

Zero Surface Tension (ZST) Theory of Micellization

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A theory of micellization is proposed describing micelle formation as an interrupted droplet nucleation process. The aggregation stops when a surface tension of the micelle close to zero or negative is produced by the growing surface concentration of polar heads. The decrease in surface tension is caused by repulsive forces between head groups of steric or electrostatic origin.

From data on aggregation numbers of oligo-oxyethylene derivatives of n-alkanoles, the distance of displacement of the surface of tension from the surface of the hypothetical hydrocarbon core of the micelle is calculated. The surface of tension is positioned from 5 to 11 Å *inside* the hydrocarbon core. Those figures are somewhat higher than calculated by Tolman for liquids in equilibrium with vapor or by Nielsen and Sarig for droplet nucleation within a miscibility gap in a ternary liquid system. The reason is probably the large size of the head groups of the amphiphiles considered.

The zero surface tension model mostly coincides with the phase separation model with regard to data on critical micelle concentration (cmc). From such data the thermodynamics of transfer of the hydrophobic part of the amphiphile can be calculated because of the small or vanishing contribution of surface free energy in a zero surface tension model.

The mean shape of micelles is assumed spherical rather than ellipsoidal. For large micelles a "central hole" is avoided by head group burial or water inclusion in the hydrophobic core. Because of the low surface tension, micelles are vigorously oscillating and dividing/coalescing predominantly according to a "peanut shape". Some observed anomalies in rheology and light scattering may be explained that way. The cloud point observed for nonionic micelles is possibly the temperature where the surface tension becomes exactly zero and long surfactant cylinders are formed by secondary aggregation of micelles.

The diffuse electric double layer lowers the surface tension more at low ionic strength than at high. Therefore, the aggregation number of ionic

micelles increases sharply with increasing ionic strength and approaches a nonionic limit with bound counterions.

In the past decade, a number of important contributions to the theory of micelles has appeared from the point of view of phenomenological thermodynamics¹⁻⁴ and from the point of view of reaction kinetics (relaxation processes).⁵⁻⁸ Nevertheless, the field of micelle research still appears to be confusing, and it is hard to make genuine predictions from the existing theories. As an example, take the theory of Tanford where we have two adjustable parameters: one correction for "surface roughness" and a coefficient of "opposing forces" of steric origin. The latter is not calculable from first principles, see the 1980 edition of Ref. 1, pp. 72–73.

It is the purpose of the present paper to propose a *simple* picture of micellization by using some of the features of the previous thermodynamic models and suggesting some modifications which seem inevitable. The most important modification made in the present paper is the introduction of a micellar surface tension which varies with the aggregation number of the micelle according to simple laws known from the surface chemistry of monolayers. The approximation made here is to regard the micelle interior as an oil phase and the polar heads at the oil-water interface as "surfactants" which lower the interfacial tension. Now, steric effects become calculable by means of an excluded area approach.

The surface concentration of heads increases with aggregation number, and the surface tension becomes lower. Finally, a situation is reached, where the surface tension becomes close to zero or even negative. Then, the micelle will be destabilized by

Brownian motion or micro-Marangoni effects, and dissolution of the micelle occurs. Thus, the picture of micellization which is given here is one which might be described as an "interrupted nucleation process". The difference between classical theory of nucleation and the present theory of micellization is precisely the *variable surface tension* in the latter theory. The value zero of the surface tension provides an upper bound for the size of the micelle and prevents phase separation in any macroscopic sense taking place.

THEORY OF NONIONIC, SPHERICAL MICELLES

Free amphiphile molecules in aqueous solution (A) associate into a cluster of aggregation number m according to the equilibrium K_m being the association constant. Assuming ideality we have from the law of mass action eqn. (1), where X and X_m

$$m\text{A} \rightleftharpoons \text{A}_m$$

$$K_m = \frac{X_m}{X^m} = \exp\left[\frac{-\Delta G_m^\ominus}{kT}\right] \quad (1)$$

are the mol fractions of free amphiphile and m -mer, respectively. ΔG_m^\ominus is the standard free energy of

formation of one m -cluster, k is Boltzmann's constant and T is the absolute temperature. For the standard free energy we have eqn. (2), μ_m^\ominus being the

$$\Delta G_m^\ominus = \mu_m^\ominus - \mu_A^\ominus m \quad (2)$$

standard chemical potential of the aggregate and μ_A^\ominus the standard chemical potential of the free amphiphile. The standard chemical potential of the aggregate can be divided into two parts, eqn. (3),

$$\mu_m^\ominus = m\mu_B^\ominus + \mu'_m \quad (3)$$

where μ_B^\ominus is the size-independent part (due to hydrophobicity) and μ'_m the size-dependent part [eqn. (4)].

$$\mu'_m = f(m) \quad (4)$$

Following Ruckenstein and Nagarajan³ we introduce a rescaled mol fraction of free amphiphile, eqn. (5).

$$\xi \equiv X \exp\left[\frac{\mu_A^\ominus - \mu_B^\ominus}{kT}\right] \quad (5)$$

From the preceding equations we obtain eqn. (6).

$$X_m = \xi^m \exp\left[\frac{-\mu'_m}{kT}\right] \quad (6)$$

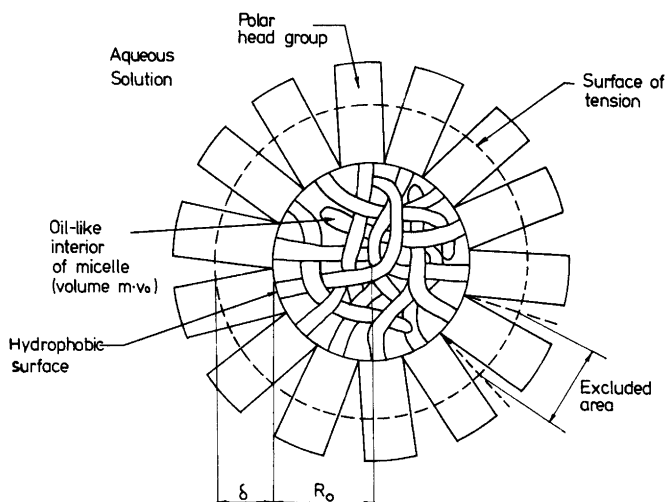


Fig. 1. Model of the micelle as a spherical oil-like droplet surrounded by polar heads. For simplicity, the surface of tension is situated outside the hydrophobic core as assumed by previous authors. In reality δ shows up to be negative. The polar heads are not in their state of closest packing, but in the state yielding zero surface tension, but the difference in area/head is not great.

Fixing the mol fraction of free amphiphile, the rescaled mol fraction ξ is fixed, and from any assumed functional dependence $f(m)$ in eqn. (4), the size distribution of micelles can be calculated from eqn. (6).

The picture of the micelle is the one given schematically in Fig. 1. The hydrocarbon chains of the amphiphile molecules are assumed to form an "oil-like" hydrophobic core. The core is surrounded by polar head groups floating as "surfactants" at the oil-water interface. The volume of the hydrophobic core is simply given by mv_o , where v_o is the volume of a single hydrocarbon chain given by eqn. (7),^{1,3} n_C being the number of carbon atoms in the hydrocarbon chain. Eqn. (7) is based on

$$v_o(\text{\AA}^3/\text{amphiphile}) = 27.4 + n_C \cdot 26.9 \quad (T = 298.2 \text{ K}) \quad (7)$$

volume measurements of Reiss-Husson and Luzzati on pure alkanes.⁹ Thus, the radius of the hydrophobic core is given as eqn. (8), with β given in eqn. (9).

$$R_o = \beta \cdot \sqrt[3]{m} \quad (8)$$

$$\beta \equiv \sqrt[3]{\frac{3v_o}{4\pi}} \quad (9)$$

The so-called *surface of tension* for small droplets is located in such a way that the overpressure in the droplet satisfies the Laplace equation, eqn. (10), with γ = surface tension.

$$\Delta p = \frac{2\gamma}{R_o + \delta} \quad (10)$$

For more details, the papers of Tolman¹⁰ and Kondo¹¹ should be consulted.

The size-independent part of the standard free energy of transfer ($\mu_A^\ominus - \mu_B^\ominus$) is assumed to be a linear function of n_C as estimated from data of solubilities of hydrocarbons in water (Ref. 1, Chapter 2). We shall return to this later and confine ourselves here to the size-dependent part of the standard free energy of the micelle μ'_m , eqn. (11), where a is the area available for one polar head at the surface of tension, *viz.* eqn. (12).

$$\mu'_m = \gamma ma + \frac{2\gamma}{R_o + \delta} \left[\frac{4}{3} \pi (R_o + \delta)^3 \right] \quad (11)$$

$$a = \frac{4\pi}{m} (R_o + \delta)^2 \quad (12)$$

The first term on the r.h.s. of eqn. (11) is the contribution from the surface free energy of the micelle. The second term is the contribution from the Laplace overpressure to the standard chemical potential of the micelle. Eqn. (11) may be rewritten as eqn. (13).

$$\mu'_m = \frac{44}{3} \pi \gamma [\beta \cdot \sqrt[3]{m} + \delta]^2 \quad (13)$$

It should be remembered, however, that the surface tension γ is a function of m . The relation between γ and the area per polar head will be assumed to be similar to the relation between those quantities at an oil-water interface with surfactants. We shall use the simplest possible relation, *viz.* the Szyszkowski isotherm, which is obtained by combination of the Langmuir adsorption isotherm with the Gibbs adsorption isotherm.^{12,13} Thus, we have eqn. (14), where Π is the surface pressure, γ_o is the surface tension of the pure oil-water interface and a_{\min} is the *excluded area* of a polar head group.

$$\Pi \equiv \gamma_o - \gamma = -\frac{kT}{a_{\min}} \ln \left[1 - \frac{a_{\min}}{a} \right] \quad (14)$$

Eqn. (14) is valid for plane interfaces or for curved interfaces with large radii of curvature. Tolman¹⁰ has shown that the surface tension has to be corrected for very small droplets, however, when the surface of tension is displaced from the surface of no superficial density of the drop material. Strictly speaking, Tolman's correction was derived for a droplet in equilibrium with its own vapor, but the experimental nucleation study of Nielsen and Sarig¹⁴ of droplet formation within the miscibility gap of the ternary liquid system methanol-water-tribromomethane seems to indicate the correction to be approximately valid also for liquid-liquid interfaces. In the present case, the surface of no superficial density should be taken approximately to be the hydrophobic surface at R_o , and Tolman's correction would imply that the surface tension given by eqn. (14) should be divided by the factor $1 - 2\delta/(R_o + \delta)$. The final expression for the micellar surface tension is therefore eqn. (15), where γ_o^∞ is the surface tension of a pure oil-water interface with an infinite radius of curvature.

$$\gamma = \left(\frac{R_0 + \delta}{R_0 - \delta} \right) \cdot \left(\gamma_0^\infty + \frac{kT}{a_{\min}} \ln \left[1 - \frac{a_{\min}}{a} \right] \right) \quad (15)$$

The machinery is now ready for the calculation of the distribution of aggregation numbers by means of eqns. (6), (13) and (15). For simplicity, we shall first assume $\delta=0$ and only introduce δ as a correction to fit experimental data.

On Fig. 2 the calculations of surface tension and of the variable part of the standard free energy of the micelle are shown for $a_{\min}=60 \text{ \AA}^2$ and 8 carbon atoms in the hydrophobic chain ($n_C=8$). The surface tension is seen to be a decreasing function of aggregation number m . If we consider for a moment m to be a continuous variable, we can calculate the aggregation number corresponding to zero surface tension from eqn. (15) with $\delta=0$. The result is $m_0=30.9$ which means that $m=30$ is the last stable cluster size. The pure surface tension γ_0^∞ has been put equal to 50 mN/m all over in the present paper

as an average value for the surface tension between the higher alkanes and water at 298.2 K.

The mol fractions of clusters with $m=2, 5, 10, 29$ and 30 have been calculated for several fixed values of $\ln \xi$ in Table 1. It has been assumed that $X_m=0$ for $m=31, 32$ etc. It is seen that the mol fraction of $m=30$ becomes important above $\ln \xi$ -values around 9.2. In a very narrow range of ξ -values X_{30} grows rapidly from negligible values to values above unity corresponding to unattainable ξ -values (unattainable concentrations of free amphiphile). This narrow ξ -range corresponds to the concentration range around the *critical micelle concentration* (cmc).

In comparison to X_{30} we have negligible amounts of clusters with $m=29$ around ξ_{cmc} . It is also remarkable that X_2 is negligible although $\mu'_2/kT < \mu'_{30}/kT$, but the fluid sphere model is of course inappropriate for low aggregation numbers. It is seen that the cmc-behaviour as well as the appearance of a definite micelle size around and

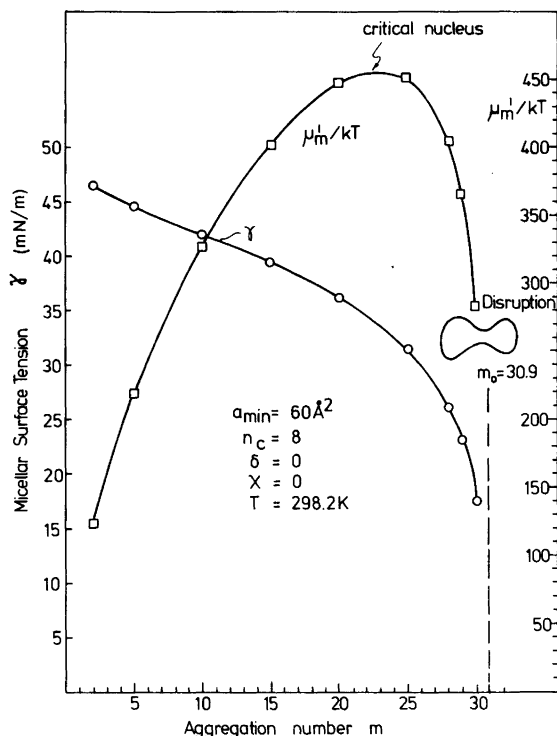


Fig. 2. Micellization described as a nucleation process with disruption at zero surface tension. Due to the large excluded area and the short hydrocarbon chains, the aggregation numbers have small values. The micellar surface tension and the micellar, variable free energy are shown as function of aggregation number.

Table 1. Mol fractions of aggregates of selected aggregation numbers as a function of $\ln \xi$ in the vicinity of ξ_{cmc} . Conditions as for Fig. 2.

m	$\ln \xi$					
	5	8	9	9.2	9.3	9.4
2	4.2×10^{-50}	1.7×10^{-47}	1.2×10^{-46}	1.9×10^{-46}	2.3×10^{-46}	2.8×10^{-46}
5	8.3×10^{-85}	2.5×10^{-78}	4.0×10^{-76}	1.1×10^{-75}	1.8×10^{-75}	3.0×10^{-75}
10	1.5×10^{-120}	7.2×10^{-108}	1.6×10^{-103}	1.2×10^{-102}	3.2×10^{-102}	8.7×10^{-102}
29	1.9×10^{-96}	1.2×10^{-58}	4.6×10^{-46}	1.5×10^{-43}	2.7×10^{-42}	5.0×10^{-41}
30	1.4×10^{-58}	1.7×10^{-19}	1.85×10^{-6}	7.46×10^{-4}	1.50×10^{-2}	3.01×10^{-1}

above cmc is inherent in the present model. We shall go into details with other examples in the next sections.

HEAD GROUP BURIAL AND "OPPOSING FORCES"

Tanford (Ref. 1, Chapter 6) has given some arguments for the larger micelles being of an ellipsoidal rather than a spherical shape. Experimental evidence should be the high intrinsic viscosity and the high light scattering dissymmetry exhibited by such micellar solutions. A purely geometric consideration is the following: In the case of large aggregation numbers, the radius of an assumed spherical hydrophobic core becomes larger than the maximum length of a fully extended alkane chain of a single amphiphile. According to Tanford it is impossible to maintain the spherical shape of the micelle, since no micelle can have a hole in the middle.

In the opinion of the present author, many arguments *against* an ellipsoidal shape can be raised, however. Firstly, it is not possible to use viscosity models for rigid ellipsoids for fluid-like micelles with rapid exchange of amphiphiles with the surrounding solution (relaxation times around 10^{-4} s or greater^{5,8}). Secondly, it is not possible to imagine an *equilibrium* shape of a fluid droplet which is not spherical. Either there will be pressure differences or surface tension gradients and Marangoni effects in an ellipsoidal droplet.

How do we then avoid the central hole in large micelles? I can here suggest two ways: (1) Inclusion of water pockets in the micelle as suggested by Menger,¹⁵ (2) by the mechanism of *head group burial* in the hydrophobic core. Even in large micelles, a central hole may easily be filled out by pulling a small fraction of the head groups into the interior of

the micelle. Both mechanisms will give rise to adverse energetic effects or "opposing forces" in the terminology of Tanford.

Thus, it is believed that the equilibrium shape of the micelle is always spherical. A micelle is a small thermodynamic system,¹⁶ however, with vigorous fluctuations around the equilibrium state. Since micelles with low surface tensions will dominate according to the present theory, those micelles are easily deformable and will almost never be in the equilibrium spherical shape. In an appendix it is shown that the dominant mode of deformation due to Brownian motion and due to micro-Marangoni effects from thermal fluctuations is a *peanut shape* of the micelle. Since all the micelles are oscillating around the spherical shape, and since a snapshot of a solution of micelles would show a collection of randomly oriented peanuts, Tanford's concept of ellipsoidal micelles is quite precise, but the interpretation is more subtle. The light scattering data and the high intrinsic viscosities should be understood from this "fluctuating peanut" picture of a micellar solution.

We shall now discuss the influence of head group burial on the distribution of micellar aggregation numbers. The Szyszkowski isotherm [eqn. (14)] is linked to a Langmuir adsorption isotherm for the surfactant (here the polar heads), see Sheludko.¹² Therefore, we can write eqn. (16), where K is the

$$\frac{a_{\min}}{a} = \frac{Kc}{1+Kc} \quad (16)$$

adsorption constant and c is the concentration of polar heads in the interior of the micelle. For c we have eqn. (17).

$$c = \frac{a_{\min}/a}{K(1-a_{\min}/a)} \quad (17)$$

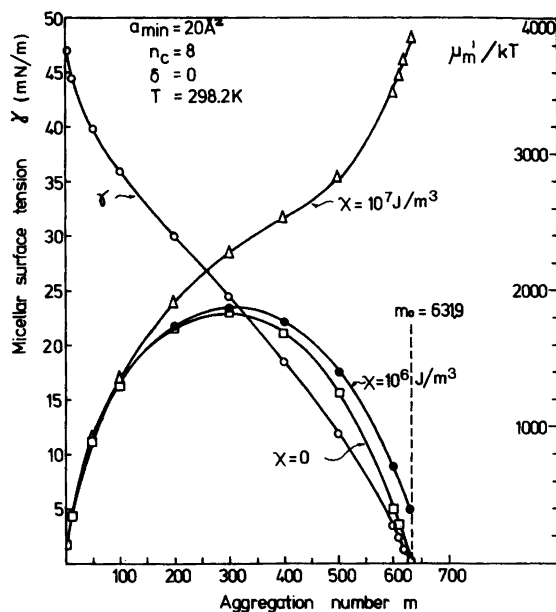


Fig. 3. Smaller excluded areas lead to higher aggregation numbers and a closer approximation to zero surface tension of the micelles. The energetic effects of head group burial (χ) is also shown. When χ -effects become dominating, the free energy becomes monotonously increasing, and a size distribution of micelles is produced above cmc.

It is reasonable to assume that the *free energy density* in the interior of the micelle is proportional to the concentration of buried head groups. The contribution to μ'_m from head group burial is therefore given by eqn. (18), where χ is a coefficient

$$\mu'_m(\text{burial}) = \chi \cdot \frac{a_{\min}/a}{1 - \frac{a_{\min}}{a}} \cdot m v_0 \quad (18)$$

characteristic for the type of head group. (The singularity at $a = a_{\min}$ has no importance, since a reaches the area of zero surface tension a_0 before it reaches a_{\min} for growing size of the micelle). Instead of eqn. (13) we have now eqn. (19).

$$\mu'_m = \frac{44}{3} \pi \gamma [\beta \sqrt[3]{m} + \delta]^2 + \chi \cdot v_0 \frac{a_{\min} m^2}{4\pi(\beta \sqrt[3]{m} + \delta)^2 - a_{\min} m} \quad (19)$$

From eqn. (19) and eqns. (6) and (15) the aggregation number distribution can be calculated.

In Fig. 3 calculations for $a_{\min} = 20 \text{ \AA}^2$, $\delta = 0$ and $n_c = 8$ are shown ($T = 298.2 \text{ K}$). The aggregation "number" corresponding to zero surface tension is $m_0 = 631.9$, and for $m_{\max} = 631$, γ as well as μ'_m/kT come very close to zero in comparison to the case in Fig. 2. Free energy curves are also shown for $\chi = 10^6$ and 10^7 J/m^3 . In the latter case the free energy maximum ("critical nucleus") disappears and μ'_m/kT

Table 2. Mol fractions of the two most frequent aggregation numbers in the case $n_c = 8$ and $a_{\min} = 20 \text{ \AA}^2$. $\chi = 0$. See also Fig. 3.

m	ln ξ	0.005	0.010	0.015	0.018
	0				
630	6.6×10^{-12}	1.5×10^{-10}	3.6×10^{-9}	8.4×10^{-8}	5.6×10^{-7}
631	6.0×10^{-6}	1.39×10^{-4}	3.28×10^{-3}	7.69×10^{-2}	5.11×10^{-1}

Table 3. The influence of a_{\min} and χ on micellar aggregation number and on cmc.

a_{\min} (\AA^2)	60	20	20	20	20
χ (J/m^3)	0	0	10^5	10^6	10^7
m_{\max}	30	631	631	631	631
m_{micelle}	30	631	631	631	535–555
ξ_{cmc}	9.25×10^3	1.00447	1.0675	1.844	2.61×10^2

becomes monotonously increasing.

In Table 2 the mol fractions corresponding to the two most frequent aggregation numbers for $\chi=0$ are shown. It appears that we have also in this case a practically monodisperse distribution of aggregates with aggregation number equal to $m_{\max}=631$ for $\ln \xi$ -values above around 0.005.

Table 3 summarizes the influence of a_{\min} and χ on micellar aggregation numbers and on cmc. A lower value of the excluded area yields higher aggregation numbers and values of ξ_{cmc} closer to unity (for $\chi=0$). For very high values of χ where the free energy maximum disappears, a *distribution* of molecular weights and aggregation numbers is introduced. The distribution is shown in Fig. 4 for two values of $\xi \geq \xi_{\text{cmc}}$. It is seen that opposing forces caused by head group burial also increase ξ_{cmc} well above unity.

Different kinds of empirical or semi-empirical expressions for "opposing force" contributions to μ_m

have been considered by Tanford,^{1,2} Ruckenstein and Nagarajan³ and Israelachvili *et al.*⁴ They all lead to a distribution of aggregation numbers as above. The "opposing force" contribution is claimed to be caused by steric or electrostatic repulsion between head groups, however. The present author fundamentally disagrees with that position for the following reasons: The effect of increased steric repulsion (increased excluded area) is to *increase* the surface pressure. Thus, the surface tension and the variable free energy *decrease* because of repulsion between head groups. As we shall see later, the same can be said for electrostatic repulsion. Thus, to have an *increase* in surface free energy a Π - a -relationship including *attractive* forces between the head groups in the monolayer should be invoked, *e.g.* a Frumkin isotherm.^{1,2}

In a certain sense, the position of the above-mentioned authors is correct, however. Repulsive forces between head groups lead to a faster decrease

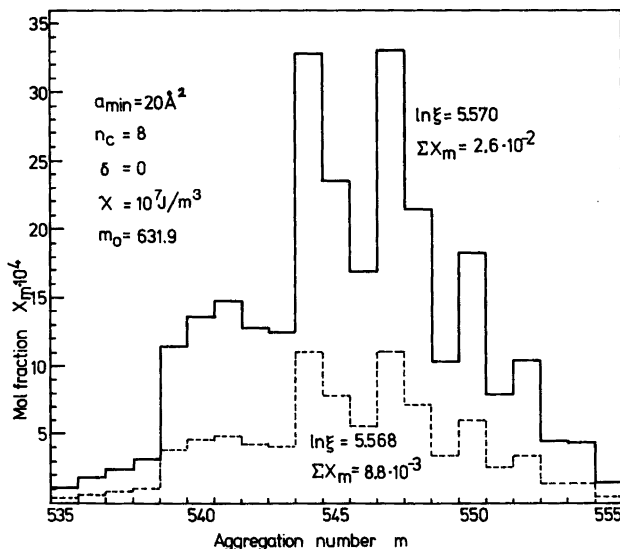


Fig. 4. Histograms showing the size distribution produced by large energetic effects in connection with head group burial ($\chi=10^7 \text{ J/m}^3$). Two different values of $\ln \xi$ have been taken, exhibiting the sharp increase in total micelle mol fraction (ΣX_m) around ξ_{cmc} .

of surface tension with aggregation number. Therefore, the surface tension is brought to zero faster. From eqn. (6) and the fact that we assume $X_m = 0$ for all $m \geq m_o$ it appears that we assume an "opposing force" contribution which rises from zero to infinity at $m = m_o$. Therefore, the interpretation of the "principle of opposing forces" is indeed a subtle one (Ref. 1 pp. 70–77).

To summarize, I have assumed a "switch-on" opposing force of infinity above m_o . Apart from that, opposing forces are believed to originate in attractive forces between head groups or in head group burial or water inclusion in the hydrophobic core.

COMPARISON WITH EXPERIMENTAL RESULTS FOR NONIONIC MICELLES

In this section we shall test the ZST model of micellization on data for mean aggregation numbers for oligo-ethylene oxide derivatives of n-alkanoles. Such data have been reported earlier by Becher.¹⁷ The amphiphiles are characterized by the number of carbon atoms in the alkane chain (n_c) and the number of ethylene oxide groups (n_{EO}).

If the micellar size distribution is assumed approximately monodisperse with aggregation number $\bar{m} = m_{max} \cong m_o$, we obtain from eqns. (8), (9), (12) and (15) with $\delta = 0$ and $\gamma = 0$ the relation (20).

$$\bar{m} \cong m_o = \frac{36\pi v_o^2}{a_{min}^3} \left[1 - \exp\left(-\frac{\gamma_o^\infty a_{min}}{kT}\right) \right]^3 \quad (20)$$

Isolating instead a_{min} and taking $\delta \neq 0$ we obtain eqn. (21).

$$\frac{a_{min}}{1 - \exp\left(-\frac{\gamma_o^\infty a_{min}}{kT}\right)} = \frac{\sqrt[3]{36\pi v_o^2}}{\sqrt[3]{\bar{m}}} \left(1 + \frac{\delta}{\beta \sqrt[3]{\bar{m}}} \right)^2 \quad (21)$$

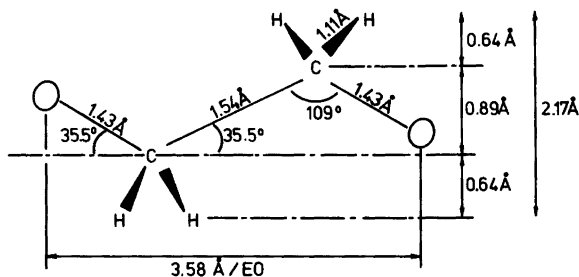


Fig. 6. Characteristic dimensions of a monomeric unit of an oligo-ethylene oxide chain.

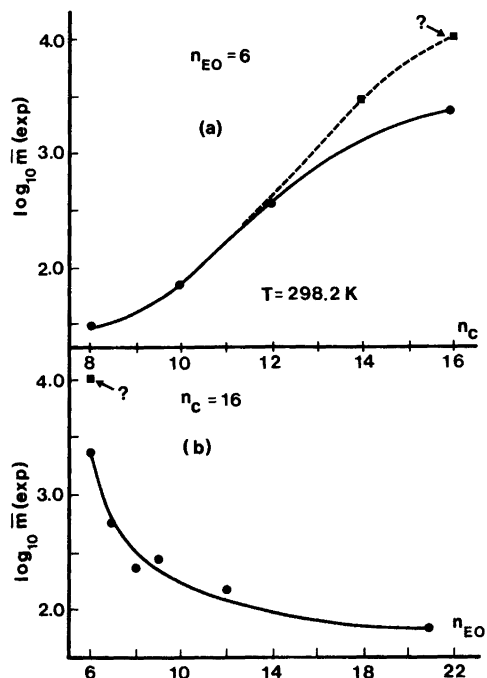


Fig. 5. (a) Experimental aggregation numbers of hexoxyethylene alkanol ether micelles as a function of the number of carbon atoms in alkane chain. Data from Becher.¹⁷ Question mark indicates a probably erroneous value. (b) Influence of varying n_{EO} on experimental aggregation numbers of Becher. $n_c = 16$. Question mark corresponds to question mark on Fig. 5(a).

Since the volume v_o of the hydrocarbon chain grows linearly with the number of carbon atoms, we see from eqn. (20) that we should expect a drastic increase in aggregation number for increasing length of the hydrocarbon chain. It is indeed observed that for $n_{EO} = 6$, the aggregation number

Table 4. Influence of varying n_c on experimental aggregation numbers of hexa-ethylene oxide derivatives of n-alkanols. $n_{EO}=6$. $T=298.2$ K.

n_c	$\bar{m}(\text{exp})^a$	$\bar{m}(\text{corr})^b$	$v_o (\text{\AA}^3)$	$R_o (\text{\AA})$	$\delta (\text{\AA})$ for $a_{\min}=15 \text{\AA}^2$	δ for 20\AA^2
8	32	32	243	12.3	-5.5	-4.8
10	73	73	296	17.3	-7.1	-6.0
12	400	400	350	32.2	-8.3	-5.8
14	3100	—	404	66.9	(-0.33)	(+6.7)
14	—	1400	404	51.3	-6.7	-1.9
16	2430	2430	458	64.3	-5.5	+0.85
16	10500	—	458	104.7	(+17.6)	(+30.7)
Average and range of displacement of surface of tension					-6.6 ± 1.7	-3.5 ± 4.4

^a Experimental data from Becher, Ref. 17. ^b Corrected data according to Fig. 5(a).

increases from 32 for $n_c=8$ to 2430 for $n_c=16$ (perhaps even higher aggregation numbers, see Fig. 5 and Table 4). In order to obtain quantitative agreement, one has to assume $\delta \neq 0$, however.

Fig. 6 shows the dimensions of a segment of a fully stretched poly-oxethylene segment. When rotated around the longitudinal axis, the methylene hydrogen atoms describe a cylindrical surface with a cross sectional diameter equal to 2.17 Å. Adding twice the van der Waal radius for hydrogen (1.2 Å) we obtain an efficient diameter equal to 4.57 Å and a cross sectional area equal to 16.4 Å². The circumscribed quadrangle has an area equal to 20.9 Å². One could also imagine, however, that the excluded area were less than 16.4 Å² due to interpenetration of poly-oxethylene chains. We

shall therefore consider $a_{\min}=15$ and 20 Å², respectively. From eqn. (21) we obtain eqn. (22), where the value 1.924 corresponds to $a_{\min}=15 \text{\AA}^2$ and the value 2.130 corresponds to $a_{\min}=20 \text{\AA}^2$. Values of δ have been calculated and the results are shown in Table 4 and Table 5.

$$\frac{\delta}{R_o} = \left\{ \begin{matrix} 1.924 \\ 2.130 \end{matrix} \right\} \cdot \frac{\sqrt[6]{\bar{m}}}{[27.4 + 26.9n_c]^{1/3}} - 1 \quad (22)$$

When n_{EO} is fixed and n_c varies one should not expect any great variation in δ . This is indeed the case in Table 4 for $a_{\min}=15 \text{\AA}^2$, but *not* for $a_{\min}=20 \text{\AA}^2$. Two of the experimental values of the aggregation numbers seem to be in error, however, see also Fig. 5. The average value of δ for $a_{\min}=15$

Table 5. Influence of varying n_{EO} on aggregation numbers. $T=298.2$ K.

n_{EO}	$\bar{m}(\text{exp})^a$	$\bar{m}(\text{corr})^b$	$R_o (\text{\AA})$	$\delta (\text{\AA})$ for $a_{\min}=15 \text{\AA}^2$	δ for 20\AA^2
$n_c=13$					
8	71	—	18.6	-8.5	-7.4
10	61	—	17.6	-8.3	-7.3
12	55	—	17.0	-8.2	-7.2
$n_c=16$					
6	2430	2430	64.3	-5.5	+0.85
7	594	594	40.2	-11.1	-8.0
8	240	316	32.5	-11.3	-9.0
9	279	224	29.0	-11.2	-9.2
12	150	125	23.9	-10.6	-9.1
21	70	70	19.7	-9.7	-8.6

^a Experimental data from Becher, Ref. 17. ^b Corrected data according to Fig. 5(b).

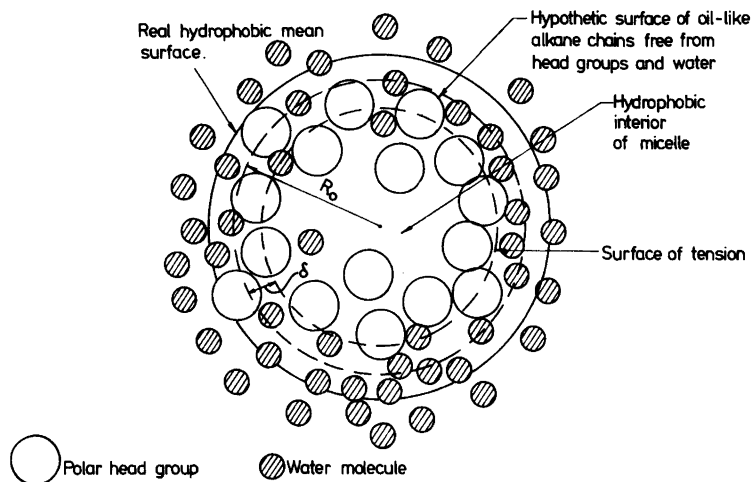


Fig. 7. Revised picture of a nonionic micelle. The surface of tension is displaced into the hydrophobic core due to water penetration and head group burial, and the distributions of molecules are statistical rather than regular as in Fig. 1.

\AA^2 is -6.6\AA with a range equal to $\pm 1.7 \text{\AA}$. Thus, the surface of tension seems to be positioned *inside* the surface of the hydrophobic core. In comparison, for plane interfaces between liquids and their vapors, Tolman has found the surface of tension to be positioned around $1.0-3.5 \text{\AA}$ inside the "surface of no superficial density of liquid". For very small spherical droplets (radii $14-32 \text{\AA}$) of tribromomethane in methanol-water mixtures, Nielsen and Sarig¹⁴ have used Tolman's equation for the curvature correction of the interfacial tension in connection with the classical Volmer-Becker-Döring theory of homogeneous nucleation. A value of $-\delta$ equal to $+2.4 \text{\AA}$ was estimated for those critical nuclei. The larger values of $-\delta$ in Table 5 are not surprising in view of the bulky poly-oxyethylene groups present at the surface.

Fig. 5(b) and Table 5 show that also n_{EO} has an appreciable effect on aggregation numbers. The calculated values of $-\delta$ seem to be somewhat larger for longer poly-oxyethylene chains than $n_{\text{EO}}=6$ (Table 4), especially for the larger micelles with $n_{\text{C}}=16$. This may be seen as some evidence of increased water penetration into the micelle with increased poly-oxyethylene chain length and of increased head group burial for the larger micelles, although the data are far from conclusive.

The schematic picture of a micelle given in Fig. 1 should therefore be revised in the sense of Fig. 7 which shows the negative displacement of the

surface of tension, the fluctuating head groups delving sometimes into the hydrophobic core and the water molecules penetrating quite far into the micelle.

THERMODYNAMICS OF TRANSFER

In addition to the aggregation number another important parameter is the *critical micelle concentration* (cmc). From Table 1 and Table 2 we see that the value of ξ_{cmc} may be estimated as the value yielding a molar fraction of $m=m_{\text{max}}$ equal to 10^{-4} , say. From eqn. (6) we have then eqn. (23).

$$\ln \xi_{\text{cmc}} \cong \frac{1}{m_{\text{max}}} \cdot \left[\frac{\mu'_{m_{\text{max}}}}{kT} - 9.21 \right] \quad (23)$$

For $m=m_{\text{max}}$ and $\chi=0$ (or at least not too great) we usually have $\mu'_m/kT \cong 0$ because of the low surface tension. Since m_{max} is mostly of the order of 100 or more, $\ln \xi_{\text{cmc}}$ will normally be quite close to zero and ξ_{cmc} quite close to unity. A very sharp transition takes place around this value for the molar fraction of $m=m_{\text{max}}$ because of the large power to which ξ is raised in eqn. (6).

With ξ_{cmc} close to unity we obtain from eqn. (5) the relation (24) between cmc and the free energy of transfer of the hydrocarbon part of the amphiphiles from water to the hydrophobic core of the micelle;

$$\ln X_{\text{cmc}} \cong \ln \frac{[\text{cmc}]}{55.5} \cong \frac{\mu_{\text{B}}^{\ominus} - \mu_{\text{A}}^{\ominus}}{kT} \quad (24)$$

$[\text{cmc}]$ is in mol/dm³ and 55.5 is the number of mol H₂O per dm³ pure water. Thus, the ZST-theory yields the same basic result as the incorrect phase separation model as far as cmc is concerned. The reason is the very small contribution of the polar heads to the free energy of micellization. This fact serves as an explanation of why the phase separation model has maintained its popularity in thermodynamic studies of micellization based on cmc-measurements. Just to cite one recent example among numerous, see the paper by Kucharski.¹⁸ However, the phase separation model can by its very nature give no idea whatsoever about aggregation numbers.

It should be remarked that ξ_{cmc} may not be close to unity for small micelles where m_{max} is small and $\mu_{\text{m}}^{\ominus}/kT$ may still be appreciable for $m = m_{\text{max}}$, see for example Fig. 2. The approximation may also break down for very large micelles if head group burial and water inclusion become energetically dominant.

If it is correct that cmc largely reflects the thermodynamics of transfer of the hydrocarbon chains, then cmc-data for oligo-oxyethylene derivatives of n-alkanoles should depend only on n_{C} ,

but not on n_{EO} . This is indeed the case as shown in Fig. 8 where data for $\ln([\text{cmc}]/55.5)$ vs. n_{C} for $n_{\text{EO}} = 3, 6$ and 9 are fitted by the same regression line. A comparison is made also with the regression lines for the transfer of n-alkanes from water to liquid alkane and for solubilization of n-alkanes from 0.1 mol/dm³ NaCl solution into sodium dodecyl sulphate micelles. The latter regression lines are taken from Tanford¹ and correspond to $T = 298.2$ K.

It is remarkable that the standard free energy of transfer from water to micelles of the alkane chains is greater than the free energy of transfer of the corresponding n-alkane from aqueous solution to liquid alkane. Probably, this is due to the more restricted motion of alkane chains in the micelle. The smaller hypervolume occupied in the statistical mechanical phase space gives rise to a greater chemical potential in the micelle in comparison with bulk, liquid alkane. Also, the effect of buried head groups and water inclusion will tend to elevate the chemical potential. A great part of the micelles is rather to be described as a surface region than as a bulk fluid.

Alkanes solubilized in micelles seem to occupy an intermediary position from Fig. 8. The chemical potential is higher for an alkane solubilized in a

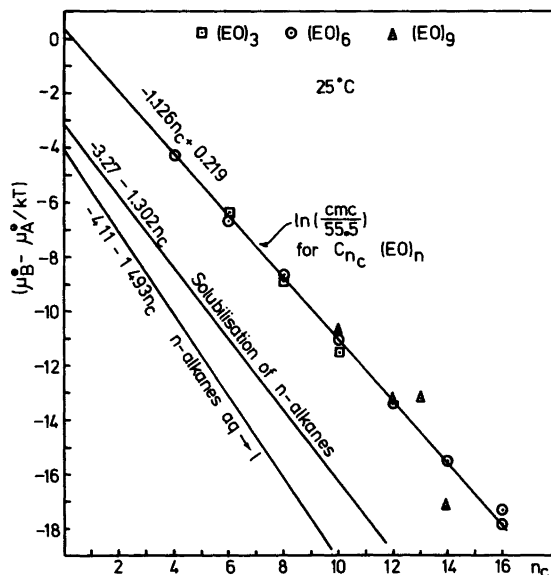


Fig. 8. Thermodynamics of transfer into nonionic micelles of the hydrophobic part of the amphiphiles as compared with the thermodynamics of solubilization of n-alkanes in SDS micelles and of n-alkanes from water into liquid n-alkanes as given by Tanford (1).

micelle than for an alkane dissolved in bulk alkane. However, the chemical potential of a solubilized alkane is lower than the chemical potential of the hydrocarbon chain of an amphiphile, since a solubilized alkane is more free to move in the interior of the micelle, being not restricted by a polar head group.

PRELIMINARY TREATMENT OF IONIC MICELLES

In order to be able to treat ionic micelles, it is necessary to know the influence of the electric forces on surface tension. The situation here is quite parallel to the situation arising in the thermodynamic description of microemulsions. Ruckenstein and Krishnan^{19,20} have calculated equilibrium droplet radii of microemulsions formed with ionic surfactants and nonionic cosurfactants. In the case of ionic micelles, the charged heads are considered as "surfactants" and there are no cosurfactants. In that case the equation of Ruckenstein and Krishnan for the interfacial tension (Ref. 19, eqn. 36) reads as eqn. (25), where ψ_s

$$\gamma = \gamma_0 - \frac{kT}{a_{\min}} \ln[1 + K'c_A] - \int_0^{\psi_s} \sigma d\psi'_s \quad (25)$$

is the surface potential and σ the surface charge density. The Langmuir adsorption constant K' has a contribution from the surface potential, *viz.* eqn. (26),

$$K' \equiv K \exp(-z_A \psi_s / kT) \quad (26)$$

z_A being the charge of the amphiphile. Now, the Langmuir isotherm yields for the surface concentration of occupied states eqn. (27) or eqn. (28).

$$\Gamma = \frac{1}{a} = \frac{1}{a_{\min}} \cdot \frac{K'c_A}{1 + K'c_A} \quad (27)$$

$$1 + K'c_A = \left[1 - \frac{a_{\min}}{a} \right]^{-1} \quad (28)$$

When eqn. (28) is introduced into eqn. (25) we obtain eqn. (29), which is simply a Szyszkowski isotherm

$$\gamma = \gamma_0 + \frac{kT}{a_{\min}} \ln \left[1 - \frac{a_{\min}}{a} \right] - \int_0^{\psi_s} \sigma d\psi'_s \quad (29)$$

with a contribution from surface charge. The last term represents the free energy of formation of the diffuse double layer. The interpretation of γ_0 is still that of a pure oil-water interfacial tension, since the hypothetical "adsorption process" is carried out at constant micellar radius starting from a "micelle" with no head groups on the surface.

Strictly speaking, a Tolman correction for γ should be introduced. The correction drops out, however, for zero surface tension. Ruckenstein and Krishnan did not correct for curvature either, but they found also for microemulsions that the interfacial tension was zero to a good approximation. Microemulsions of the type studied by Ruckenstein and Krishnan may be described as highly oil-solubilized micelles formed with surfactants and cosurfactants, so those calculations support the zero surface tension theory of micellization proposed in the present paper.

If we neglect the radius of the counterions in comparison to the radius of the micelle, and if we take the surface charge as being located at the hydrophobic surface ($\delta=0$), the surface potential according to simple Debye-Hückel theory (see for example Ref. 21) is given as eqn. (30), where m is the

$$\psi_s = \frac{mF}{4\pi N_0 \epsilon R_0} [1 + \kappa R_0]^{-1} \quad (30)$$

number of head groups, F the Faraday, N_0 Avogadro's number, ϵ the absolute permittivity of water and κ the inverse Debye-Hückel length. The charge density on the surface is given by eqn. (31)

$$\sigma = \frac{mF}{4\pi R_0^2 N_0} \quad (31)$$

and m may be used as the integration variable remembering to leave R_0 constant during the integration. With the integration performed and with $\delta=0$, eqn. (29) can now be written as eqn. (32).

$$\gamma = \gamma_0 + \frac{kT}{a_{\min}} \left[1 - \frac{a_{\min} \sqrt[3]{m}}{4\pi \beta^2} \right] - \frac{1}{2} \frac{F^2 m^2 (1 + \kappa \beta \sqrt[3]{m})^{-1}}{16\pi^2 \epsilon N_0^2 \beta^3 m} \quad (32)$$

Note that we have (afterwards!) introduced the m -dependence of R_0 . The aggregation number leading to zero surface tension can now be determined by eqn. (33). In practice, it is easier to determine κ as a function of m_0 ; eqn. (34).

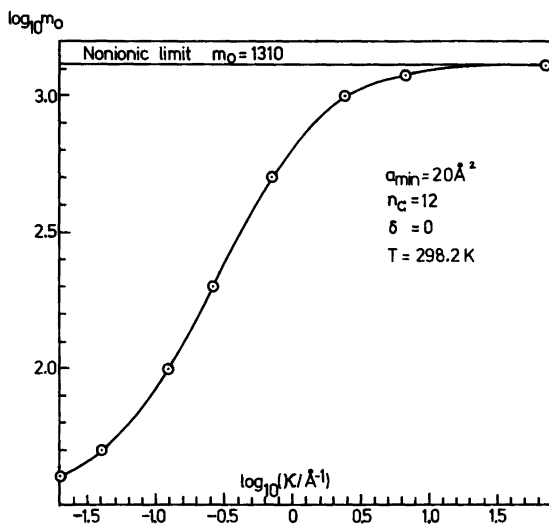


Fig. 9. The increase and saturation of aggregation numbers of ionic micelles with $n_c = 12$ with increase in the inverse thickness of the diffuse double layer.

$$(1 + \kappa\beta\sqrt{m_0}) \left[\frac{\gamma_0 a_{\min}}{kT} + f_2(m_0) \right] = f_1(m_0) \quad (33)$$

$$\kappa\beta = m_0^{-1/3} \left[\frac{f_1(m_0)}{\frac{\gamma_0 a_{\min}}{kT} + f_2(m_0)} - 1 \right] \quad (34)$$

In eqns. (33) and (34) the functions (35) and (36) have

$$f_1(m_0) = \frac{a_{\min} F^2 m_0}{32kT\pi^2 N_0^2 \epsilon \beta^3} \quad (35)$$

$$f_2(m_0) = \ln \left[1 - \frac{a_{\min} \sqrt[3]{m_0}}{4\pi\beta^2} \right] \quad (36)$$

been introduced. As an example, we may take an amphiphile with $n_c = 12$, $\beta = 4.37 \text{ \AA}$ and $a_{\min} = 20 \text{ \AA}^2$. The temperature is 298.2 K, γ_0 is 50 mN/m and $\epsilon = 6.954 \times 10^{-10} \text{ A s/V m}$.

The aggregation number m_0 is shown as a function of κ in Fig. 9. Values of m_0 below about 40 yield negative values of κ as calculated from eqn. (34). Therefore, aggregation numbers below 40 cannot exist under any circumstances. At $\kappa \geq 0$, the aggregation number is around 40 corresponding to very small ionic strengths where electrostatic repulsion is very efficient in lowering the surface tension. At higher values of κ and the ionic strength,

the aggregation number rises sharply to orders of magnitude 10^2 and 10^3 .

Such a behaviour has indeed been found experimentally by Mazer, Benedek and Carey²² in a light scattering study of micellar weights of (impure) sodium dodecyl sulphate (SDS) as a function of NaCl concentration. The behaviour has been confirmed for pure SDS samples using membrane osmometry by Birdi, Dalsager and Backlund.²³ Both studies were carried out at 40 °C, however. The latter authors found aggregation numbers rising from 103 at 0.1 mol/dm³ to 700 at 0.8 mol/dm³ of added NaCl.

In the case of cationic micelles, it should be mentioned that Dalsager²⁴ has also observed an increase in the aggregation number of TTAB-micelles (tetradecyl trimethyl ammonium bromide) with added KBr-concentration from 126 (30 °C) or 148 (40 °C) at 0.1 mol/dm³ KBr to 546 at 0.8 mol/dm³ KBr and 30 °C or 345 at 0.7 mol/dm³. In the simplified theory given here there should be no difference in that respect between anionic and cationic micelles, since the electrostatic term lowering the surface tension in eqn. (32) is proportional to the squared charge on the micelle.

None of the above-mentioned authors have observed the saturation effect shown in Fig. 9. It is seen that the aggregation number in the model example approaches 1310 at high ionic strengths.

That limit will be called the *nonionic limit*, since it is the aggregation number calculated from eqn. (20) without regard to electrostatic effects. The double layer is so narrow here that the counterions are best described as being bound to the ionic amphiphiles.

If the Debye-Hückel theory were strictly valid, κ^2 would be proportional to the ionic strength. It is well-known, however, that the Debye-Hückel approach yields only qualitatively correct results for higher ionic strengths than 0.01 mol/dm³. I have used it here only for preliminary survey purposes. A better approach would be to invoke solutions of the non-linear Poisson-Boltzmann equation as done by Ruckenstein and Krishnan for microemulsions.^{19,20} Furthermore, one would expect an asymmetry between anionic and cationic micelles. For small inorganic ions, activity and conductance data suggest that only the cations are hydrated and not the anions, see for example Sørensen.^{25,26} For micelles one should then expect a more developed Stern layer of polarized water molecules around cationic micelles than around anionic micelles. Model refinements of that kind will be the object of a forthcoming paper.

DISCUSSION

The ZST model of micellization seems to be quite successful in explaining aggregation numbers and cmc-values in the case of nonionic micelles and probably also for ionic micelles. In contrast to earlier theories, the "opposing forces" in the surface layer of the micelles are assumed to lower the free energy of the micellar surface rather than to increase the free energy of the micelle. When the surface tension comes close to zero or becomes negative, the aggregates become destabilized. The aggregates then disintegrate predominantly into two (highly unstable) parts. The dominating stable aggregates have a quite low surface tensions and will tend to oscillate in a "peanut mode" around the equilibrium, spherical shape. Thus, high intrinsic viscosities and light scattering dissymmetries may at least partially be explained that way instead of in terms of ellipsoid equilibrium shapes.

A simple model such as the ZST theory will necessarily have shortcomings, however. One of the most serious seems to be the prediction of monodispersity. Experimentally, one finds some dependence of molecular weights of micelles on concentration, and Hall and Pethica²⁷ have shown

that such a dependence would be produced by a molecular weight distribution of micelles. Aniansson *et al.*⁶ have demonstrated by chemical relaxation studies on sodium alkyl sulphates at 298.2 K that there is an aggregation number distribution width ranging from 6 to 16. The distribution has little or no effect on micelle polydispersity expressed as M_w/M_n , however. I would like to stress here that the prediction of monodispersity is not essential in the ZST-theory. It is very likely that the crude Szyszkowski isotherm exaggerates the decrease in surface tension in the neighbourhood of zero surface tension. A more "flat approach" produced by a more realistic adsorption isotherm would produce polydispersity in the ZST model too. As we have seen, a distribution of aggregation numbers is also produced by water inclusion, head group burial and attractive surface forces.

Another phenomenon which seems hard to explain by the ZST-model is the so-called "cloud point" of poly-oxyethylene surfactants. The size of the aggregates increases rapidly as the temperature is raised towards that cloud point.²⁸⁻³¹ Most authors have seen this as an increase in micellar aggregation numbers, but Tanford *et al.*³² has suggested that what is observed is aggregation of micelles. An NMR-study by Staples and Tiddy seems to confirm that proposal.³³ From eqn. (21) only a slight temperature dependence of m_0 is predicted, since a_{\min} , v_0 and β are expected to be only slightly dependent on temperature and since the exponential is small in comparison to unity. However, one could imagine a phase transition in the poly-oxyethylene surface layer or a change in water structure which altered a_{\min} or changed the nature of the equation of surface tension. If the aggregation theory is correct, it may be taken as support for the ZST-theory. Long rods could form by aggregation of spherical micelles, but only at ultralow surface tensions. Any finite surface tension would lead to breakdown of a surfactant cylinder due to a kind of Rayleigh instability. Imagine then that the most stable micelles have a surface tension close to zero, but not exactly equal to zero at a given temperature. By raising the temperature, the surface tension decreases slightly and reaches zero at the cloud temperature where long rods form. Such lines of thought seem worthwhile to pursue in the future.

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APPENDIX

Destabilization of droplets of low surface tension. The kinetic energy of a droplet in one spatial direction during Brownian motion is in the mean (root mean square) $kT/2$. The free energy increase in the process of formation of n equally sized droplets from one droplet of radius R is equal to

$$\left(\frac{20}{3}\right)\pi\gamma \cdot [\sqrt[3]{n}-1]R^2$$

where the "Kelvin effect" (increase in free energy due to increase in Laplace overpressure) has been included. Those two energies have to be comparable to each other to have a significant destabilization, *i.e.* eqn. (A1). It is seen that $n=2$ (peanut division)

$$\gamma_{\text{critical}}(n) = \frac{kT}{\frac{40}{3}\pi[\sqrt[3]{n}-1]R^2} \quad (\text{A } 1)$$

becomes unstable before $n=3, 4, \dots$ when the surface tension γ decreases. For a small micelle with $R=10 \text{ \AA}$, the critical surface tension is around 0.10 mN/m . For a large micelle with $R=70 \text{ \AA}$, $\gamma_{\text{critical}} \cong 2 \times 10^{-3} \text{ mN/m}$. Both figures are indeed close to zero in comparison to the pure oil-water interfacial tension around 50 mN/m .

Sørensen and Hennenberg³⁴ and Sørensen³⁵ have considered the destabilizing effect of low surface tension during the diffusion of surfactants into droplets. A considerable decrease of the critical thresholds for Marangoni instability was predicted. By the analogy between heat and mass transfer, the results may immediately be transferred to heat conduction instabilities. A solution of micelles is of course an equilibrium system, but a single micelle may be far from equilibrium by, for example, thermal fluctuations. According to elementary statistical mechanics we have for the standard deviation of the temperature fluctuations of a small volume of heat capacity C_v immersed in a heat bath at temperature T , eqn. (A2). If C_{sp} is the specific heat

$$\sigma(T) = T \sqrt{\frac{k}{C_v}} \quad (\text{A } 2)$$

of fluid alkanes and ρ the density of fluid alkanes, we can write eqn. (A3), where C_{sp} has been taken as

$$\frac{\sigma(T)}{T} \cong \sqrt{\frac{k}{C_{sp}mv_o\rho}} \cong \frac{3.14}{\sqrt{mv_o}} \quad (\text{A } 3)$$

2090 J/kg deg and ρ as 700 kg/m^3 . The value of v_o should be inserted in \AA^3 as calculated from eqn. (7) for $T=298.2 \text{ K}$. For simplicity, we assume in a given moment a parabolic temperature distribution in the micelle, eqn. (A4), and the temperature T outside the

$$T_{\text{micelle}} = T_{\text{middle}} + \theta \left(\frac{r}{R}\right)^2 \quad r \leq R \quad (\text{A } 4)$$

micelle. Thermal fluctuations in surface tension are given by eqn. (A5).

$$\delta\gamma = -\alpha\delta T_{\text{surface}} \quad (\text{A } 5)$$

The thermal Marangoni number according to the theory of Sørensen and Hennenberg is defined as eqn. (A6), where $l=2, 3, 4, \dots$ is the quantum number

$$Ma \equiv \frac{-2\theta\alpha R}{(2l-1)(2l-3) \left[\frac{l+1}{l} \kappa_2 + \kappa_1 \right] \eta_1} \quad (\text{A } 6)$$

characterizing the considered spherical harmonics of surface deformation, κ_1 is the thermal diffusivity in the drop and κ_2 the thermal diffusivity outside. The dynamic viscosity in the drop is equal to η_1 . For low surface tensions, the theory predicts a critical Marangoni number equal to eqn. (A7), with a

$$Ma_{cr} = -\hat{\gamma}\hat{V} \quad (\text{A } 7)$$

dimensionless surface tension number, eqn. (A8), and a dimensionless viscosity number, eqn. (A9)

$$\hat{\gamma} \equiv \frac{\gamma \cdot R}{\kappa_1 \cdot \eta_1} \quad (\text{A } 8)$$

$$\hat{V} \equiv \frac{(l+2)l(l-1)}{(2l-1)(2l-3)} \cdot \frac{1 + \eta_2/\eta_1}{l-1 + (l+2)\eta_2/\eta_1} \quad (\text{A } 9)$$

(surface viscosity has been neglected). For positive surface tensions Ma_{cr} will be negative. Therefore, θ has to be positive and heat transfer from outside

and into the micelle to obtain instability. We derive that γ should be less than γ_{cr} ; eqn. (A 10). The

$$\frac{\gamma_{cr}}{\theta\alpha} = \frac{2}{(l+2)(l-1)} \cdot \frac{l-1+(l+2)^{n_2/\eta_1}}{1+n_2/\eta_1} \cdot \frac{\kappa_1}{\frac{l+1}{l}\kappa_2 + \kappa_1} \quad (\text{A } 10)$$

viscosity of water is $\eta_2 = 8.9 \times 10^{-4}$ kg/m s at 25 °C. At the same temperature, the viscosity of n-hexadecane is 30×10^{-4} kg/m s. However, Shinitsky *et al.*³⁶ have calculated the microviscosity in the interior of cationic micelles with n_c from 12 to 16 by measuring the fluorescence depolarization of aromatic hydrocarbon probes. Values as high as 170 to 320×10^{-4} kg/m s are found at 27 °C. The high values are probably reflecting the more restricted motion of the hydrocarbon chains in the micelles. We shall assume $\eta_1 = 250 \times 10^{-4}$ kg/m s. The thermal diffusivity in water at 25 °C is $\kappa_2 = 14.6 \times 10^{-8}$ m²/s. In the micelle we use the value for transformer oil³⁷ $\kappa_1 = 7.4 \times 10^{-8}$ m²/s. The following table can now be calculated from eqn. (A 10):

Critical surface tension for thermal Margangoni instability for micelles as a function of the spherical harmonic number.

l	$\gamma_{cr}/\theta\alpha$
2	0.0690
3	0.0383
4	0.0246
5	0.01724
7	0.00983
10	0.00527
15	0.00252
∞	$(2/3l^2)$

The size dependence of the critical surface tension enters only indirectly through the magnitude of the thermal fluctuations. We take approximately

$$\theta \cong \sigma(T) \cong \frac{3.14T}{\sqrt{mv_0}} \quad (\text{A } 11)$$

For α we take the value for a n-decane/water interface 0.05 mN/m deg.³⁸ For $n_c = 8$ and $m = 32$ we calculate a critical surface tension equal to 0.038 mN/m for the $l=2$ normal mode (peanut). For $n_c = 16$ and $m = 10^4$ we obtain $\gamma_{cr} = 0.0017$ mN/m. We

see that for both very small and very large micelles it is necessary with very low surface tensions to trigger instability. The critical surface tensions for thermal fluctuations are of the same order of magnitude as the critical surface tensions estimated for momentum fluctuations (Brownian motion). Again, the peanut mode is the mode triggered first when γ decreases.

REFERENCES

1. Tanford, C. *The Hydrophobic Effect. Formation of Micelles & Biological Membranes*, Wiley-Interscience, New York 1980. (1st edition 1973).
2. Tanford, C. *J. Phys. Chem.* 78 (1974) 2469.
3. Ruckenstein, E. and Nagarajan, R. *J. Phys. Chem.* 79 (1975) 2622.
4. Israelachvili, J. N., Mitchell, D. J. and Ninham, B. W. *J. Chem. Soc. Faraday Trans. 2*, 72 (1976) 1525.
5. Aniansson, E. A. G., Wall, S. N., Almgren, M., Hoffmann, H., Kielmann, I., Ulbricht, W., Zana, R., Lang, J. and Tondre, C. *J. Phys. Chem.* 80 (1976) 905.
6. Aniansson, E. A. G. *Ber. Bunsenges. Phys. Chem.* 82 (1978) 981.
7. Sams, P. J., Wyn-Jones, E. and Rassing, J. J. *Chem. Soc. Faraday Trans. 2*, 69 (1973) 180.
8. Rassing, J., Sams, P. J. and Wyn-Jones, E. *J. Chem. Soc. Faraday Trans. 2*, 70 (1974) 1247.
9. Reiss-Husson, F. and Luzzati, V. *J. Phys. Chem.* 68 (1964) 3504.
10. Tolman, R. C. *J. Chem. Phys.* 17 (1949) 333.
11. Kondo, S. *J. Chem. Phys.* 25 (1956) 662.
12. Sheludko, A. *Colloid Chemistry*, Elsevier, Amsterdam-London-New York 1966, pp. 114 – 119.
13. Szyszkowski Z. *Physik. Chem.* 64 (1908) 385.
14. Nielsen, A. E. and Sarig, S. *J. Crystal Growth* 8 (1971) 1.
15. Menger, F. M. *J. Phys. Chem.* 83 (1979) 893.
16. Hill, T. L. *Thermodynamics of Small Systems*, Benjamin, New York 1963 (Part I), 1964 (Part II).
17. Becher, P. In Schick, M. J., Ed., *Nonionic Surfactants*, Dekker, New York 1967, Chapter 15.
18. Kucharski, S. *J. Colloid Interface Sci.* 77 (1980) 488.
19. Ruckenstein, E. and Krishnan, R. *J. Colloid Interface Sci.* 75 (1980) 476.
20. Ruckenstein, E. and Krishnan, R. *J. Colloid Interface Sci.* 76 (1980) 188.
21. Tanford, C. *Physical Chemistry of Macromolecules*, Wiley, New York 1961, pp. 461 – 466.

22. Mazer, N. A., Benedek, G. B. and Carey, M. C. *J. Phys. Chem.* 80 (1976) 1075.
23. Birdi, K. S., Dalsager, S. U. and Backlund, S. J. *Chem. Soc. Faraday Trans. 1*, 76 (1980) 2035.
24. Dalsager, S. U. *Teoretisk og Eksperimentel Analyse af Micelledannelse*, Ph.D. Thesis, Technical University of Denmark, Lyngby 1980.
25. Sørensen, T. S. *Acta Chem. Scand. A* 32 (1978) 571.
26. Sørensen, T. S. *Acta Chem. Scand. A* 33 (1979) 583.
27. Hall, D. G. and Pethica, B. A. In Schick, M. J., Ed., *Nonionic Surfactants*, Dekker, New York 1967, Chapter 16.
28. Balmbra, R. R., Clunie, J. S., Corkill, J. M. and Goodman *Trans. Faraday Soc.* 58 (1962) 1661.
29. Balmbra, R. R., Clunie, J. S., Corkill, J. M. and Goodman *Trans. Faraday Soc.* 60 (1964) 979.
30. Elworthy, P. H. and Macfarlane, C. B. *J. Chem. Soc.* (1963) 907.
31. Atwood, D. J. *Phys. Chem.* 72 (1968) 339.
32. Tanford, C., Nozaki, Y. and Rohde, M. F. *J. Phys. Chem.* 81 (1977) 1555.
33. Staples, E. J. and Tiddy, G. J. T. *J. Chem. Soc. Faraday Trans. 1*, 74 (1978) 2530.
34. Sørensen, T. S. and Hennenberg, M. In Sørensen, T. S., Ed., *Dynamics and Instability of Fluid Interfaces, Lecture Notes in Physics No. 105*, Springer, Berlin-Heidelberg-New York 1979, pp. 276–315.
35. Sørensen, T. S. *J. Chem. Soc. Faraday Trans. 2*, 76 (1980) 1170.
36. Shinitzky, M., Dianoux, C., Gitler, C. and Weber, G. *Biochemistry* 10 (1971) 2106.
37. Isachenko, V. P., Osipova, V. A. and Sukomel, A. S. *Heat Transfer*, MIR Publishers, Moscow 1977, Appendices, Tables 5 and 7, pp. 481–482.
38. Landolt-Börnstein, *Zahlenwerte und Funktionen, II. Band, 3. Teil*, Springer-Verlag, Berlin 1956, 6th Ed., p. 462, Tabelle 23, 1321.

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