

$$\frac{1}{\tau} \cong k_{n,n-1}/(n - n/e) = \frac{1.6k_{n,n-1}}{n} \quad (17)$$

This is in accord with the intuitive notion that for a sequence of $n - 2$ equally slow irreversible steps the overall relaxation time must be of the order of n times the average time required for each step.

Turning to the T-jump experiments, one must deal with a process occurring under conditions never greatly different from equilibrium. A first approximation to the relaxation time may then be obtained by examining the sequence of steps leading to the complete dissolution of one particular micelle A_n . The overall process may be considered as a series of unit size changes with an average lifetime between successive changes of the order of $\Delta t = 1/2k_{n,n-1}$. Because the system is nearly at equilibrium, the forward and reverse rates for each reaction 11 are nearly equal, and at any stage size changes in either direction have almost the same probability. The dissolution process thus resembles a one-dimensional random walk with steps of unit size and with the final state $n - 2$ steps away from the initial state. Standard treatments¹² show that the mean distance travelled after s steps is $s^{1/2}$ times the step length. On the average, the number of steps taken during the transition from reactant to product is then $(n - 2)^2$, or for large micelles essentially n^2 . The time required $n^2\Delta t$ is of the same order as the relaxation time, so that

$$\tau \cong n^2/2k_{n,n-1} \quad (18)$$

This expression, like (10) above, fails to account for the observed increase of $1/\tau$ with increasing concentration. However, using typical T-jump data for sodium dodecyl sulfate,³ *i.e.*, $1/\tau = 600 \text{ sec}^{-1}$ and $n = 95$, it yields an estimated $k_{n,n-1}$ of $3 \times 10^6 \text{ sec}^{-1}$, well above the lower limit based on nmr data for trifluorododecyl sulfate and given in (4) above.

Although (18) is only a rough approximation it appears to represent the relation between $k_{n,n-1}$ and the τ values found in the T-jump experiments much more adequately than either eq 6 or 10, based on the KHDS model, implying that micellization does involve a succession of many steps with similar rates. Our model suggests that in stopped-flow experiments where the final concentration is far below the cmc, the relaxation should appear to be faster, with τ given approximately by (17). The results presented here further suggest that if fluorine nmr spectra were obtained in a 52-kG field, where the term $\nu_{\text{mic}} - \nu_{\text{aq}}$ of eq 2 or 3 would become 240 Hz, line broadening due to the exchange process might become observable, allowing $k_{n,n-1}$ to be evaluated more accurately and much more directly.

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Micelle Shape and Size^{1a}

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Simple geometrical considerations indicate (as previously noted in 1955 by Tartar) that most of the common small soluble micelles must be ellipsoidal rather than spherical in shape. It is shown that spherical and ellipsoidal micelles represent a family of micellar shapes within which the micelle aggregation number and the surface area available to polar head groups are continuously variable, and it is suggested that amphiphiles with a single hydrocarbon chain per polar head group form micelles with a distribution of sizes and shapes within this family. Amphiphiles with two hydrocarbon chains per head group require a smaller surface area per hydrocarbon chain, and geometrical considerations then indicate a preference for extended bilayers or vesicles rather than spherical or ellipsoidal micelles, in agreement with experimental observation.

The purpose of this paper is to consider the relation between the size and shape of micelles formed in aqueous solution by amphiphilic molecules or ions with aliphatic hydrocarbon tails. The surface area available to hydrophilic head groups will also be considered.

The calculations are similar to calculations previously reported by Tartar,² whose paper appears to have been

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ignored in more recent papers considering the shape of small micelles. The calculations are based on two assumptions.

(1) The micelle contains a hydrophobic core consisting entirely of portions of the hydrocarbon chains. It is assumed that the terminal CH_3 groups are always contained in this core, but one or more methylene groups near the amphiphile head group may not be.³ It is assumed that no solvent enters the core. It should be noted that, though this overall assumption is generally supported by a variety of studies,⁷⁻¹¹ evidence against it has been presented for amphiphiles with fluorinated (CF_3) terminal groups.¹²

(2) The density of this core is predictable to within a few per cent. The data given by Reiss-Husson and Luzzati¹³ have been used to obtain the volume occupied by an alkyl chain of n_C carbon atoms embedded in the hydrocarbon core. Near room temperature, with the volume v in $\text{\AA}^3/\text{chain}$, one obtains

$$v = 27.4 + 26.9n_C \quad (1)$$

Essentially the same relation would have been obtained on the basis of the published densities of liquid hydrocarbons or even by the empirical volume additivity rule of Traube.¹⁴

Because no holes may exist within the micelle, one or more dimensions are always limited by the maximum possible extension of a hydrocarbon chain. This distance is obtained from the distance of 2.53 \AA between alternate carbon atoms of a fully extended chain,¹⁵ with the addition of the van der Waals radius of the terminal methyl group (2.1 \AA)¹⁶ and one-half the bond length to the first atom not contained within the hydrophobic core ($\approx 0.6 \text{\AA}$). The maximum length l_{max} for a chain with n_C embedded carbon atoms, in \AA , becomes

$$l_{\text{max}} = 1.5 + 1.265n_C \quad (2)$$

Globular Micelles

The radius of the hydrophobic core of a spherical micelle may not exceed l_{max} and the maximum number of hydrocarbon chains per micelle is thus uniquely determined for each value of n_C by combination of eq 1 and 2. For amphiphiles with a single hydrocarbon chain this is equivalent to the maximum value for the micelle aggregation number, m . Table I shows calculated values for several values of n_C and comparison of these with experimental micelle aggregation numbers immediately shows that most of the common small compact micelles cannot be truly spherical in shape. For example, the weight-average aggregation number (\bar{m}_w) of dodecyl sulfate micelles ranges from 62 in the absence of added salt to 126 in 0.5 M NaCl.^{17,18} The maximum number for a spherical micelle depends on the choice of a value for n_C , but even with $n_C = 12$ the maximum value of m is only 56. There is good evidence that at least one and perhaps more of the CH_2

Table I: Micelle Aggregation Number for Globular Micelles^{a,b}

	n_C				
	6	10	12	15	20
Sphere, $r_0 = l_{\text{max}}$					
	17	40	56	84	143
Ellipsoids, $b_0 = l_{\text{max}}$					
Prolate					
$a_0/b_0 = 1.25$	21	50	70	105	178
$a_0/b_0 = 1.5$	25	60	84	126	214
$a_0/b_0 = 1.75$	29	70	97	146	250
$a_0/b_0 = 2.0$	33	80	111	167	285
Oblate					
$a_0/b_0 = 1.25$	26	63	87	131	223
$a_0/b_0 = 1.5$	38	90	125	188	321
$a_0/b_0 = 1.75$	51	123	171	256	437
$a_0/b_0 = 2.0$	67	160	223	335	570

^a n_C represents the number of carbon atoms in that portion of the alkyl chain which is incorporated in the hydrophobic core. This will generally be less than the total length of the hydrocarbon chain. ^b The tabulated figures are the number of hydrocarbon chains per micelle. This is equal to the micelle aggregation number m for amphiphiles with a single hydrocarbon chain. It would be equal to $2m$ for amphiphiles with two chains, each of n_C carbon atoms.

groups of amphiphile alkyl chains do not in fact enter the hydrophobic core in micelle formation, so that n_C for a dodecyl chain should be assigned a value less than 12, leading to smaller maximal values for m . Thus for $n_C = 10$ the maximal value of m for a spherical micelle is only 40.¹⁹

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- (19) Tartar² came to the same conclusion. Only one of the systems analyzed by him, alkyl sulfonates in the absence of added salt, had micelle aggregation numbers consistent with a spherical shape, but this result was based on the assumption that the entire hydrocarbon chain is used in the formation of the hydrophobic core. With n_C smaller than the actual length of the alkyl chain, an ellipsoidal shape would be required for this system also.

To incorporate a larger number of hydrocarbon chains in a micelle, a distortion in the micelle shape is required. The simplest possibilities are ellipsoids of revolution: the minor semiaxis b_0 of an ellipsoid may not exceed l_{\max} , but the major semiaxis a_0 is not limited and an increase in the available volume is thus provided. Table I shows pertinent calculations, for selected values of n_C , for both prolate and oblate ellipsoids. It is seen that only small values of the ellipsoidal axial ratio (a_0/b_0) are required for a substantial gain in the micelle aggregation number, sufficient to account for experimentally observed values.

Formation of an ellipsoid ($b_0 = l_{\max}$) from a sphere ($r_0 = l_{\max}$) is accompanied by an increase in total surface area (S), but the increase is less than the increase in volume. The surface area per hydrocarbon chain is thus diminished. For amphiphiles with a single hydrocarbon chain this is equivalent to the surface area per molecule (S/m) and this is an important quantity because it is a measure of the separation between amphiphile head groups. Because the head groups extend away from the surface of the hydrophobic core, one is generally interested in knowing the value of S/m at some distance d outside the core surface, *i.e.*, at the surface of a sphere with radius $r = r_0 + d$ or at the surface of an ellipsoid defined by semiaxes $a = a_0 + d$, $b = b_0 + d$.

Figure 1 shows a typical example of the dependence of S/m on micelle aggregation number. The calculations are for $n_C = 12$ and $d = 2 \text{ \AA}$, and for the values of m given in Table I for spheres and ellipsoids with r_0 or $b_0 = l_{\max}$. Additional data have been generated by making calculations for globular micelles with hydrophobic cores smaller than maximal size, *i.e.*, spheres with $r_0 < l_{\max}$ and ellipsoids with $b_0 < l_{\max}$. The figure shows that, within the range of m values considered, it is a good approximation to consider S/m as a single-valued function of m for all globular micelles with a given value of n_C , only minimally affected by the actual micelle shape.

It is evident from Figure 1 that spherical and ellipsoidal micelles represent a family of conformations within which the micelle aggregation number is continuously variable, with a parallel variation in S/m . Any actual system that forms globular micelles will undoubtedly consist of a distribution of sizes and corresponding shapes about an optimal value of S/m . This optimal value will be determined (at a given total amphiphile concentration) by the opposing influences of repulsion between head groups and the tendency to avoid contact between the surface of the hydrophobic core and the solvent. Repulsion between head groups will tend to increase S/m , but will become unimportant when S/m becomes sufficiently large. When S/m becomes large there will necessarily be contact between water molecules and the core surface, and a consequent pressure to reduce S/m . The optimal value of S/m

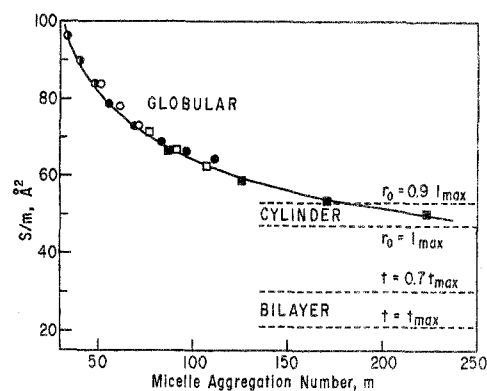


Figure 1. Surface area per amphiphile molecule possessing a single alkyl chain, with 12 carbon atoms per chain embedded in the hydrophobic core. The values of S/m are calculated at a distance of 2 \AA outside the core surface: ●, dimensions as in Table I (sphere and prolate ellipsoids); ■, dimensions as in Table I (oblate ellipsoids); ○, spheres with $r_0 < l_{\max}$ to $r_0 = 0.85l_{\max}$; □, prolate ellipsoids ($a_0/b_0 = 1.5$) with $b_0 < l_{\max}$ to $b_0 = 0.85l_{\max}$; □, same for oblate ellipsoids. Values for cylindrical micelles and bilayers are also shown. They are independent of m , apart from end effects, which have not been taken into consideration.

will be determined by proper balance between these factors. (These are the only energetic factors for an isolated micelle in equilibrium with its environment. At high micelle concentrations an additional pressure for formation of large micelles exists, as mentioned below in the Discussion.)

It may be noted that the experimental observation that \bar{m}_w and \bar{m}_n may be essentially the same for most systems forming globular micelles²⁰⁻²² does not require a particularly narrow size distribution. For example, the standard deviation of a Gaussian distribution function can be as high as $\bar{m}/4$ without introducing a measurable difference between \bar{m}_w and \bar{m}_n . Systems containing large micelles often have very broad distribution functions, with \bar{m}_w significantly larger than \bar{m}_n .²²

Cylindrical Micelles, Bilayers, and Vesicles

Cylindrical micelles can grow in length without limit. Ignoring effects of the cylinder ends, the available surface area per single-chain amphiphile molecule is independent of the aggregation number. The actual value of S/m is smaller than for globular micelles, in the range of micelle size normally observed for globular micelles, as is illustrated for $n_C = 12$ in Figure 1, but for larger micelles the surface areas become about equal.

Bilayers can also accommodate a limitless number of amphiphile molecules without alteration in the available surface area per amphiphile. Values of S/m are generally much smaller than for any other type of micelle, even if the thickness (t) of the hydrophobic

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core is made substantially less than its maximum value ($t_{\max} = 2l_{\max}$), as would be true if the hydrocarbon chains are not fully extended or not perpendicular to the bilayer surface. The values of S/m are essentially independent of n_C , *i.e.*, the values shown in Figure 1 apply to any value of n_C . For bilayers there is no gain in S/m as one moves away from the surface of the hydrophobic core.

Bilayers are capable of forming spherical vesicles with an internal solvent-filled cavity. One bilayer surface is expanded in this process and the other is contracted. The net increase in S/m is small. Even if the radius of the internal cavity is as small as the thickness of the bilayer core, the increase in S/m is only 15%. As the overall vesicle size increases, S/m approaches the value for an infinite planar bilayer.

Amphiphiles with Two Alkyl Chains

All of the preceding calculations apply to amphiphile molecules consisting of one head group and one alkyl chain with n_C carbon atoms per chain participating in formation of the hydrophobic core. For amphiphiles with two alkyl chains, each with n_C carbon atoms participating in formation of the hydrophobic core, the same calculations apply, except that the number of amphiphile molecules will be one-half the m values for single chain molecules and the surface areas per head group will be twice as large. This means that the S/m values for bilayers or vesicles for two-chain amphiphiles will be comparable to the S/m values for globular micelles or cylinders for single-chain amphiphiles. It is probably not necessary to seek a more complex explanation than this simple fact to account for the experimental observation that biological phospholipids tend to form bilayers or vesicles rather than globular micelles.⁷

Discussion

The results of Figure 1 indicate that one can obtain a value of S/m for globular micelles from the aggregation number alone, the only uncertainty being in the proper value for n_C . Thus the m values previously cited for dodecyl sulfate micelles ($\bar{m}_w = 62$ in the absence of added salt, increasing with ionic strength to $\bar{m}_w = 126$ in 0.5 M NaCl) correspond to a decrease in S/m from 90 Å² in the absence of added salt to 67 Å² in 0.5 M NaCl. These values are based on an assumed value of $n_C = 10$, and represent surface areas at a distance of 4.5 Å from the surface of the hydrophobic core, which, with the choice of $n_C = 10$, would represent the approximate location of the sulfur atom of the sulfate head group. With the unrealistic choice of $n_C = 12$, and a corresponding value of 2 Å for the location of the sulfur atom beyond the core surface, the S/m values would have been 77 Å² in the absence of added salt and 60 Å² in 0.5 M NaCl. The decrease in S/m with added salt is of course to be expected as a result of the decrease in the effect of electrostatic repulsion.

Table II shows another calculation, based on the observed average micelle sizes for *N*-alkyl betaines in water, as a function of the length of the alkyl chain.²³ It is again assumed that n_C is smaller by 2 carbon atoms than the actual length of the alkyl chain. Although the head group in this case is zwitterionic, the observed values of S/m are of the same order of magnitude as those for ionic micelles, such as dodecyl sulfate, at high ionic strength. The most likely explanation is that the repulsive force in these micelles is in fact like that in an ionic micelle, resulting from coulombic repulsion between the $N(CH_3)_2^+$ groups of the betaine head groups, which, being directly attached to the alkyl chain, would have to be located close to the hydrophobic core. The negatively charged COO^- groups would lie at a greater distance, and would be more mobile, and would resemble the diffuse layer of counterions near the surface of an ionic micelle. Both the critical micelle concentrations and the micelle aggregation number for decyl and dodecyl betaines are in fact nearly the same as the corresponding figures for decyl- and dodecyltrimethylammonium bromides in the presence of about 0.2–0.3 M NaBr.^{18,24} A perhaps unexpected feature of Table II is the considerable decrease in S/m with increasing chain length. The change in the optimal value for S/m may reflect the increased magnitude of the hydrophobic effect per molecule, the repulsive force remaining constant.

Table II: Results for *N*-Alkyl Betaines^a

Alkyl chain	n_C	\bar{m}_w (exptl)	Ellipsoid		$S/m, \text{Å}^2$	
			axial ratio Prolate	Oblate	Pro- late	Oblate
C ₈	6	24	1.44	1.20	97	95
C ₁₀	8	34	1.26	1.12	92	91
C ₁₁	9	58	1.74	1.32	79	77
C ₁₃	11	87	1.84	1.35	74	71
C ₁₅	13	130	2.02	1.42	70	66

^a Experimental values of \bar{m}_w from Swarbrick and Daruwala.²³

It should be noted in conclusion that an important factor in the determination of the optimal value for S/m was not mentioned in the earlier discussion of the subject, this being the factor of total amphiphile concentration. In any system in which m is continuously variable an increase in amphiphile concentration necessarily favors the formation of larger micelles. (A rigorous thermodynamic relation for the change in \bar{m} with increasing concentration of micelles is given by eq 16.99 of Hall and Pethica²⁵). It is evident that

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this effect will lead to a decrease in S/m for globular micelles as the amphiphile concentration is increased. Figure 1 shows that the range of S/m values for cylindrical micelles overlaps the range for globular micelles at moderately large values for m and under these conditions a transition from globular to cylindrical form

would appear likely. That such transitions actually occur at high amphiphile concentration has been well established by Reiss-Husson and Luzzati.^{13,26}

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Aureole Profile in Bursting Soap Films. Surface Tension and Surface Relaxation in Rapidly Compressed Monolayers

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Reflectometric methods for studying the thickness changes occurring during the bursting of vertical soap films are described. From measurements of the thickness profile and velocities in films of sodium dodecyl sulfate, the surface tensions in the film can be calculated using the theory of Frankel and Mysels. If no desorption of surfactant molecules occurs, the aureole expands linearly with time and the bursting may be called self-similar; when desorption of surfactant occurs from the soluble monolayers comprising the outer surfaces of the film, deviations from self-similarity arise. Such deviations are observed in the film studies, and it is estimated that 25% of the molecules at the surfaces of a thin film of sodium dodecyl sulfate desorb during rapid compression (*i.e.*, thickening) of the film in less than 10^{-8} sec. From published values of the surface area per molecule of sodium dodecyl sulfate in equilibrium films it can be calculated that the minimum area which the surfactant can occupy is 28 \AA^2 .

The study of bursting soap films by means of high-speed flash photography has revealed the existence of regions of shrinking film material. Mysels called these disturbed regions aureoles.² An aureole expands rapidly in front of the growing hole. Aureoles are caused by gradients in the surface tension of the rapidly contracting film near the rim of the hole.²⁻⁷ The surfaces of bursting soap films disappear at rates of the order of 10 m sec^{-1} and therefore studies of aureoles afford a novel means of investigating the behavior of soluble monolayers in a rapidly shrinking area, *i.e.*, at an extreme rate of compression.

The postulated surface tension gradients can be calculated from the thickness profile of an aureole and the velocity of its expansion over the undisturbed film. The surface tensions σ in the aureole are then obtained by integration over the aureole surface.³ The quantitative experimental data at the basis of such computations must, however, be rather precise.

The earlier investigations of aureoles were done with flash photographic techniques. A high-speed photograph of a bursting film gives an overall view of the burst at some instant. Series of such photographs

could be obtained for comparable films and with a variation of the time interval between the initiation of the burst at t_0 and the moment when each photograph was taken.² If these time intervals were accurately known, and if also the thicknesses δ in the aureole could be deduced with sufficient precision from the interference colors or patterns in the photographs, then such series of photographs would contain all the input information for the calculation of aureole surface tensions. It is, however, very difficult and certainly impractical to extract data of the desired quality from experiments of

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