

some absorption in the region 8125–6940 Å. which is consistent with condensation to a purple solid. We did many experiments at different pressures, both at very high temperatures (up to about 1250°) and at

low temperatures (down to about 120°) but did not succeed in obtaining evidence of any other form of sulfur except S₂ and the ordinary yellow form, S₈.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY AT BROWN UNIVERSITY]

An X-Ray Study of Potassium Laurate Solutions¹

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The small-angle X-ray scattering from concentrated solutions of potassium laurate has been reinvestigated with the use of monochromatic radiation. A correction for the effect of the slit height has been applied. The measured intensity has been used to calculate the radial distribution function for the potassium gegenions which sheathe the laurate micelles. Ambiguities in the interpretation have been reduced by theoretical arguments and by comparison of the distributions calculated on the basis of alternative assumptions. For 30% (by weight) solutions, the micelle centers form a loose close-packed arrangement; the arrangement becomes less ordered as the concentration is decreased. The effective micelle diameter is 27 Å. and the average micelle contains about 63 molecules. Detailed conclusions regarding the structure of the micelles cannot be obtained from the data reported.

Introduction

Numerous studies³ have attempted by means of X-ray diffraction to obtain information about the structure of the micellar aggregates which are believed to exist in soap solutions. Differences in the interpretation of the results have, however, persisted, and serious objections to most of the published work have recently been emphasized.⁴ First, several of the models proposed^{5,6} for micelles have been based on distances calculated from the positions of diffraction maxima under the assumption that Bragg's law remains meaningful for the scattering from non-periodic structures. Second, previous workers have assumed that the use of filtered characteristic X-radiation gives scattering patterns negligibly different from those which would be produced by strictly monochromatic radiation. It may be added, third, that when slits rather than pinholes were used to define the incident beam, it has been previously assumed that no correction was necessary.

The present investigation has aimed at avoiding these sources of uncertainty by use of a crystal monochromator, by correcting for the effect of slit height and by calculating a radial distribution function from the observed data.

Experimental

A Norelco Diffraction Unit, operated at 35 kv. and 20 ma. with a copper-target tube, was used for the production of X-rays. A nearly monochromatic beam was isolated by reflection from the (001) face of a pentaerythritol crystal. The small-angle vacuum camera was similar to that described by Kiessig⁷ except that the collimating system consisted of a pair of lead-jawed slits 10 cm. apart instead of a pair of pinholes. The distance from sample to film was 22.4 cm.; this was determined by photographing a sample of

powdered lauric acid, which has a known shortest spacing of 27.4 Å. The cell for solution samples was a small brass box with mica windows spaced 0.170 cm. apart. Solutions were introduced into the cell by means of a hypodermic syringe.

Solutions of potassium laurate were freshly prepared before each exposure by neutralizing weighed amounts of lauric acid with standard potassium hydroxide solution and then adjusting the amount of water to give the desired concentrations. Lauric acid was obtained from the Paragon Testing Laboratories. It was vacuum distilled and recrystallized from absolute ethanol. The purified material melted between 43.6 and 44.3°.

Four concentrations of potassium laurate were investigated: 29.6, 24.1, 19.7 and 15.1% by weight. The exposure times were 48, 70, 95 and 135 hours, respectively, so that investigations at lower concentrations become increasingly difficult. After each exposure a calibration photograph was prepared by making a set of timed exposures of the direct beam filtered through aluminum to obtain a convenient intensity. Corresponding diffraction and calibration photographs were developed simultaneously with Kodak D-11 developer.

Film densities were measured with a Sinclair Smith recording microphotometer, which, however, was operated manually to obtain maximum reproducibility. Figure 1 represents typical microphotometer tracings. For each concentration several photographs were prepared and microphotometered, and the resulting diffraction curves were averaged. The fluctuations in the individual microphotometer tracings can only be attributed to the grain of the film.

Since, for X-rays, exposure time is proportional to intensity,⁸ it was possible to convert these traces to a (relative) energy scale by use of the calibration films. The curves of Fig. 2 which are drawn through the experimental points present the relative diffraction intensities for each concentration as functions of diffraction angles. Since the pentaerythritol monochromator crystal deteriorated in the X-ray beam, the calibration prepared at the end of an exposure of a certain solution does not allow the intensities to be placed on an absolute scale. Thus the intensities from the various concentrations are only approximately comparable. The experimental intensity values, I_a , are related to the absolute intensity values, I_a' , by the equation $I_a' = cI_a + k$ where c and k are unknown constants, differing from one solution to the next.

Corrections for absorption in the sample and for polarization of the incident beam by the monochromator were nearly constant over the range of angles studied; hence these corrections were neglected.

The Slit Height Correction.—Small angle diffraction is often observed with a beam defined by slits, rather than by pinholes, in order to decrease the long exposure times.

(1) Based upon a thesis submitted by D. E. Andersen to Brown University in partial fulfillment of the requirements for the Ph.D. degree.

(2) du Pont Predoctoral Fellow, 1950–1951.

(3) W. Philippoff, *J. Colloid Sci.*, **5**, 169 (1950) (this review contains a comprehensive bibliography); G. W. Brady, *J. Chem. Phys.*, **19**, 1547 (1951).

(4) E. W. Hughes, *Nature*, **165**, 1017 (1950).

(5) W. Philippoff, *Kolloid-Z.*, **96**, 255 (1941).

(6) W. D. Harkins, *J. Chem. Phys.*, **16**, 156 (1948).

(7) H. Kiessig, *Kolloid-Z.*, **98**, 213 (1942).

(8) K. Lonsdale, "Crystals and X-Rays," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 35.

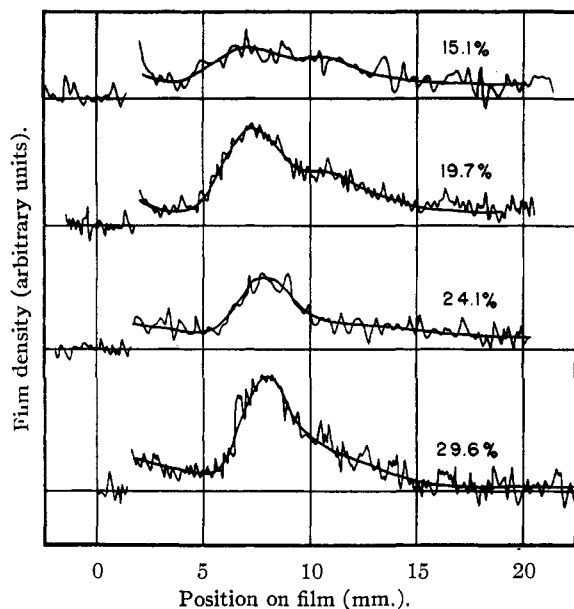


Fig. 1.—Microphotometer tracings of diffraction patterns for several concentrations of potassium laurate.

Consequently, the intensity recorded at any point on the photograph is a superposition of the true intensities scattered over a small angular range which is determined by the slit height. Methods of calculating the true intensity from the recorded intensity have been proposed⁹ for the case of an infinitely long slit. We have modified their treatment to adapt it to slits of finite height. Since the completion of this part of the work, another treatment¹⁰ of the same problem has come to our attention. Their result is of a similar form but somewhat different in detail.

If it is assumed that the beam is parallel and of uniform intensity, then the scattered intensity $I(x)$ received at a point x on the equator of the film is related to the true intensity $i(x)$ by the equation

$$I(x) = 2 \int_0^A i(\sqrt{x^2 + t^2}) dt \quad (1)$$

Here x is the distance, along the equator of the film, from the trace of the undiffracted incident beam, A is half the height of the beam (and the slit), and t is the distance, above the center, of a point in the beam.

This expression (1) may be inverted, by manipulations analogous to those suggested by Guinier and Fournet⁹ to give

$$i(x) = - (1/\pi) \int_0^A [I'(z)/z] du + \int_1^2 i(\sqrt{x^2 + A^2/\sin^2(\pi\alpha/4)}) d\alpha \quad (2)$$

where

$$z \equiv \sqrt{x^2 + u^2}$$

and $I'(z)$ is the slope of $I(z)$ and u and x are parameters of integration.

The result (2) was applied by the following procedure. $I'(x)$ was measured from graphs of I against x and $I'(x)/x$ was evaluated. Then for each of many closely-spaced values of x , $I'(z)/z$ was plotted against u and the first integral was evaluated by measuring the area under the curve with a planimeter. The second integral was calculated, beginning at the largest value of x , by approximating $i(x)$ by $I(x)$; this causes only a negligible error since $I(x)$ is practically constant at this point. The integral was then evaluated at successively smaller values of x ; the required range of $i(x)$ lies always at larger values of x , for which $i(x)$ has already been obtained.

(9) J. W. M. DuMond, *Phys. Rev.*, **72**, 83 (1947); A. Guinier and G. Fournet, *Nature*, **160**, 501 (1947).

(10) O. Kratky, G. Porod and L. Kahovec, *Z. Elektrochem.*, **55**, 53 (1951).

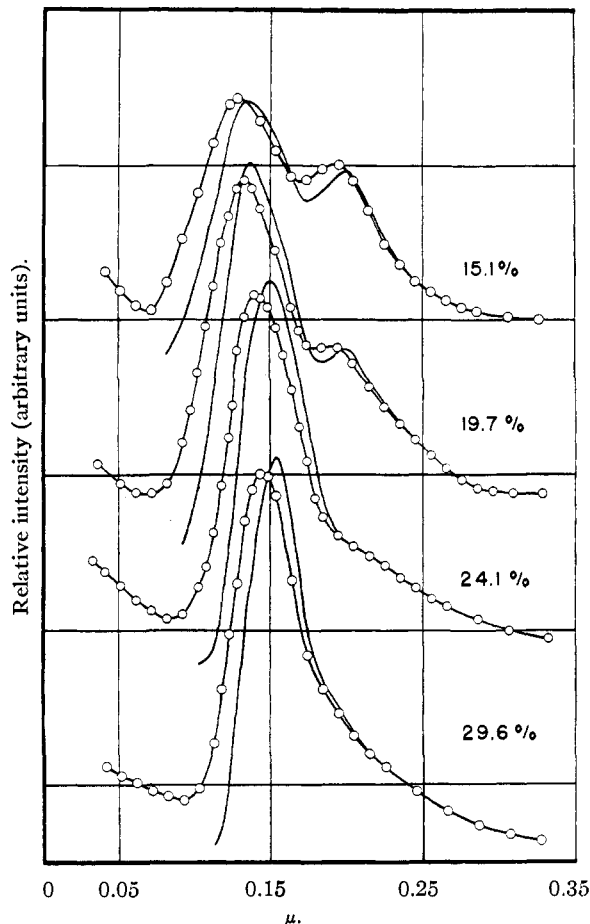


Fig. 2.—Relative diffraction intensities, for several concentrations of potassium laurate, as functions of $\mu \equiv (4\pi \sin \theta)/\lambda$. In each case the curve through experimental points is uncorrected for the effect of slit height, the unbroken curve is corrected. The origins of the curves are displaced.

In this way the solid lines of Fig. 2 have been obtained. The corrected intensity has not been extended to the smallest angles at which intensities were measured because the observed increase of intensity at these angles may be spurious.

The exact version (2) is awkward to use. If, however, the slope $i'(x)$ of the true intensity can be assumed constant over the small range of integration of the second integral, then this integral can be evaluated simply as

$$0.727i(\sqrt{x^2 + A^2}) + 0.273i(\sqrt{x^2 + 2A^2}) \text{ for } x \gg A$$

$$0.710i(\sqrt{x^2 + A^2}) + 0.290i(\sqrt{x^2 + 2A^2}) \text{ for } x = A$$

$$\text{and } x \ll A$$

Theory of the Interpretation

Studies of the Wien effect in aqueous solutions of long-chain quaternary ammonium salts¹¹ have indicated that the micelles are surrounded by a shell of gegenions. In fact, most of the gegenions in the solution are thus bound to micelles. It was assumed that here laurate ion micelles are also surrounded by potassium ion shells.

The potassium ions, of high electron density, are responsible for most of the observed scattering. Since the electron density of the laurate ions is near that of water, the electron density in the solution is composed approximately of peaks, representing potassium ions, rising above the nearly

(11) S. Gusman, Thesis, Brown University, 1950.

constant density of the "solvent." At least formally then, the total scattered intensity can be separated into components, one of which represents the heavy-ion scattering. Let A_i be the instantaneous complex scattering amplitude of a solvent atom i , defined such that the atomic scattering power (which is contained implicitly in A_i) is the average of the scattering power of water molecules and carbon and oxygen atoms in the laurate ions. Let $A_i + a_j$ be the instantaneous complex scattering amplitude of potassium ion j , so that a_j represents that part in excess of the scattering which would result from a solvent atom in the same position. The total instantaneous intensity is then

$$I = \left| \sum_{i=1}^N A_i + \sum_{j=1}^n a_j \right|^2 \quad (4)$$

where N is the number of atoms (other than hydrogen) in the sample and n is the number of potassium ions. The average intensity is then

$$\bar{I} = \left\langle \sum_{i,j=1}^N A_i^* A_j \right\rangle + \left\langle \sum_{i=1}^N \sum_{j=1}^n (A_i^* a_j + a_j^* A_i) \right\rangle + \left\langle \sum_{i,j=1}^n a_i^* a_j \right\rangle \quad (5)$$

The first term is the scattering from the solvent, the third term is that part of the potassium scattering in excess of the solvent scattering, and the second term arises from geometric interaction of solvent atoms and potassium ions. This can be re-expressed in terms of atomic scattering powers and radial distribution functions in the usual way¹² as

$$\bar{I} = N f_s^2 \left[1 + \int_0^\infty 4\pi r^2 P_{SS}(r) \frac{\sin \mu r}{\mu r} dr \right] + 2\sqrt{N} n f_s f_K \int_0^\infty 4\pi r^2 P_{SK}(r) \frac{\sin \mu r}{\mu r} dr + n f_K^2 \left[1 + \int_0^\infty 4\pi r^2 P_{KK}(r) \frac{\sin \mu r}{\mu r} dr \right] \quad (6)$$

where $\mu \equiv (4\pi \sin \theta)/\lambda$ and θ is the Bragg angle, and in which the terms correspond to the respective terms in the preceding equation. Here f_s is the average scattering power of a solvent atom and f_K is the "excess" scattering power of a potassium ion. $P_{SS}(r)$ is the density of solvent atoms at a distance r from a given solvent atom, $P_{KK}(r)$ is the excess density of potassium ions at a distance r from a potassium ion, and $P_{SK}(r)$ is an average of the density of solvent atoms about a given potassium ion and the excess density of potassium ions about a given solvent atom.

Now the diffraction described by the first and second terms should exhibit peaks at angles which are determined by the short-range structure of the solvent. The corresponding interatomic distances are small so that the maxima occur at large scattering angles. For the third term, on the other hand, the prominent distances between potassium ions include large values so that this term should represent most of the small angle scattering. This can be partially verified by considering the source of

small angle scattering from a reasonable model,¹³ in which the solvent is composed of hard spheres of radius 1.4 Å. arranged in the same structure as was found experimentally for liquid mercury, and in which the potassium ions are aggregated into thin spherical shells, similarly arranged, of radius 16 Å., each containing 50 ions. The intensities represented by the first and third terms may then be calculated from the work of Oster and Riley¹³; at that point where the third term has its first and highest maximum, it has about 100 times the intensity represented by the first term. Little change in this result would be caused by a slightly different model.

The second term is smaller, on the average, than the first term, as a consequence of the size of the numerical coefficients of the terms in (6). It is the product of structure factor contributions for the solvent and for the excess heavy ions; since these contributions have large values at different values of μ , the second term should almost always be small compared to the first term.

The unimportance of the first term was checked by photographing the scattering from a sample of pure water; it showed negligible scattering in the small-angle region when given exposures comparable to those given the solution samples. Consequently, it may be taken as a good approximation that the small-angle scattering is given by the third term only of equation (6).

The Fourier transform of this approximate expression for \bar{I} then yields¹⁴

$$4\pi r P_{KK}(r) = (2/\pi) \int_0^\infty \mu j(\mu) \sin \mu r d\mu \quad (7)$$

where

$$j(\mu) \equiv (\bar{I}/n f_K^2) - 1$$

By means of this equation the radial distribution function $P_{KK}(r)$ may be calculated from intensity of scattering as a function of angle.

The experimental procedure provides, however, not \bar{I} over the complete range in μ , but rather a relative intensity $k\bar{I}$ within a very limited range in μ , so that (7) cannot be used directly. The limited measurements can, nevertheless, give information about $P_{KK}(r)$, in terms of an expression analogous to (7) containing the quantities

$$k\bar{I}(\mu) = k[n f_K^2 j(\mu) + n f_K^2] \quad (8)$$

and

$$M(\mu) \equiv 1 \text{ for } \mu_1 \leq \mu \leq \mu_u \\ \equiv 0 \text{ for } 0 \leq \mu < \mu_1, \mu_u < \mu < \infty \quad (8')$$

where μ_1 and μ_u are the lower and upper limits, respectively, of the range of μ for which $k\bar{I}$ is measured. Corresponding to (7) a new radial distribution function may be defined by

$$4\pi r P'(r) \equiv (2/\pi) \int_0^\infty \mu M(\mu) k\bar{I}(\mu) \sin \mu r d\mu \\ = 4\pi r k [P''(r) + Q(r)] \quad (9)$$

where

$$4\pi r P''(r) = (2/\pi) n f_K^2 \int_0^\infty \mu M(\mu) j(\mu) \sin \mu r d\mu \quad (9')$$

(13) G. Oster and D. P. Riley, *Acta Cryst.*, **5**, 1 (1952).

(14) F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927).

(12) J. A. Prins, *J. Chem. Phys.*, **3**, 72 (1935).

and

$$4\pi r Q(r) = (2/\pi) n f_K^2 \int_0^\infty \mu M(\mu) \sin \mu r \, d\mu \quad (9')$$

In both cases the factor f_K^2 has been taken outside the integral because it is very nearly constant over the small range of μ for which M differs from zero.

In order to see how (9') is related to (7), it may be rewritten, by means of the convolution theorem,¹⁵ as

$$4\pi r P''(r) = (n f_K^2 / \pi) \int_0^\infty 4\pi \eta P_{KK}(\eta) [\bar{M}_c(|r - \eta|) - \bar{M}_c(r + \eta)] \, d\eta \quad (10)$$

where

$$\begin{aligned} \bar{M}_c(r) &\equiv \sqrt{(2/\pi)} \int_0^\infty M(\mu) \cos \mu r \, d\mu \\ &= \sqrt{(2/\pi)} (\sin \mu_0 r - \sin \mu_1 r) / r \end{aligned}$$

and $P_{KK}(r)$ is the same desired radial distribution function which appears in (7). Then if the function $\bar{M}_c(|r - \eta|) - \bar{M}_c(r + \eta)$ were simply a delta-function, $P''(r)$ would be identical with $P_{KK}(r)$. In fact, however, this function has one large broad maximum and several satellite maxima separated by 19 Å. in the present case. If $P_{KK}(r)$ consists of relatively isolated peaks, each one produces, in $P''(r)$, a peak which is broadened and modulated by a 19 Å. ripple.

The second term (9'') of (9) may be evaluated directly to give

$$4\pi r Q(r) = (2 n f_K^2 r / 3\pi) [\mu_0^3 \Phi(\mu_0 r) - \mu_1^3 \Phi(\mu_1 r)] \quad (11)$$

where

$$\Phi(x) \equiv (3/x^3)(\sin x - x \cos x)$$

The ratio $Q(r)/P''(r)$ shows that Q is important only for small values of r . If $P''(r)$ is replaced by its average value n/V

$$Q/P'' \cong (f_K^2 V / 6\pi^2) \mu_0^3 \Phi(\mu_0 r) \quad (12)$$

Insertion of the appropriate values shows that Q is negligible for $r > 10$ Å.

The results of the last two paragraphs show that the radial distribution function $P'(r)$ defined in (9) is obtained by modification of the true radial distribution function $P_{KK}(r)$ by a ripple and a smearing process, by then adding a distortion at small r values, and finally by multiplying by an unknown constant. Thus evaluation of $P'(r)$ from experimental measurements gives information about the form of $P_{KK}(r)$. A plot of $4\pi r^2 P'(r)$, for the 15.1% potassium laurate solution is shown in Fig. 3A.

While the calculation of $P'(r)$ makes use of all the experimental measurements, considerable undesirable distortion is introduced into the radial distribution function. It is possible to eliminate a large part of the distortion, at the expense of some of the information contained in the measurements, by a modified calculation now to be described. Finally, comparison of the two results should help to decide which features of $P'(r)$ are significant.

The modification mentioned consists in weighting

(15) I. N. Sneddon, "Fourier Transforms," McGraw-Hill Book Co., Inc., New York, N. Y., 1951.

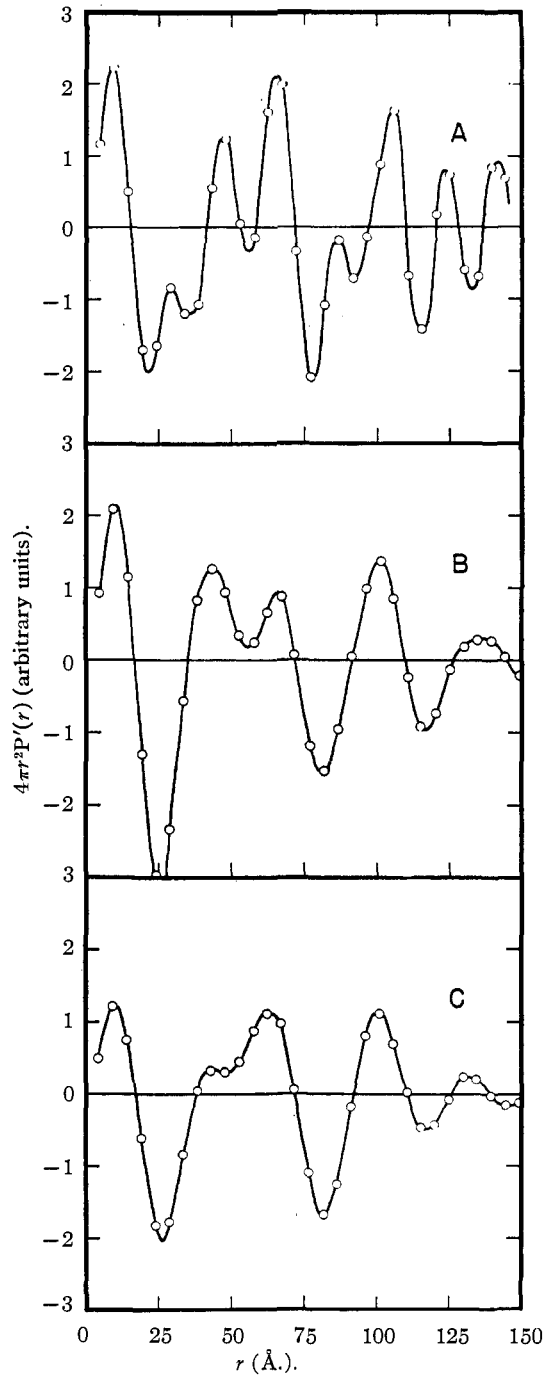


Fig. 3.—Radial distribution functions, for 15.1% potassium laurate solution, calculated on the bases of alternative assumptions (see text).

the experimental intensity, $k\bar{I}(\mu)$ by the function¹⁶

$$\mu^4 \exp[-B\mu^2]$$

where B is chosen to make the function equal to $1/10$ of its maximum value, when $\mu = \mu_0$. (Then it is equal to $2/10$ of its maximum at $\mu = \mu_1$.) This modification has the effect of decreasing the weight given to the measurements near either the upper or lower cut-off, so that the distortion due to the limitation of the measurements is reduced. Corresponding to (8')

(16) J. Waser, Thesis, Calif. Inst. of Tech., 1944.

$$M(\mu) = B^2\mu^4 \exp[-B\mu^2] \text{ (for all } \mu) \quad (13)$$

is now to be inserted into (9). The result (10) follows as before except that now

$$\bar{M}_c(r) = \sqrt{2} \frac{12B^2 - 12Br^2 + r^4}{32B^{3/2}} \exp[-r^2/4B] \quad (14)$$

This version of \bar{M}_c turns out to exhibit a wider, lower peak, with very little ripple.

The result (9') follows as before and the integral may be evaluated by substitution of (13). The result, corresponding to (11), is

$$4\pi r Q(r) = (2/\sqrt{\pi}) \frac{60B^2 - 20Br^2 + r^5}{64B^{3/2}} \exp[-r^2/4B] \quad (15)$$

Examination of this quantity shows that it represents a contribution which adds to $4\pi r P''(r)$ for r between 0 and 15 Å., subtracts between 15 and 30 Å., adds between 30 and 40 Å., and is negligible thereafter. The results of this modified calculation of $4\pi r P''(r)$ are shown in Fig. 3B. This will be compared with the previous result later.

If the experimental intensity values could be placed on an absolute scale, then (7) could be used directly to evaluate $4\pi r P_{KK}(r)$. One method of establishing the scale factor k is to extend the measurements to a value of μ large enough so that the scattering is equal to that from a random distribution of scatterers; at that point $\bar{I} = n f_K^2$ and k may be adjusted so that the observed intensity equals this value. The present measurements do not extend far enough for this to be a very plausible assumption. Nevertheless, results computed by assuming it are shown in Fig. 3C.

Distributions calculated by all three methods will be compared and discussed later.

Other workers^{3,17} have attempted to calculate the radial distribution of micelle centers in similar problems. The calculation differs only in that the present f_K is replaced by F , the average structure factor for an assumed micelle model, and the number of atoms n is replaced by the number of micelles. For the spherical micelles assumed by these workers, F decreases more rapidly with increasing μ than does f_K , so that the effect is nearly opposite to that produced by the weighting by $\mu^4 \exp[-\beta\mu^2]$. Consequently the micelle center distribution function exhibits sharper peaks than

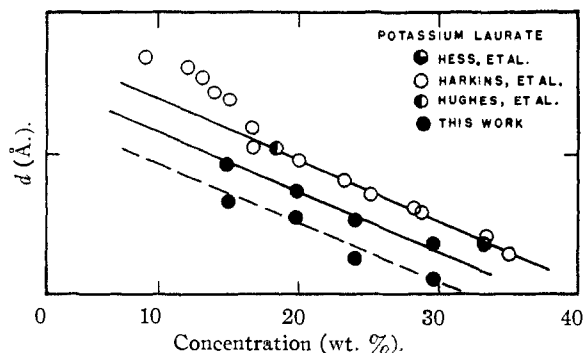


Fig. 4.—"Interplanar spacings" calculated from Bragg's law for potassium laurate solutions. The dashed line includes the slit height correction, the solid lines do not.

(17) M. L. Corrin, *J. Chem. Phys.*, **16**, 844 (1948).

does the atom center distribution function used here; but the magnified effect of the finite termination of the data introduces much more serious difficulties into the interpretation.

Calculations of the structure factor from various assumed micelle models—spheres and spheroids¹⁸ and spherical shells¹³—all lead to functions of the same general shape, more or less resembling a Gauss function. The similarity is such that no conclusions can be drawn as to which model provides the best picture for a micelle, at least from small-angle scattering. Consequently such studies can only lead to information about the distribution of micelle centers, whether calculated directly or calculated *via* the distribution of (heavy) atoms as done here.

Results and Discussion

Measurements on potassium laurate solutions by several investigators are compared in Fig. 4. For the purpose of this comparison, d values have been calculated from position of the maximum in the scattering curve, by means of Bragg's law. The present values are smaller, by a constant amount, than previous values. This is the result to be expected from the fact that the non-monochromatic radiation used by other workers contains a component of wave length less than that of the principal component. A further source of the decrease in spacings is the correction for the slit height effect. The d values reported are believed to be accurate to ± 1 Å. (However, the interatomic distances in the radial distribution function are accurate only to perhaps ± 2 Å. as a result of accumulated errors.)

Data from the solutions containing 15.1% (by weight) potassium laurate have been analyzed by the three procedures discussed. Figure 3A is a plot of the radial distribution function defined in equation (6) and Fig. 3B, of that defined in equation (13). The effect of the predicted 19 Å. ripple in A is very marked and many of the apparent features are spurious. The smoothing resulting from the second treatment is apparent in curve B. The additive distortion Q is noticeable also; in B the maxima in Q coincide approximately with those in P'' , so that the magnitudes, but not the positions, of the first few features are changed. The curve resulting from matching \bar{I} with $n f_K^2$ at μ_0 is presented in part C.

All curves are consistent in showing the main features of the distribution; taken together, with due allowance for the systematic differences from the true radial distribution, they provide a reasonably reliable picture. The third variation, C, while less well-founded theoretically than A or B, is seen empirically to represent a fair average of A and B. Hence it alone was used in the analysis of solutions of higher concentration. The results for solutions of 19.7, 24.1 and 29.6% potassium laurate are recorded in Fig. 5.

The first maximum in these distribution functions has no simple physical significance because no data sensitive to such small interparticle distances have been included; rather this maximum arises from the method of calculation.

(18) A. Guinier, *Ann. phys.*, **12**, 161 (1939).

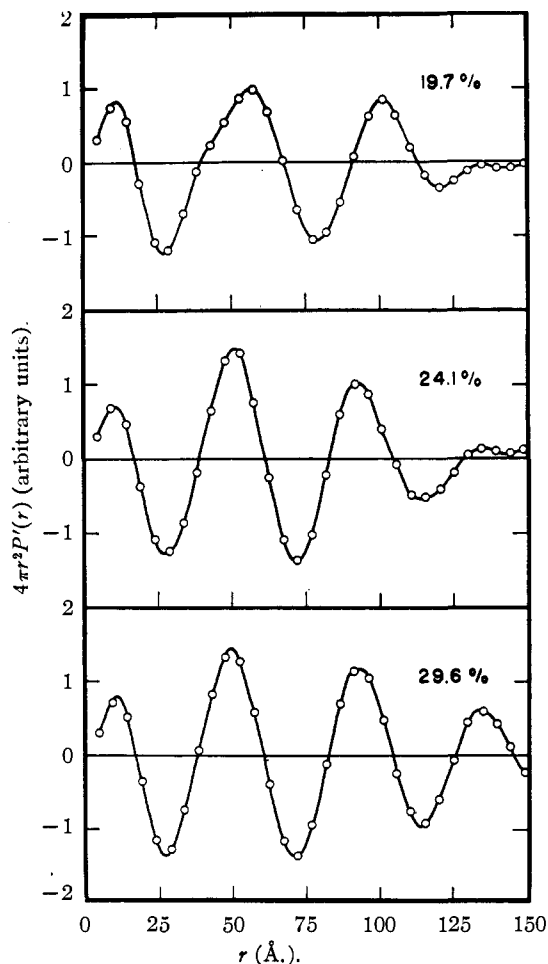


Fig. 5.—Radial distribution functions, calculated by matching \bar{I} and nf_K^2 at μ_1 , for several concentrations of potassium laurate.

The first minimum locates an effective micelle diameter or the distance of closest approach of micelle centers, if it may be assumed that micelles repel one another at small distances and thus seldom touch. The interatomic distance corresponding to this feature, at $r = 27$ Å., is slightly less than twice the length of an extended laurate anion, 16 Å.

The second maximum locates the most frequent separation of micelle pairs. Since this maximum moves to larger r values and decreases in height as the concentration decreases, it can be concluded that the packing becomes less rigid at lower concentrations. It is curious that this maximum appears to split into two components at a concentration of 15.1%, but the physical significance of this behavior is uncertain.

In the most concentrated solution, a small fourth peak appears; this indicates an increase in the degree of order of the micelle arrangement.

Because the distribution functions are on a relative scale only (*cf.* eq. (9)), the number of nearest neighbors of a micelle cannot be computed directly from the area under the second maximum. However it will be shown that, in the most concentrated solution, the distribution function is consistent with a loose cubic close-packed distribution of

micelle centers, so that there are approximately 12 nearest neighbors around any micelle.

Consider the model of a micellar solution in which the micelle centers have the same spatial arrangement as a cubic close-packed distribution of spheres, except that the micelles are not in contact. The centers then lie on a set of spheres, concentric about any given micelle, of radii S , $\sqrt{2}S$, $\sqrt{3}S$, etc. Let S be chosen to correspond to the minimum for the 29% solution. The corresponding (discontinuous) distribution function¹⁹ is illustrated in Fig. 6; the heights of the lines are proportional to the number of centers per unit area lying on each sphere. In order to represent a less rigid arrange-

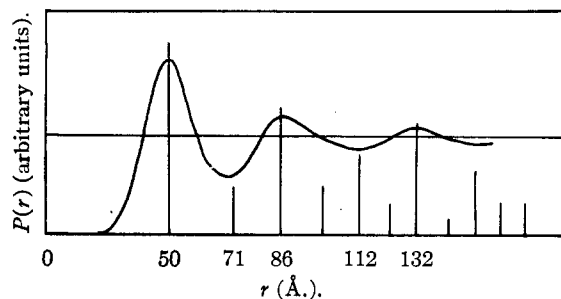


Fig. 6.—Distribution function for spheres in cubic closest packing (vertical lines) and for spheres in a flexible arrangement which is cubic close-packed on the average (smooth curve).

ment, this set of delta-functions has to be smeared out into a set of overlapping peaks with areas proportional to the number of micelles at each distance and with widths varying with the root-mean-square deviation of the centers from the completely ordered positions. The estimated appearance of the resulting curve has been sketched also in Fig. 6; the positions of the maxima correspond to the positions of the delta-functions in the curve above. This curve has the same shape as the

TABLE I
COMPARISON OF POTASSIUM LAURATE SOLUTIONS WITH SPHERES IN CUBIC CLOSE-PACKING

The upper number of each pair is the measured position of a feature in the radial distribution function for a potassium laurate solution, the lower number is the calculated position of the corresponding feature for spheres in cubic close-packing. In this calculation, the value of S is adjusted so that the first measured and calculated features coincide for each concentration.

| Concn., weight % | Position of feature, Å. | | | | |
|------------------|-------------------------|----|------|-----|-----|
| | 50 | 71 | 86 | 112 | 132 |
| 29.6 | 50 | 71 | 92.5 | 113 | 133 |
| | (50) | 71 | 86 | 112 | 132 |
| 24.1 | 51 | 72 | 93 | 113 | ... |
| | (51) | 72 | 88 | 114 | 135 |
| 19.7 | 57 | 80 | 101 | 120 | ... |
| | (57) | 81 | 99 | 128 | 151 |
| 15.1 | 64 | 88 | 102 | ... | ... |
| | (64) | 91 | 111 | 142 | 169 |
| | or 43 | 88 | 102 | ... | ... |
| | (43) | 61 | 74 | 96 | ... |

(19) R. W. James, "The Optical Principles of the Diffraction of X-Rays," G. Bell and Sons, Ltd., London, 1948, p. 475.

distribution function for the 29% solution, so the model is believed to represent a good picture of the solution. Table I lists the results for the other concentrations and indicates that this close-packed arrangement becomes less and less ordered as the concentration decreases.

The number of molecules in the average potassium laurate micelle, at various concentrations, can now be computed²⁰ from the number of molecules per unit volume and the number of micelles

(20) R. W. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.*, **16**, 644 (1948).

per unit volume. The number of molecules is calculated from the concentration and the density (1.018 g./cm.³ for the 29% solution). The results for the 29.6, 24.1, 19.7 and 15.1% solutions, respectively, are 63, 55, 64 and 70 molecules per micelle. At the lowest concentration the micelles may deviate enough from the close-packed arrangement to cause appreciable error in the corresponding figure. The error of $\pm 2 \text{ \AA}$. in the determination of the separation of micelle centers introduces an uncertainty of ± 8 molecules in these results.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

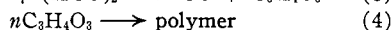
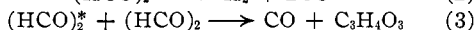
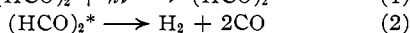
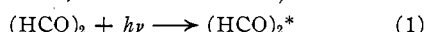
The Photolysis of Glyoxal Vapor at Wave Length 3130 Å.¹

BY JACK G. CALVERT AND GILBERT S. LAYNE

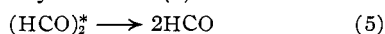
RECEIVED SEPTEMBER 29, 1952

A quantitative study of the rates of formation of carbon monoxide and hydrogen products from the vapor phase photolyses of pure glyoxal vapor was made in experiments at several temperatures, intensities of 3130 Å. radiation, and concentrations of pure glyoxal and in mixtures of glyoxal with carbon dioxide. The data indicate that the quantum yields of carbon monoxide and hydrogen, about 1.2 and 0.13, respectively, are relatively insensitive to changes in all of the experimental variables. The results are consistent with the reaction mechanism (1), (2) and (9) given in the text. It seems probable that no glyoxal molecules absorbing 3130 Å. radiation are deactivated and that all of the activated glyoxal molecules decompose by either reaction (2) or (9) with the probabilities for each mode of decomposition being 0.15 and 0.85, respectively.

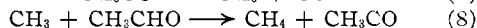
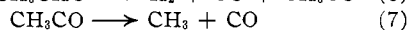
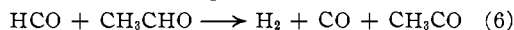
Norrish and Griffiths² found the following reaction mechanism was consistent with the products identified and the rate studies made in glyoxal photolyses in unfiltered mercury arc light (chiefly wave lengths 4360, 4050 and 3660 Å.)



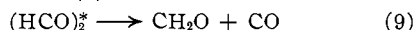
$(\text{HCO})_2^*$ indicates a light activated glyoxal molecule; $\text{C}_3\text{H}_4\text{O}_3$ represents a molecule of glycerosone. The effect of added acetaldehyde and carbon dioxide on the ratio of the products of glyoxal photolysis at 3660 Å. was investigated by Blacet and Moulton.³ Methane could not be detected in the products of the photolysis of glyoxal with added acetaldehyde. It was concluded that formyl radical formation by reaction (5)



does not occur in glyoxal photolysis at 3660 Å. since reaction (5) would be followed presumably by a sequence of reactions producing methane



Blacet and Moulton explained their results qualitatively in terms of the Norrish mechanism and the additional reaction (9)

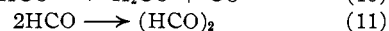
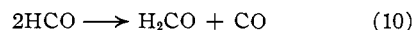


(1) Presented in part before the Division of Physical and Inorganic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1952.

(2) R. G. W. Norrish and J. G. A. Griffiths, *J. Chem. Soc.*, 2829 (1928).

(3) F. E. Blacet and R. W. Moulton, *THIS JOURNAL*, **63**, 868 (1941).

For several reasons the evidence given for the proposed glyoxal photolysis scheme is not compelling. A very limited range of the experimental variables was used in these studies; *e.g.*, all of the photolyses were carried out at the one temperature of 25°. In addition the experiments were complicated by the occurrence of the rapid thermal reaction of glyoxal polymerization. The exclusion of reaction (5) on the basis of the previous work is also open to question. Provided that sufficient energy per quantum of adsorbed light is available to cause (5) and that this reaction occurs in glyoxal photolysis, then it is probable that reactions such as (10) and (11)



would be the dominant modes of formyl radical reaction at 25°,^{4,5} and reaction (6) and the subsequent reactions (7) and (8) would be unimportant at this low temperature. If this is the case the presence of the radicals and the occurrence of (5) could not have been detected in the previous work. The present study was made to provide a more rigorous test of the proposed mechanism of glyoxal photolysis and to investigate the possible use of this photodecomposition as a source of formyl radicals at wave lengths energetically favorable to reaction (5).

Experimental Procedure

Photolysis Equipment and Procedure.—The photolysis, gas handling and optical systems, and the 3130 Å. light source and light measuring equipment used in this study were similar to those described previously.⁶ The metal

(4) F. E. Blacet and W. J. Blaedel, *ibid.*, **62**, 3374 (1940).

(5) F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 661 (1951).

(6) J. G. Calvert and B. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951).