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P. Seryz

ANGULAR DISSYMMETRY OF SCATTERING AND SHAPE OF PARTICLES*

P. Debye

I. Introduction

It now seems well established that a measurement of the intensity of the scattered light emitted by a polymer solution as compared to that of the primary light or any other measurement which can yield a numerical value for the turbidity τ of the solution is a practical method for the determination of the molecular weight M of the polymer.**

Briefly the procedure is as follows:

Prepare a solution of concentration c expressed in grams per cubic centimeter and determine the *refraction difference* of this solution against the solvent. If μ is the index of refraction of the solution and μ_0 that of the solvent it turns out that $\mu - \mu_0$ is within very narrow limits proportional to the concentration. (In most cases $\mu - \mu_0$ is of the order of 1 unit in the third decimal for a 1% solution.)

Next calculate from the observed value of $(\mu - \mu_0)/c$ a constant K which characterizes the solution as to its scattering power from the relation:

$$K = \frac{32\pi^3}{3} \frac{\mu_0^2}{N\lambda^4} \left(\frac{\mu - \mu_0}{c} \right)^2$$

in which N is Avogadro's number ($N = 6.061 \times 10^{23}$) and λ is the wavelength in centimeters of the primary light measured in vacuum. (The usual values of K are of the order 10^{-6} cm.²/g.²).

Now determine the *turbidity* τ in cm.⁻¹ for different concentrations c (ranging practically from a few tenth of 1% to a few per cent). Plotting finally $K\frac{c}{\tau}$ as ordinates against c as abscissas a straight line is found with an intercept for which is equal to $1/M$, in which M is the molecular weight.

*Technical Report No. 637 to Rubber Reserve Company, April 9, 1945.

**The turbidity τ is defined as the fractional decrease of the primary intensity over unit distance. In the following the letter τ always refers to the additional turbidity of the solution due to the presence of the polymer. It represents the difference in turbidity of solution and pure solvent.

LIGHT SCATTERING

For polymers of the same kind but with different degrees of polymerization all measured in the same solvent the straight lines are nearly parallel to each other and differ only in their intercepts. The better the solvent the steeper is the slope of these lines.

If the polymer is a mixture of particles with different degrees of polymerization the average molecular weight measured by the intercept is the *weight-average* molecular weight.

The statement as it is presented here implies that the particles in the solution are small compared with the wavelength of the light measured in the solution. If we are dealing with coiling polymers it seems at a first glance that this condition is amply verified up to rather high molecular weights. Let us suppose as an example that we have to deal with a straight polystyrene chain consisting of 10,000 linked monomers. This would correspond to a molecular weight $M = 104 \times 10^6$. The chain would contain $N = 20,000$ carbon-to-carbon links. According to the usual calculation the average distance R from beginning to end of the chain (defined as the square root of the average value of the square of this distance) is:

$$R = \sqrt{2Na^2} = 308 \text{ A.U.}$$

if we take a , the C-C distance, equal to 1.54 A.U. This would still be at least 10 times smaller than the wavelength.*

At this stage of the argument it can be questioned whether we are right to judge the size of the polymer by such an average distance R , since we know that the molecule is continuously changing its shape and will pass through forms with a much larger distance from beginning to end. Our subsequent calculation will show, however, that this objection does not carry weight. In the averaging process involved in the calculation of the scattering of an assembly of all possible kinds of shapes it is again the same average distance R as before which is important.

The first observable effect to be expected as soon as the size becomes comparable with the wavelength would be that the angular distribution of the scattered intensity loses its symmetry around the 90° direction, the scattering becoming more pronounced in the forward direction. As well our own experience as that from other laboratories, accumulated during the last year, indicates that such an effect can be observed for polymers for which it would not be expected, judging from the value of the average distance R as calculated from the customary formula. Although from an experimental point of view there can be no question as to the existence of such a dissymmetry effect, questions can be raised as to its interpretation.

*For the formula compare for instance H. Mark, "Physical Chemistry of High Polymeric Systems," Interscience, New York, 1940, p. 72.

The most straightforward interpretation is that in reality the average distance R in a polymer molecule of the coiling type is larger than the value calculated from the customary formula. This is rather to be expected if we consider the assumptions which are made in deriving the relation. It is assumed that the chain consists of links with perfectly free rotations around each other with no amount of hindering at all. It is further assumed that the monomeric parts of the chain do not occupy any space, this even to such an extent that in the theoretical picture of the molecule links can cut through each other without any hindrance. This leads us to believe that the chains in nature will be considerably "stiffer" than those of the picture and as a consequence we have to anticipate larger values of R .

However, there exist other less fundamental reasons why a solution can show angular dissymmetry of scattering. Apart from the obvious effect of large size impurities, the dissymmetry may be due to gel content. An example of this is contained in Report CR-578 of W. O. Baker, J. H. Heiss, Jr., and R. W. Walker. Two solutions of identical composition of a GR-S copolymer are compared (A) containing no gel, (B) containing 50% of microgel. Whereas with respect to the intensity of the 90° scattering A:B = 2.38:3.06, the total turbidities are much farther apart. For these, A:B = 4.8:33.1, demonstrating that in the solution with a high gel content a large portion of the light is scattered in directions approaching the directions of the primary beam. This part of the scattered light obviously is not observed in the 90° scattering, whereas on the other hand it has to be counted as contributing to the total turbidity.

What an investigation of the dissymmetry effect shows immediately is the existence or nonexistence of particles of relatively large size in the solution. If such particles are observed the question still remains as to the constitution of those particles. It is evident that in order to answer this last question additional evidence, preferably independent of experiments on light scattering alone, will be very important.

In the following the case of unbranched polymers of the coiling type is considered. The angular distribution of scattering is calculated and expressed with the help of the average distance R from beginning to end of the chain. It is further shown how abnormally large values of R can be explained by hindered rotation and a simple formula is found which connects the increase in R with the restriction of rotation for a special type of hindrance.

II. Light Scattering by an Unbranched Chain

As a model to start with, we assume a chain of $N + 1$ atomic groups, each with its center at the intersection of two links. Each link may have the length a and for the present these bonds

LIGHT SCATTERING

are considered to make a valence angle with each other and to have perfect freedom of rotation.

The amplitude of the scattered light emitted by a molecule of this kind will be proportional to:

$$\sum_{n=1}^{n=N+1} e^{ik(\bar{s}, \bar{r}_n)}$$

We define $k = 2\pi/\lambda$ with λ equal to the wavelength of the primary light, measured in the medium; \bar{s} is the vectorial difference between two unit vectors, one drawn in the direction of the scattered beam, the other in the direction of the primary beam; \bar{r}_n is the vectorial distance of the position of the center of the n^{th} atomic group from a fixed reference point. In this formula the proportionality factor measuring the response of the monomeric atomic group is left out, since we will only be interested in the angular distribution of the scattered intensity and not in its absolute value.

A definite configuration of the chain can still have all possible orientations in space, without changing the shape of the molecule by bond rotations. So we will first obtain the intensity averaged with respect to all possible orientations by multiplying the expression for the amplitude with its conjugate and then averaging about all the orientations. The result of this procedure is:

$$I = \sum_m \sum_n \frac{\sin[ksr_{mn}]}{ksr_{mn}} \quad (1)$$

I is the intensity, s is the length of the vector \bar{s} , which is equal to $2 \sin \vartheta/2$ with ϑ equal to the angle between the primary and the scattered beam and r_{mn} is the distance from group m to group n . The averaging process used in obtaining this expression for I is the same as that used in calculating the scattering of x-rays or electrons from a gas molecule. The equality sign is to be interpreted as mentioned before. For polymers another averaging process is still to be carried out, since the shape of the molecules will vary continuously. This can be done if we know for every distance r_{mn} what the probability is that such a distance will occur in an interval between r_{mn} and $r_{mn} + dr_{mn}$. Now it is well-known that for a chain of the kind here considered this probability for the distance r of beginning to end of the chain is:

$$w(r) dr = 4\pi \left(\frac{3}{2\pi R^2} \right)^{3/2} e^{-3r^2/2R^2} r^2 dr \quad (2)$$

in which the factor is so adjusted that $\int w(r) dr = 1$ and in which R^2 is the average value of r^2 . We know also that for free rotating bonds:

$$R^2 = zu^2 \frac{1 + p}{1 - p} \quad (3)$$

if the chain consists of z links ($z + 1$ groups) and p is the cosine of the angle between two bonds. The relation for the probability of occurrence of the distance r is the customary expression, which from a mathematical point of view is only exact in the limit for an infinitely long chain. The same is true for the relation expressed by equation (3). We will accept the validity of both relations for any chain lengths, a procedure which can be shown not to introduce any appreciable errors in all practical cases to be considered.

Knowing the probability function for r we can now determine at once the average value of one of the terms contained in the double sum representing the intensity I . We find:

$$\text{Av} \frac{\sin [ksr]}{ksr} = e^{-k^2 s^2 R^2 / 6} \quad (4)$$

and substituting this in equation (1) with due regard to equation (3), which expresses R^2 in terms of the number of links, we obtain:

$$I = \sum_{mn} \exp\left(-\frac{k^2 s^2 a^2}{6} \frac{1 + p}{1 - p} |m - n|\right) \quad (5)$$

Each summation index m , as well as n , goes from 1 to $N + 1$; of the difference $m - n$ the absolute value is to be taken, which is indicated by writing $|m - n|$. If this summation is performed, the result is:

$$I = N^2 \frac{2}{x^2} \left[e^{-x} - (1 - x) \right] \quad (6)$$

with:

$$x = \frac{1 + p}{1 - p} \frac{k^2 s^2}{6} Na^2 = \frac{k^2 s^2 R^2}{6} \quad (7)$$

in which R^2 now indicates the average square of the distance from beginning to end of the whole chain.

LIGHT SCATTERING

Details of the Calculation

If one term of the sum in equation (5) is written as $t_z = e^{-zb}$ with:

$$b = \frac{k^2 s^2 a^2}{6} \frac{1+p}{1-p}$$

the whole double sum can be arranged in a quadratic scheme of the following form:

$$I = \begin{vmatrix} t_0 + t_1 + t_2 + \dots + t_N \\ t_1 + t_0 + t_1 + t_2 + \dots + t_{N-1} \\ t_2 + t_1 + t_0 + t_1 + \dots + t_{N-2} \\ \dots \dots \dots \\ t_N + t_{N-1} + t_{N-2} + \dots + t_1 + t_0 \end{vmatrix}$$

Taking out the diagonal terms first and then observing that the part in the upper right is equal to the part in the lower left, the result is:

$$I = (N + 1) + 2 \left\{ \sum_{z=1}^{z=N} t_z + \sum_{z=1}^{z=N-1} t_z + \dots + \sum_{z=1}^{z=N-(N-1)} t_z \right.$$

or:

$$I = (N + 1) + 2 \sum_{z=0}^{N-1} \sum_{z=1}^{N-1} t_z$$

Since t_z is an exponential function the series over which the summations have to be carried out are simple geometrical series and we find:

$$I = (N + 1) + 2 \frac{e^{-b}}{1 - e^{-b}} N - \frac{1 - e^{-Nb}}{e^b - 1}$$

Now in every case b has a very small numerical value and only Nb can be finite provided the chain is long enough. The way of interpreting the result therefore is to put $Nb = x$ and $b = x/N$, and to determine the value of I in the limit for finite x and increasingly large values of N . In this way we find:

$$I = (N + 1) + 2 \frac{N^2}{x} \left(1 - \frac{1}{2} \frac{x}{N} + \dots \right) \left(1 - \frac{1 - e^{-x}}{x} \left(1 - \frac{1}{2} \frac{x}{N} + \dots \right) \right)$$

Retaining only terms of the order N^2 this yields the final result:

$$I = N^2 \frac{2}{x} \left[1 - \frac{1 - e^{-x}}{x} \right] = N^2 \frac{2}{x^2} \left[e^{-x} - (1-x) \right]$$

Since we do not care about the strength of the scattering but are only concerned with the angular distribution, we will omit the factor N^2 and have in this way normalized the scattered intensity so as to make $I = 1$ for $s = 0$, which, since $s = 2 \sin \theta/2$, corresponds to $\theta = 0$. In the following discussion we therefore take:

$$I = \frac{2}{x^2} \left[e^{-x} - (1-x) \right] \dots x = k^2 R^2 s^2 \quad (8)$$

For small values of the angle θ we will have:

$$I = 1 - \frac{k^2 R^2}{18} s^2 + \frac{k^4 R^4}{72} s^4 - \dots$$

If the size of the polymer is so large that for large angles our variable x itself becomes large the intensity can be represented by the relation:

$$I = \frac{12}{k^2 R^2} \frac{1}{s^2} - \frac{72}{k^4 R^4} \frac{1}{s^4}$$

In order to facilitate applications, Table I gives I as a function of x .

Table I

x	I	x	I	x	I
0	1	1.0	0.736	3.5	0.413
0.2	0.937	1.5	0.643	4.0	0.377
0.4	0.878	2.0	0.568	5.0	0.321
0.6	0.828	2.5	0.506	6.0	0.278
0.8	0.780	3.0	0.455	∞	0

The largest value $s = 2 \sin \vartheta/2$ can have in the angular range at our disposition is $s = 2$. Taking the polystyrene polymer mentioned in the introduction of the molecular weight $M = 1.04 \times 10^6$ as an example, we found $R = 308$ A.U. For $\vartheta = 180^\circ$ ($s = 2$) and with a wavelength of 3000 A.U. (measured in the solvent) we find $x = 0.31$. According to (8) this means that only a slight dissymmetry effect should exist, which would decrease the intensity to be observed in the backward direction ($\vartheta = 180^\circ$) to 90% of the intensity in the forward direction ($\vartheta = 0^\circ$). The reason for the

LIGHT SCATTERING

small effect is of course our small assumed value of R (308 A.U.), which is only 1/10 of the wavelength. This average distance was the result of the usual formula which follows from calculations assuming highly idealized conditions. According to our discussion in the introduction we have every reason to believe that in this calculation the distance is underestimated.

As can easily be seen the whole reasoning which leads to equation (8) as an expression describing the angular distribution is independent of the special way in which R^2 is supposed to follow from the atomic distances of the chain (equation 3). The only important thing is that R^2 be proportional to the number of links, which is characteristic for all molecules of the coiling type. The factor entering in the relation between the average square of the distance of the ends and the number of links will depend essentially on the "stiffness" of the chain and we can safely surmise that the value given to this factor in equation (3) is the lowest estimate possible. Realizing this situation, we suggest that relations (8) be taken as describing the angular distribution and that the parameter R^2 be determined not by calculation from a model of the molecule but be derived from the experimental evidence. In this way we learn experimentally something about the actual size of the polymer. This done, we can then speculate about the experimental value of R as compared to theoretical values derived from a model. Attempts of this kind are to be found in Fred W. Billmeyer's report CR622.

III. Influence of Hindrance of Rotation on the Average Chain Length

In order to estimate how much increase of the size of a polymer can result from hindered rotation the following special model is considered. We again have N links each of length a making the valence angle with each other, the projection of one bond on the next being pa . But now instead of assuming free rotation we restrict it in the following manner. Two consecutive bonds define instantaneously a plane, we assume that the third following bond can rotate freely only, within an angle 2α around its central position which is in the plane and parallel to the first bond of the three. The rotation is in this way restricted to an interval $-\alpha$ to $+\alpha$ and we would have free rotation only if we took $\alpha=\pi$. We want to know the average square of the distance from beginning to end of this chain.

Considering the bonds as vectors $\bar{a}_1 \dots \bar{a}_N$, the vectorial distance from beginning to end is the sum of these vectors. In order to obtain the square of this distance we have to take the scalar product of this sum with itself. In this way we obtain N^2 terms each of which represents the scalar product of one vectorial bond with another. So if we are going to determine the average value R^2 , we will have to know first what the average

is of the scalar product of two vectorial bonds taken at random.

Now considering a continuous part of the chain containing the bonds \bar{a}_{n+1} to \bar{a}_{n+z} inclusive and supposing that we want to find the average value of $(\bar{a}_{n+1} \bar{a}_{n+z})$ the averaging process can be built up of consecutive steps. First we allow the bond $n+z$ to perform its motion and calculate the resulting average, then we do the same with the following bond $n+z-1$ and so on. Now it can be shown that the result of the first step transforms the product:

$$(\bar{a}_{n+1} \bar{a}_{n+z})$$

into:

$$\varepsilon(\bar{a}_{n+1} \bar{a}_{n+z-1}) + \eta(\bar{a}_{n+1} \bar{a}_{n+z-2}) \quad (9)$$

with two constants ε and η defined by the relations:

$$\varepsilon = \rho \left(1 - \frac{\sin \alpha}{\alpha}\right) \quad (9')$$

$$\eta = \frac{\sin \alpha}{\alpha}$$

Details of the Calculation

Let Figure 1 represent a picture of the situation with respect to the 3 last bonds and let us draw the vector \bar{a}_{n+1} from the center of the circle over which the end of vector \bar{a}_{n+z} can move. Let further $\bar{u}_0, \bar{u}'_0, \bar{v}_0, \bar{v}$, and \bar{w} represent vector components of the main vectors to be considered, as indicated in Figure 1.

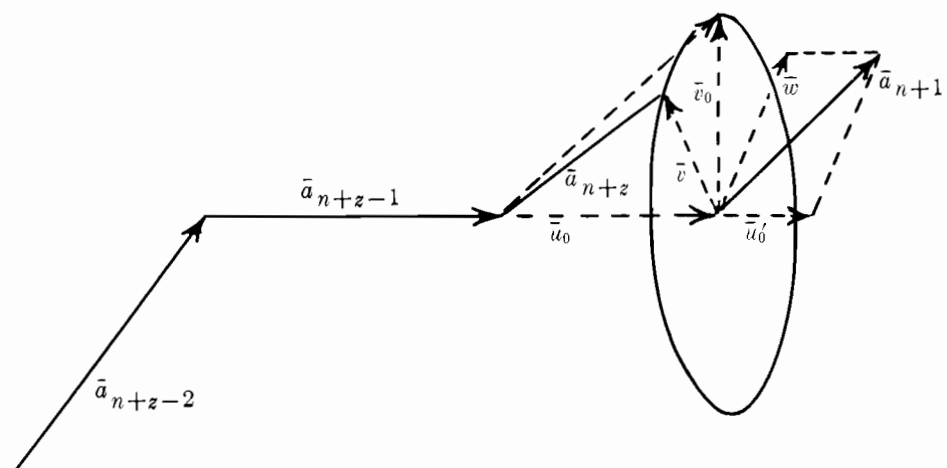


Figure 1

LIGHT SCATTERING

We then have;

$$(\bar{a}_{n+1} \bar{a}_{n+z}) = (\bar{a}_{n+1} \bar{u}_0) + (\bar{a}_{n+1} \bar{v})$$

but:

$$(\bar{a}_{n+1} \bar{v}) = (\bar{w} \bar{v}) + (\bar{u}'_0 \bar{v}) = (\bar{w} \bar{v})$$

since \bar{u}'_0 is perpendicular to \bar{v} . So we can write:

$$(\bar{a}_{n+1} \bar{a}_{n+z}) = (\bar{a}_{n+1} \bar{u}_0) + (\bar{w} \bar{v})$$

The first term is constant through the motion of bond $n + z$. If ψ is the angle between \bar{w} and \bar{v} and ψ_0 the angle between w and v_0 the motion of bond $n + z$ will be confined to the interval $\psi = \psi_0 + \alpha$ to $\psi = \psi_0 - \alpha$. For the average value of the second term we therefore find:

$$wv \frac{1}{2\alpha} \int_{\psi_0 + \alpha}^{\psi_0 - \alpha} \cos \psi d\psi = \frac{\sin \alpha}{\alpha} wv \cos \psi_0$$

However:

$$wv \cos \psi_0 = (\bar{w} \bar{v}_0) = (\bar{a}_{n+1} \bar{v}_0)$$

So we can say that the result of the first step in our averaging process of $\bar{a}_{n+1} \bar{a}_{n+z}$ is:

$$(\bar{a}_{n+1} \bar{u}_0) + \frac{\sin \alpha}{\alpha} (\bar{a}_{n+1} \bar{v}_0)$$

The two vectors \bar{u}_0 and \bar{v}_0 are both situated in the plane of the two vectors \bar{a}_{n+z-1} and \bar{a}_{n+z-2} . Therefore the first two are linear combinations of the second two. It is easily seen that

$$\bar{u}_0 = p \bar{a}_{n+z-1}, \quad \bar{v}_0 = \bar{a}_{n+z-2} - p \bar{a}_{n+z-1}$$

Substituting this in our last result, relations (9) and (9') of the text are obtained.

Let us now call P_z the average value of the product $(\bar{a}_{n+1} a_{n+z})$ after all the steps of the averaging process are carried out. From (9) it then follows immediately that:

$$P_z = \varepsilon P_{z-1} + \eta P_{z-2} \quad (10)$$

We further know that:

$$P_1 = a^2 \text{ and } P_2 = pa^2 \quad (10')$$

and from these two relations (10) and 10') an expression for P_z can be calculated. The result is:

Define λ_1 and λ_2 as the two roots of the quadratic equation:

$$\lambda^2 - \varepsilon\lambda - \eta = 0 \quad (11)$$

then:

$$\frac{P_z}{a^2} = \frac{p-\lambda_2}{\lambda_1-\lambda_2} \lambda_1^{z-1} - \frac{p-\lambda_1}{\lambda_1-\lambda_2} \lambda_2^{z-1} \quad (12)$$

Details of the Calculations

In order to solve the recurrence equation (10) we put $P_z = \lambda^z$ and see immediately that this can be done provided λ is a root of the quadratic equation (11). We then assume $P_z/a^2 = A_1 \lambda_1^z + A_2 \lambda_2^z$ in which λ_1 and λ_2 are the 2 roots and A_1 and A_2 arbitrary constants. We can then determine these 2 constants by the 2 conditions that $P_1 = a^2$ and $P_2 = pa^2$, which leads to:

$$A_1 \lambda_1 + A_2 \lambda_2 = 1$$

$$A_1 \lambda_1^2 + A_2 \lambda_2^2 = p$$

or:

$$A_1 = \frac{1}{\lambda_1} \frac{p - \lambda_2}{\lambda_1 - \lambda_2}, \quad -A_2 = \frac{1}{\lambda_2} \frac{p - \lambda_1}{\lambda_1 - \lambda_2}$$

LIGHT SCATTERING

As mentioned before, the required average R^2 is the sum of the N^2 average values of all the products $(\bar{a}_m \bar{a}_n)$. In a quadratic arrangement this summation appears in the following form:

$$R^2 = \begin{vmatrix} P_1 + P_2 + P_3 + \dots + P_N \\ P_2 + P_1 + P_2 + \dots + P_{N-1} \\ \dots \\ \dots \\ P_N + P_{N-1} + P_{N-2} + \dots + P_1 \end{vmatrix} \quad (13)$$

This summation is of the same kind as that which has to be carried out in the case of free rotation. The final result (in the limit for large values of N) is:

$$\frac{R^2}{a^2} = \frac{1 + (\sin \alpha/\alpha)}{1 - (\sin \alpha/\alpha)} \frac{1 + p}{1 - p} \quad (14)$$

Details of the Calculation

If we substitute in (13) the values of P_z following from equation (12) we see that R^2 can be expressed by two sums Σ_1 and Σ_2 in the form:

$$\frac{R^2}{a^2} = \frac{p - \lambda_2}{\lambda_1 - \lambda_2} \Sigma_1 - \frac{p - \lambda_1}{\lambda_1 - \lambda_2} \Sigma_2$$

Each of these sums can be written in a quadratic scheme in the form:

$$\Sigma = \begin{vmatrix} 1 + \lambda + \lambda^2 + \dots + \lambda^{N-1} \\ \lambda + 1 + \lambda + \dots + \lambda^{N-2} \\ \dots \\ \dots \\ \lambda^{N-1} + \lambda^{N-2} + \lambda^{N-3} + \dots + 1 \end{vmatrix}$$

For Σ_1 we have to substitute $\lambda = \lambda_1$ and for Σ_2 the other root $\lambda = \lambda_2$. Taking the diagonal terms first and observing that the upper right part is equal to the lower left part, it follows that:

$$\Sigma = N + 2 \sum_{\sigma=1}^{\sigma=N-1} \sum_{z=1}^{z=N-1} \lambda^z$$

In the limit for large values of N this reduces to:

$$\Sigma = N \left\{ 1 + \frac{2\lambda}{1-\lambda} \right\}$$

and we find:

$$\frac{R^2}{a^2} = N \left\{ 1 + 2 \frac{p - \lambda_2}{\lambda_1 - \lambda_2} \frac{\lambda_1}{1 - \lambda_1} - 2 \frac{p - \lambda_1}{\lambda_1 - \lambda_2} \frac{\lambda_2}{1 - \lambda_2} \right\}$$

or:

$$\frac{R^2}{a^2} = N \left\{ 1 + 2 \frac{p - \lambda_1}{(1 - \lambda_1)(1 - \lambda_2)} \lambda_2 \right\}$$

since λ_1 and λ_2 are the roots of equation (11) we have (considering also equation 9'):

$$\lambda_1 + \lambda_2 = \varepsilon = p(1-\eta), \quad \lambda_1 \lambda_2 = 1-\eta$$

Substituting gives:

$$\frac{R^2}{a^2} = N \frac{1 + \eta}{1 - \eta} \frac{1 + p}{1 - p}$$

Since according to (9') we have $\eta = \sin \alpha / \alpha$ this is the final result indicated in the text in equation (14).

The relation (14) for R^2 is the same as that of the current literature in the limit for free rotation, since in this case we have to substitute $\alpha = \pi$. In general for hindered rotation R^2 will be larger by a factor:

$$\frac{1 + (\sin \alpha / \alpha)}{1 - (\sin \alpha / \alpha)}$$

Since the quotient $\sin \alpha / \alpha$ approaches unity when the angle α becomes small the relation illustrates how R^2 increases with increasing hindrance.

As an illustration for the use which can be made of the relations presented in this report let us suppose the same linear

LIGHT SCATTERING

polystyrene polymer, which we already discussed, of a molecular weight $M = 1.04 \times 10^6$ containing $N = 20,000$ C-C bonds, each of length $a = 1.54$ A.U. Formerly we calculated for free rotating bonds $R = 308$ A.U. and concluded that if this was the actual distance we could expect only a small dissymmetry effect, the backward scattering being 90% of the intensity in the forward direction if observed with a wavelength of 3000 A.U. (measured in the medium).

Let us now assume that the experiment yielded a larger effect, say 25% more scattering under an angle $\vartheta = 60^\circ$ than under the angle $\vartheta = 120^\circ$. (For actually observed values see Report CR622). The two values of $s = 2 \sin \vartheta/2$ corresponding to $\vartheta = 60^\circ$ and $\vartheta = 120^\circ$ are $s = 1$ and $s = 3$. According to equation (8) the two values of the parameter x will therefore be in the ratio 1:3. If x has a numerical value say β for $\vartheta = 60^\circ$, it will be 3β for $\vartheta = 120^\circ$ and since we have observed that $I_\beta = 1.25 I_{3\beta}$ we have to choose $x = \beta$ so that this relation holds. This can easily be done with the help of the Table I and we find $x = \beta = 0.37$. This means that we should have:

$$\frac{k^2 R^2}{6} s^2 = \frac{\pi^2}{6} \frac{R^2}{\lambda^2} = 0.37$$

in order to explain the 25% difference in intensities. With $\lambda = 3000$ A.U. it follows then that $R = 711$ A.U. If finally we want to interpret this larger distance as due to hindering of rotation, we have to determine the angle α from the relation (see equation 14).

$$\frac{1 + (\sin \alpha / \alpha)}{1 - (\sin \alpha / \alpha)} = \left(\frac{711}{308} \right)^2$$

since we calculated $R = 308$ A.U. for the case of free rotation. The result is:

$$\alpha = 84^\circ$$

A restriction to a total angle 2α of 168° instead of the 360° in the case of free rotation would explain the 25% intensity difference assumed to be the result of the experiment.

MICELLE SHAPE FROM DISSYMMETRY MEASUREMENTS¹ *

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INTRODUCTION

In work (2) previously carried out in this laboratory it was found that the addition of inorganic salts to aqueous solutions of various detergents causes the colloidal aggregates to increase in size. The molecular weights of these aggregates, called micelles, in the presence of low salt concentrations indicate that the micelles are still too small to cause dissymmetry in the intensity of the scattered light. It was one of the aims of the present investigation to check this point.

Solutions of the longer-chain detergents to which relatively large amounts of salt have been added are visibly turbid. The aggregates are undoubtedly large. A second aim of this investigation was to measure the dissymmetry of light scattered by these solutions and to gain thereby some information regarding the shape of the micelle.

THEORY

The question of the shape of the micelle has received considerable attention from many investigators. McBain (7) has proposed models which are spherical and lamellar. Hartley (6) believes that only the spherical model is tenable. Harkins (5) and coworkers have supported a lamellar model on the basis of x-ray measurements. Recently Corrin (1) has stated that the x-ray scattering of soap solutions can also be explained by the spherical micelle. Debye (3) has shown from energy considerations that in aqueous solutions of the detergents or in solutions of low salt concentration the lamellar model is feasible and consistent with light-scattering measurements.

Dissymmetry measurements are incapable of resolving the problem of the shape of the micelle in aqueous solutions or in solutions of low salt concentration. The micelles are too small to cause appreciable dissymmetry in the scattered light. However, in the presence of relatively high salt concentrations the micelles of the longer-chain detergents are large enough to cause measurable dissymmetry in the intensity of the scattered light. This dissymmetry may be used to calculate characteristic dimensions of various models. Assuming a reasonable density of the aggregate, one may calculate from these characteristic dimensions molecular weights for each of the models. These molecular weights in turn may be compared with the molecular weight determined by 90° scattering. The value which agrees best with the experimentally determined molecular weight indicates the model which approximates most closely the correct one.

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The theoretical relationship which connects the intensity of the scattered light, the angle of observation, and a length characteristic of the given model is usually written as a function of the parameter X , which is defined as:

$$X = \frac{2\pi L}{\lambda} \sin \frac{\theta}{2} \quad (1)$$

λ is the wave length of the light in the scattering medium, L is the characteristic dimension of the model, and θ is the angle of observation. One may proceed in two ways to obtain the characteristic dimension from the experimental data. One may plot the intensity of the scattered light, I , as a function of θ for various chosen values of L . From these plots one obtains $I_{\theta}/(I_{180-\theta})$ for any given pair of angles symmetrical about 90° as a function of L and plots the results. This plot is then entered with the experimentally determined ratio $I_{\theta}/(I_{180-\theta})$ for the same pair of angles and a value of L is read off immediately. This method has advantages, in that it is relatively rapid and requires no correcting of the observed intensities for polarization and change in scattering volume with angle of observation. This assumes, of course, that the correction factors are symmetrical about 90° .

In the second method, one computes for various values of X corresponding values of I , using the theoretical scattering equation. Then a plot is made of $\log I$ vs. $\log X$. One then plots the experimentally determined $\log I$ as a function of $\log \sin \theta/2$, using a separate transparent sheet of graph paper. The two plots are superimposed and moved relative to each other, keeping the corresponding coordinate axes parallel, until the best alignment of the curves is found. The separation of the origins on the $\log X$ and $\log \sin \theta/2$ axes is equal to $\log 2\pi L/\lambda$, from which L may be obtained. This method takes more time than the first to carry out, but it is more accurate, as the intensity values over a considerable range of angles are employed.

EXPERIMENTAL TECHNIQUES

All dissymmetry measurements were made in an instrument recently designed by A. M. Bueche. An AH-4 mercury arc serves as the light source and is housed outside the instrument. The primary light enters the instrument through a pin hole in one end, is collimated by a single lens, and then proceeds through an aperture direct to the scattering cell. The primary beam is trapped after passage through the solution under observation. The pin hole and aperture are adjustable with respect to size, and the aperture and lens with respect to position.

A mirror located outside the cell reflects the scattered light downwards through a monochromatic filter and onto a phototube (electron multiplier type). The intensity of the scattered light is recorded as a deflection of the galvanometer connected to the phototube. The mirror may be moved in a semicircle about the cell to the desired position. The phototube moves as a unit with the mirror.

The scattering cell is an upright glass cylinder, sealed off on the bottom and open at the top. It has two horizontal arms extending outward from opposite sides of the cell and coaxial with the primary beam. A piece of microscope slide glass is sealed to the end of the arm nearer the light source; it serves as the

LIGHT SCATTERING

entrance window of the cell. The extremity of the other cell arm is drawn down and to a point to form a light trap. The arms and one side of the cell are painted black. Any light reflected from the cell entrance is not permitted by this design to reach the traveling mirror.

The *n*-tetradecyl- and *n*-hexadecyl-trimethylammonium bromides were of the same lot prepared for earlier work (2). In this investigation they were twice recrystallized from water for additional purification. Stock solutions were prepared from the wet crystals; other solutions of varying detergent concentration were prepared from the stock solutions by dilution. The concentration of detergent in the stock solutions was determined by refractive-index measurements. The potassium bromide was of reagent grade and not further purified. All water was slowly distilled from an alkaline potassium permanganate solution. It showed very little dissymmetry. Since the intensity of the light scattered from this water was little more than the sensitivity of the instrument as used, no values can be given. Except for low concentrations, the intensities of the light scattered from detergent solutions were considerably larger than that from water. It was observed in the course of the work that undistilled water could seemingly be cleaned up to show very little dissymmetry by the addition of small amounts of salt and subsequent filtration. This observation was not investigated thoroughly.

All solvents and solutions were filtered slowly through an ultra-fine Pyrex sintered-glass filter into receiving tubes from which they were poured into the scattering cell. Receiving tubes were cleaned in dichromate solution, rinsed with tap water, and then copiously rinsed with the carefully distilled water. Steaming out by the use of external heat concluded the treatment. The scattering cell was rinsed repeatedly with solvent until no further decrease in intensity of scattered light at 40° was observed. It was then filled with the detergent solution of lowest concentration. After all data for this solution had been obtained, the detergent solution was poured out of the cell and the solution of immediately higher concentration poured in. Some error in detergent concentration, due to dilution, occurs in this procedure, but contamination of the cell by dust is kept to a minimum. Since the cell takes a relatively large amount of solution (60 ml.) and the difference in concentration between successive solutions is taken small, it is felt that the dilution error is not of serious consequence. On several occasions two detergent solutions of the same concentration have been introduced successively into the scattering cell after a solution of lower detergent concentration had been in the cell. Little or no difference in the intensities of the light scattered from the solutions of identical detergent concentration was observed, indicating that the error of dilution is not serious.

Intensity measurements for both solutions and solvents were made at 10° intervals from $\theta = 40^\circ$ to $\theta = 140^\circ$, inclusive. θ is the angle of observation, as measured in the horizontal plane from the forward direction of the primary beam. Turbidities (as measured by 90° scattering) were obtained by comparing the 90° galvanometer deflections with the 90° galvanometer deflection produced by the light scattered from a Styron block placed in the primary beam. The

Styron block was calibrated with the aid of a solution of polystyrene in toluene. The difference in turbidity between the polystyrene solution and toluene was determined in the absolute intensity camera designed by P. P. Debye (4).

All measurements were made with the mercury blue line, $\lambda = 4358 \text{ \AA}$. Because unpolarized light was used and because the scattering volume is a function of angle, the observed intensities must be corrected. This may be accomplished in one of two ways. One may calculate experimental correction factors from the intensity *vs.* angle curve obtained from a solution which has no dissymmetry. Or one may correct for unpolarized light with the factor $1/(1 + \cos^2 \theta)$ and for different scattering volumes with the factor $\sin \theta$. Both methods are open to objections. Because the mirror accepts scattered light over a small range of angles instead of at a given angle, the experimentally determined correction factor will be somewhat dependent upon the refractive index of the solution used. The correction factor $\sin \theta/(1 + \cos^2 \theta)$ does not take into account the refractive-index difference between the solution and the glass of the cell and may not completely correct for scattering volume differences. Throughout this work the correction factors calculated from $\sin \theta/(1 + \cos^2 \theta)$ have been used.

DISCUSSION AND RESULTS

In table 1 are given the results of two runs with *n*-tetradecyltrimethylammonium bromide in 0.202 *M* potassium bromide. θ is the angle of observation, I is the galvanometer deflection in excess of that produced by the solvent alone, and $I_\theta/(I_{180-\theta})$ represents the dissymmetry for a pair of angles symmetrical about 90° . Dissymmetry measurements on solutions of this same detergent at lower detergent and lower potassium bromide concentrations were also made. The values of I_{40}/I_{140} for these runs are given in table 2.

Unless a scattering particle has some dimension greater than about 0.1 the wave length of the exciting radiation, no dissymmetry in the intensity of the light scattered by it will be detected. The observance of extremely little or no dissymmetry in the systems just mentioned enables us to say that, aside from the possibility of the existence of a minute fraction of large particles, the micelles have a maximum dimension no greater than 330 \AA .

In earlier work (2) it was found that the effect of a given amount of added salt in increasing the molecular weight of the micelle was more pronounced the longer the hydrocarbon tail of the detergent molecule. It was found, for example, that *n*-decyltrimethylammonium bromide increased in molecular weight from 10,200 to 10,700 when the solvent was changed from water to 0.0130 *M* potassium bromide. For the same shift in solvents the molecular weight of the micelle of *n*-tetradecyltrimethylammonium bromide increased from 25,300 to 32,100. Because of this dependence of molecular weight on chain length, the sixteen-carbon atom trimethylammonium bromide was picked for dissymmetry work at the high salt concentrations.

It was found necessary to conduct the experiments with *n*-hexadecyltrimethylammonium bromide at temperatures somewhat above 30°C ., since precipitation readily occurred below this temperature. All measurements were made at

LIGHT SCATTERING

TABLE 1

n-Tetradecyltrimethylammonium bromide in 0.302 M potassium bromide

1.1 PER CENT C ₁₄		θ	2.1 PER CENT C ₁₄	
<i>I</i>	$\frac{I_{\theta}}{I_{180-\theta}}$		<i>I</i>	$\frac{I_{\theta}}{I_{180-\theta}}$
5.64	1.027	40	11.61	1.017
4.26	1.012	50	8.69	0.992
3.33	1.006	60	6.97	1.007
2.73	1.000	70	5.72	1.004
2.41	1.004	80	5.03	1.000
2.28	1.000	90	4.81	1.000
2.40		100	5.03	
2.73		110	5.70	
3.31		120	6.92	
4.21		130	8.76	
5.49		140	11.41	

TABLE 2

n-Tetradecyltrimethylammonium bromide

SYSTEM	$\frac{I_{40}}{I_{140}}$
0.13% C ₁₄ in 0.083 M KBr	1.005
0.16% C ₁₄ in 0.083 M KBr	1.024
0.18% C ₁₄ in 0.083 M KBr	1.028

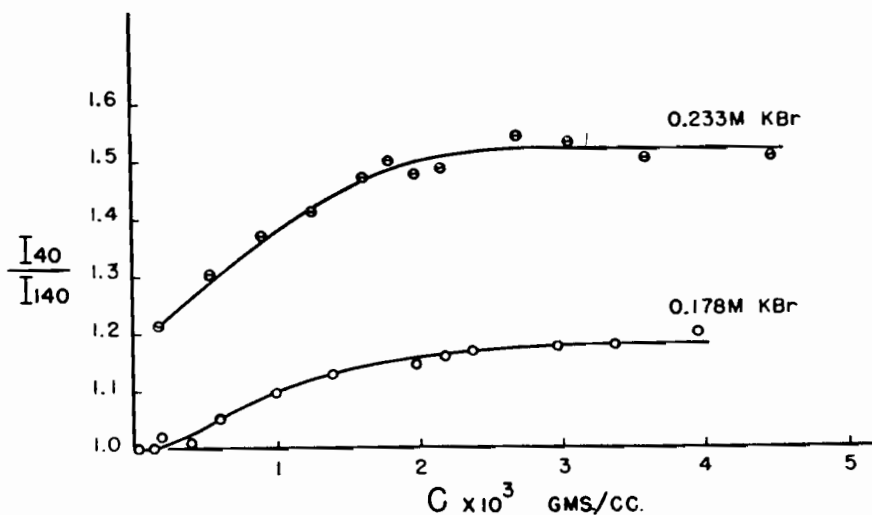


FIG. 1. Dissymmetry vs. detergent concentration for *n*-hexadecyltrimethylammonium bromide.

LIGHT SCATTERING

34°C. \pm 1°. At the higher soap concentrations it was found that the intensity of the scattered light decreased for a period of time after the solutions were placed in the scattering cell. Mixing with the previous solution still clinging to

TABLE 3
n-Hexadecyltrimethylammonium bromide

SOLVENT: 0.178 M KBr			SOLVENT: 0.233 M KBr		
C ₁₆ CONCENTRATION	$\tau \times 10^3$	$\frac{I_{40}}{I_{140}}$	C ₁₆ CONCENTRATION	$\tau \times 10^3$	$\frac{I_{40}}{I_{140}}$
<i>g./ml.</i>	<i>cm.⁻¹</i>		<i>g./ml.</i>	<i>cm.⁻¹</i>	
0.000039	0.074	1.00	0.000179	0.389	1.215
0.000138	0.179	1.00	0.000537	2.15	1.304
0.000198	0.205	1.02	0.000896	4.08	1.372
0.000395	0.606	1.01	0.001254	6.27	1.414
0.000593	1.29	1.05	0.001612	9.15	1.474
0.000988	2.42	1.098	0.001791	10.0	1.503
0.001384	3.79	1.129	0.001970	10.7	1.480
0.001977	6.48	1.147	0.002149	11.0	1.489
0.002175	7.49	1.161	0.002687	15.1	1.545
0.002372	8.28	1.170	0.003045	17.3	1.535
0.002966	10.4	1.178	0.003582	18.0	1.508
0.003361	12.1	1.181	0.004478	21.4	1.511
0.003954	14.5	1.202			

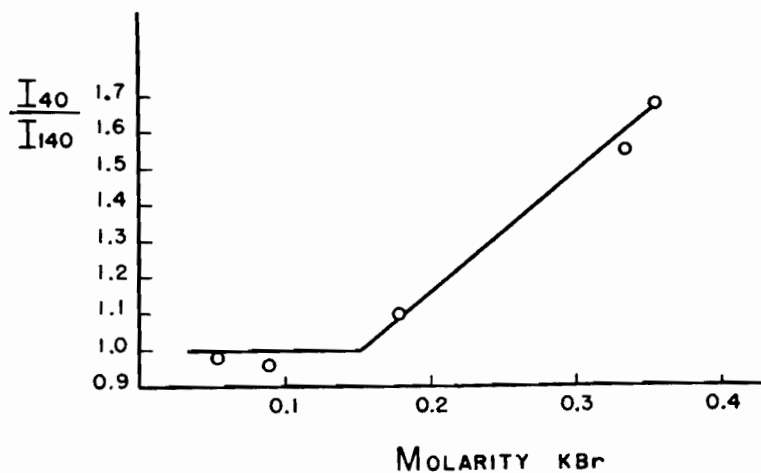


FIG. 2. Dissymmetry vs. concentration of potassium bromide. Concentration of *n*-hexadecyltrimethylammonium bromide = 0.00272 M.

the walls of the cell or an attainment of temperature equilibrium may have been responsible. Final readings were not taken until the scattered intensities appeared to remain constant with time.

In figure 1 are plotted experimentally determined ratios of I_{40}/I_{140} as a function of detergent concentration for two separate runs at different potassium

LIGHT SCATTERING

bromide concentrations. The striking feature of these plots is the rise in dissymmetry as the detergent concentration increases. An initial drop in the dissymmetry curve before the levelling-off process takes place is the usual behavior. The limiting value of the dissymmetry is theoretically characteristic of the scattering particle. In the case at hand the micelles evidently increase rapidly

TABLE 4
n-Hexadecyltrimethylammonium bromide
Concentration = 0.00272 *M*

KBr CONCENTRATION <i>M</i>	$\frac{I_{45}}{I_{145}}$
0.053	0.98
0.089	0.96
0.178	1.10
0.335	1.55
0.356	1.68

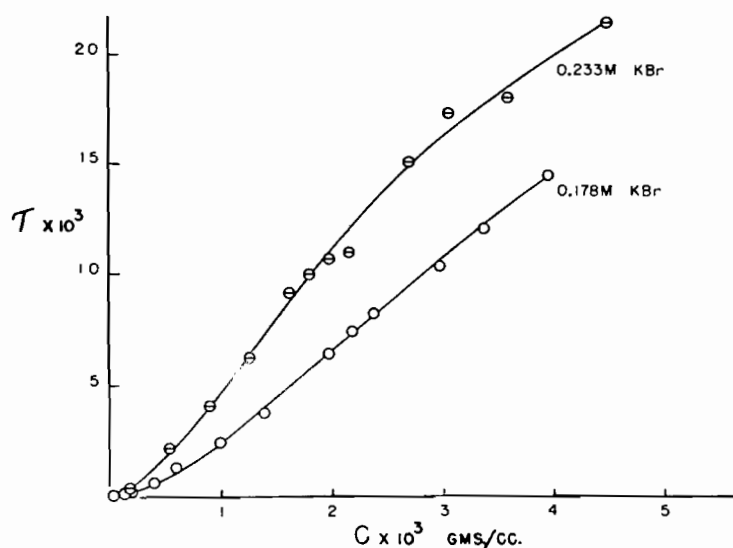


FIG. 3. Turbidity, τ , from 90° scattering measurements vs. concentration of detergent (*n*-hexadecyltrimethylammonium bromide).

in size in a concentration range starting roughly at the critical concentration. Presumably only after a certain detergent concentration is reached do the micelles attain constant size. In this work intensity curves obtained at the highest detergent concentrations on the relatively level portions of the curves have been used in the determinations of the characteristic dimensions. The experimental data used to plot figure 1 are given in table 3.

In figure 2 are plotted the results of an experiment (data in table 4) in which

the detergent concentration was maintained constant and the concentration of the added potassium bromide varied. The increase in dissymmetry with increase in salt concentration is independent proof that salt increases the size of the micelle.

Turbidity *vs.* concentration plots as obtained from 90° scattering (data in table 3) make up figure 3. Considerable rounding off in the region of the critical concentration is evident. In figure 4 are the corresponding $H(C - C_0)/\tau$ plots. H is the well-known refraction constant (2). C_0 , the critical concentration, was

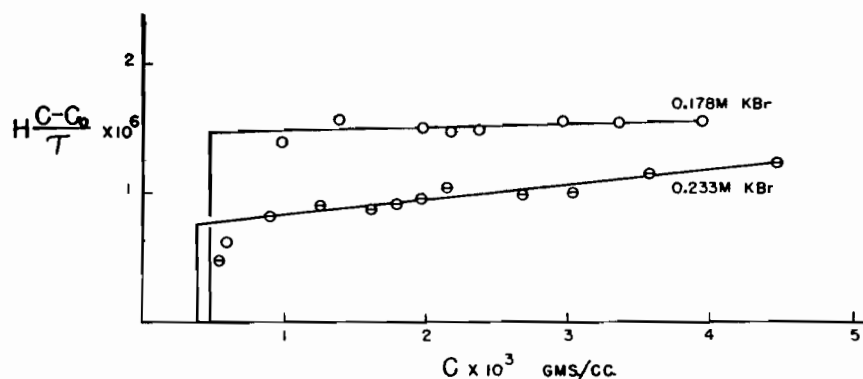


FIG. 4. Plots of $H(C - C_0)/\tau$ vs. C used for determination of the molecular weight of *n*-hexadecyltrimethylammonium bromide.

TABLE 5

n-Hexadecyltrimethylammonium bromide

SOLVENT: 0.178 M KBr	SOLVENT: 0.233 M KBr
$L_d = 683 \text{ \AA}$.	$L_d = 1020 \text{ \AA}$.
$L_s = 615 \text{ \AA}$.	$L_s = 920 \text{ \AA}$.
$L_r = 870 \text{ \AA}$.	$L_r = 1312 \text{ \AA}$.
MW (disk) = 10.6×10^6	MW (disk) = 23.6×10^6
MW (sphere) = 73.4×10^6	MW (sphere) = 246.0×10^6
MW (rod) = 0.948×10^6	MW (rod) = 1.44×10^6
Experimental MW = 0.690×10^6 (not corrected)	Experimental MW = 1.34×10^6 (not corrected)
Experimental MW = 0.795×10^6 (corrected for dissymmetry; rod model)	Experimental MW = 1.86×10^6 (corrected for dissymmetry; rod model)

obtained for each run by a least-squares method, which gives also the best plot of $H(C - C_0)/\tau$. C is the detergent concentration and τ is the turbidity of the detergent solution in excess of that of the solvent. The molecular weight of the solute is equal to the reciprocal of the intercept of the $H(C - C_0)/\tau$ plot at the critical concentration. When dissymmetry is present these molecular weights must be corrected accordingly. Values are given in table 5.

Since the two most frequently mentioned models for the micelle have been the cylinder and the sphere, it was decided to apply the experimental data to

them first. In the cylindrical lamellar model of the micelle the polar heads form the ends of the cylinder, while the hydrocarbon tails aligned in two adjacent layers make up the body. Such a micelle would approach the shape of a disk if large enough to produce dissymmetry of a measurable value. Its thickness would be approximately twice the length of the detergent molecule. A disk of negligible thickness (negligible compared with the wave length) was calculated to scatter light (incident light polarized perpendicular to the plane of observation) according to the relation:

$$I = 1 - \frac{X^2}{6} + \frac{X^4}{72} - \frac{X^6}{1440} + \frac{X^8}{43200} - \dots \quad (2)$$

This expression may be written

$$I = \frac{X^0}{1} - \frac{X^2}{6} + \sum_{n=3}^{n=\infty} \frac{X^{2(n-1)}}{\left(2n + \frac{b_{n-1}}{b_{n-2}}\right) b_{n-1}} \cos(n+1)\pi \quad (3)$$

in which b_n represents the denominator of the n^{th} term. $b_1 = 1$ and $b_2 = 6$. $X = 2\pi L_d/\lambda \sin \theta/2$. L_d is the diameter of the disk. The intensity of the light scattered in the forward direction is taken as unity.

Debye has calculated that a sphere will scatter light according to the relation

$$I = \left[\frac{3}{X^3} (\sin X - X \cos X) \right]^2 \quad (4)$$

where

$$X = \frac{2\pi L_s}{\lambda} \sin \frac{\theta}{2}$$

L_s is the diameter of the sphere.

With the aid of relationships 2 and 4 and the second method of determining characteristic dimensions described under the heading of theory, disk and sphere diameters for two detergent-potassium bromide systems were calculated. Micelle molecular weights were computed from these diameters, assuming a density of unity³ and a length for the detergent molecule of 24 Å. The results are

³ In our calculations we have assumed the density of the micelle to be unity. Although this value is not likely to be exact, it is a good enough approximation for our purpose. We have estimated micelle densities (d) from the results of viscosity measurements made in this laboratory and Einstein's formula for the rigid sphere:

$$[\eta] = \frac{2.5}{d}$$

In the case of *n*-dodecyltrimethylammonium bromide in 0.0235 *M* potassium bromide a density of 0.612 g./ml. was calculated for the aggregates.

The application of Einstein's equation to the micelle is, of course, open to criticism as to details. However, the deduction that in solution soap micelles have a very high density as compared with the usual polymers is reliable, whereas the accuracy of the calculated value of the density must be poor.

LIGHT SCATTERING

listed in table 5; there is no agreement between the calculated and observed molecular weights. Therefore it was decided to repeat the procedure, using the rod as a model for the micelle.

TABLE 6
Intensity of light scattered by rigid rod of length L

$$I = \frac{1}{X} \int_0^{2X} \frac{\sin u}{u} du - \left(\frac{\sin X}{X} \right)^2$$

$$X = \frac{2\pi L}{\lambda} \sin \frac{\theta}{2}$$

X	I	X	I
0.10	0.9990	1.50	0.7902
0.20	0.9956	1.75	0.7313
0.30	0.9901	2.00	0.6724
0.40	0.9824	2.25	0.6156
0.50	0.9728	2.50	0.5627
0.60	0.9611	3.00	0.4727
0.70	0.9476	3.50	0.4056
0.80	0.9324	4.00	0.3578
0.90	0.9156	4.50	0.3228
1.00	0.8973	5.00	0.2949
1.25	0.8465		

According to Debye a rod of negligible diameter will scatter light in accordance with the relation

$$I = \frac{1}{X} \int_0^{2X} \frac{\sin u}{u} du - \left(\frac{\sin X}{X} \right)^2 \quad (5)$$

where

$$X = \frac{2\pi L_r}{\lambda} \sin \frac{\theta}{2}$$

L_r is the rod length. In table 6 the values of this function are given for a series of values of the parameter X .

In figure 5 the plot of $\log I$ vs. $\log \sin \theta/2$ for one of the runs (solvent 0.233 M potassium bromide) has been projected upon the theoretical $\log I$ vs. $\log X$ plot for the rod. The separation of the origins for the horizontal axes is 0.405 and equal to $\log 2\pi L_r/\lambda$. L_r is computed to be 1312 Å. The molecular weight of a rod of this length, a diameter twice the length of the *n*-hexadecyltrimethylammonium bromide molecule (a value of 48 Å. was taken), and density of unity is calculated to be 1.44×10^6 . The experimentally determined molecular weight is 1.86×10^6 .

For the second run (solvent 0.178 M potassium bromide), L_r is found to be 870 Å. From this L_r a molecular weight of 9.48×10^5 is calculated. The experi-

LIGHT SCATTERING

mentally determined molecular weight for this run is 7.95×10^5 . With the rod model the agreement is as good as can reasonably be expected.⁴

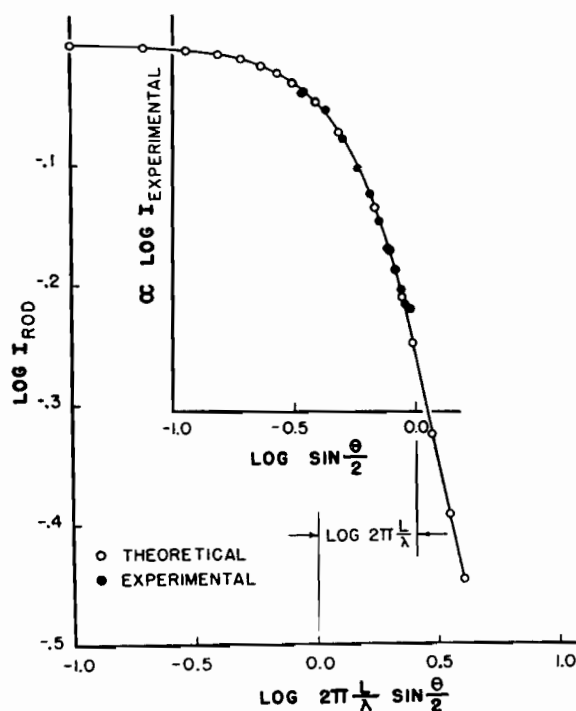


FIG. 5. Superposition of experimental data and theoretical curve, assuming a rod model for the micelle (*n*-hexadecyltrimethylammonium bromide).

CONCLUSIONS AND SUMMARY

1. No real dissymmetry was detected in solutions of *n*-tetradecyltrimethylammonium bromide in 0.083 *M* and 0.202 *M* potassium bromide. The detergent micelles in these solutions cannot have a dimension greater than roughly 300 Å.

2. The micelles of *n*-hexadecyltrimethylammonium bromide in 0.178 *M* and 0.233 *M* potassium bromide are large enough to produce measurable dissymmetry in the scattered light. Dissymmetry measurements showed conclusively that these micelles are not spherical or disk-like in shape; analysis of the data indicates that the micelles are rod-like. The cross section of such a rod would

⁴ The objection might be raised that an experimental molecular weight derived for concentrations near the critical is being compared with molecular weights calculated for higher concentrations at which the dissymmetry of scattering is well developed. However, figure 4 shows only a small slope for the straight lines representing $H(C - C_0)/\tau$ versus C and this means that an unsophisticated calculation of the molecular weight directly from the observed turbidity values at higher concentrations will not differ materially (at least for our purpose) from the value given in the table. As a matter of fact, this admittedly rough calculation yields values ranging from 0.808×10^6 to 1.01×10^6 for the four highest concentrations in the case of 0.233 *M* potassium bromide (before correction for dissymmetry).

be circular, with the polar heads of the detergent lying on the periphery and the hydrocarbon tails filling the interior. The ends of such a rod would most certainly have to be rounded off with polar heads. This rod would differ from the cylindrical model, in that the hydrocarbon tails would be perpendicular to the axis of the symmetry rather than parallel to it.

3. The angular distribution of scattering for disks of negligible thickness has been calculated.

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