six hours on medium speed film. [d] Weak. [e] Fifteen hours on fast film. [f] Eight hours on fast film. [g] *None* indicates no lines on film.

for adjustment. The maximum sample film distance is 36.5 cm., but 15.00 cm. has been used in the present work. Most parts of the camera are made of brass. The rectangular cover fits into a groove with a gum rubber gasket. A fore-pump is used for evacuation. The over-all dimensions are 57 cm. long, 17.7 cm. wide, and 12 cm. high.

The long spacing cell for holding the solutions is also shown in Fig. 6. The body consists essentially of a slotted web 1 mm. thick connected to a top and bottom reservoir through a hole 0.7 mm. in diameter. Pure beryllium windows 0.010″ mm. thick are cemented with glyptal on the front and rear of the web and are supported in place by a front and rear framework screwed on. The cell is filled through glass capillary tubes and sealed by two screw plugs, the junction being covered by melted beeswax and rosin (1:1) to ensure vacuum tightness. A small bubble of air above the solution allows thermal expansion and reduces leakage. The thickness of the solution which is X-rayed is 1.0 mm.

This cell may be constructed of brass for use with soap solutions, but, with electrolytes added, such as salts, electrolysis due to contact with the two metals, brass and beryllium, causes holes to develop through the beryllium. Consequently, the brass is entirely replaced by a non-conducting plastic such as methyl methacrylate. Plastic cells have the advantage of being transparent. Glass cells would be ideal.

Photographic film 8.8 × 2.5 cm. is used. Typical exposures for soap solutions, illustrated in Fig. 7, are five hours on Eastman fast Type K film or ten hours on medium-grain Blue Brand film. The final measurements are made from a photometer trace of the film.

The short spacing photographs are taken on a standard pinhole powder camera of 3 cm. radius (Fig. 6) fitted with a special plastic cell similar to the one just described. Typical exposures for soap solutions, illustrated in Fig. 7, are three hours on Eastman medium-grain Blue Brand film.

VIII. Purification of Materials.—The commercial lauric and myristic acids were crystallized once from alcohol and once from acetone and then hydrogenated in alcohol solution over platinum oxide at 50° and 3 to 4 atmospheres. Finally, they were distilled twice in a high vacuum, retaining only the middle third fraction each time. No special precautions were taken to exclude carbon dioxide from the potassium hydroxide solution, which was made by dissolving washed potassium hydroxide sticks in carbon dioxide-free distilled water.

The commercial oleic acid was frozen twice in an ice-salt mixture and the remaining liquid, amounting to about one-fourth of the total, was decanted off and retained each time. This was then distilled twice in a molecular still at 10^{-4} mm. and only the middle third fraction was retained each time. In color it was water clear, not pale yellow. The freshly distilled acid was neutralized with sodium hydroxide, with minimum exposure to air.

The caprylic acid was of only ordinary commercial purity. The laurylamine hydrochloride was a highly purified sample.

In all cases the solution of the base was added to the fresh fatty acid plus distilled water to make the soap solution of the required concentration. After neutralization the particular soap concentration was doubly checked by evaporation of water from two samples. The experimental error in concentration is ±0.1%. In nearly all cases the soap solutions were X-rayed within a few days after being made.

Summary

1. In not too dilute aqueous solutions of soap, X-ray diffraction photographs, when interpreted by the theory of molecular orientation in interfaces, indicate the existence of double layers of soap molecules with "water" layers between them (Fig. 1). In the double layers the hydrocarbon chains are oriented toward each other, with the polar groups toward the water. The micelles seem to be about 4, or somewhat more, double layers thick. With an ordinary soap the polar groups constitute a negatively charged layer, while the water layer contains diffuse layers of positive ions. Presumably, it is the interaction of these ions which gives a definite thickness to the water layer: repulsion between positive ions and attraction between positive and negative ions. This thickness is related to the amount of water in the soap solution.

2. The long or layer spacing (d) of soap micelles has been found to be expressed by either a logarithmic relation

$$d = 2l + k \log (1/c) \qquad (1)$$

or a linear relation

$$d = b - ac \qquad (3)$$

where k, b, and a are constants and c is the weight fraction of soap.

3. On the basis of the structure assumed, the amount of water in the micellar water layers has been calculated, and this is designated as bound water, while the remainder of the water is designated as free water. On the basis of the free water it has been found that the logarithmic equation (1) above is still valid but the linear equation (3) no longer holds.

4. The micelle layer spacings thus far found vary from 30 to 100 Å. In the plane of the layers of soap the Bragg short spacings is found to be very nearly constant at 4.5 Å. for any of the normal long paraffin chain soaps at all concentrations from 4.5 to 35%. The structure in this direction is that of a liquid, but in any group in which there is close packing this gives a chain-to-chain distance of 5.4 Å. and an area per molecule of 26.4 sq. Å. The liquid state of these layers is indicated by the diffuseness of the X-ray lines obtained for short spacing.

5. It is shown that there is an extremely large decrease of free energy when a hydrocarbon chain of a soap changes from the state in which it is entirely separated and surrounded by water to the state in which it is surrounded by other hydrocarbon chains. This may be considered as the cause of the aggregation of single soap molecules into the aggregates designated as micelles. The probability of this aggregation is reduced by the increase in electrical energy associated with the charges of the ions and other factors.

6. A 16.4% solution of potassium laurate exhibits a layer spacing of 51.3 Å., while an equimolar (18.3%) solution of potassium myristate gives a spacing of 61.5 Å. When the number of soap molecules in mixtures of these soap is kept constant, there is a linear variation of the layer spacing with the ratio of laurate to myristate in the mixture. It might seem that in such mixtures as, for example, a 1:1 molar mixture of the two soaps, the X-ray lines would be broadened to represent both spacings, *i. e.*, 51.3 and 61.5 Å. However, this is not the case, since the lines are not broadened, but simply occupy an intermediate position, which, for the 1:1 ratio, gives a spacing just half-way between the two extreme values.

7. The addition of salts such as potassium or sodium chloride to a soap solution produces marked effects both upon the layer micelle spacing and upon the intensity of the X-ray pattern. The addition of either salt increases the layer spacing, and therefore presumably, although not certainly, the water spacing. However, the short spacing is not materially affected. Sodium chloride makes the intensity of the line stronger and potassium chloride makes it weaker. It is probable that the potassium salt makes the micelles smaller while the sodium salt makes them larger.

8. The vacuum X-ray camera used in this work has a very simple design. The window (used to admit the X-rays) in the vacuum box or chamber, consists of a sheet of beryllium 0.1 mm. thick. The cell used for holding the solutions is very simple and effective. It is 1 mm. thick with a window of beryllium 0.1 mm. thick on each side.

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