Molecular Packing Parameter and Surfactant Self-Assembly: The Neglected Role of the Surfactant Tail†

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Molecular Packing Parameter and Surfactant Self-Assembly: The Neglected Role of the Surfactant Tail[†]

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The concept of molecular packing parameter is widely invoked in the literature to explain, rationalize and even predict molecular self-assembly in surfactant solutions. The molecular packing parameter is defined as $v_0/a_e l_0$, where v_0 is the surfactant tail volume, l_0 is the tail length, and a_e is the equilibrium area per molecule at the aggregate surface. A particular value of the molecular packing parameter can be translated via simple geometrical relations into specific shape and size of the equilibrium aggregate. This is the predictive application of the concept of molecular packing parameter, as discussed in the literature. In calculating the packing parameter, the dominant notion in the literature is that the surfactant headgroup determines the surface area per molecule of equilibrium aggregates a_e. It follows that, given a headgroup, the molecular packing parameter $v_0/a_e l_0$ is fixed, because the volume-to-length ratio (v_0/l_0) of the tail is a constant independent of the tail length for common surfactants. Therefore, in this view, the surfactant tail has no role in determining the size and shape of equilibrium aggregates. We show that this is contrary to fact, by focusing on the *neglected role of the surfactant tail*. Illustrative calculations are presented in this paper to demonstrate that the surfactant tail does also control equilibrium aggregate structures. It is shown that the role of the tail can be either explicit via modification of the area a_e and thus of the packing parameter, or implicit via other means, without modifying a_e or the packing parameter.

Introduction

The self-assembly of surfactants in solutions has been widely investigated both experimentally and theoretically, because numerous practical applications take advantage of the resulting multimolecular aggregates. The structure of these aggregates influences the properties of surfactant solutions, such as, for example, their solubilization capacity for hydrophobic substances or their viscous and viscoelastic properties, and consequently, the performance of surfactants in various applications. To select molecules that would yield desired structures such as spherical, globular or rodlike micelles, or spherical bilayer vesicles (Figure 1), it is necessary to know how the molecular structure of the surfactant controls the shape and size of the resulting aggregate.

Tanford[1] and Israelachvili, Mitchell and Ninham[2] pioneered two of the most important ideas to answer the above question, more than 25 years ago. Tanford proposed the concept of opposing forces to formulate a quantitative expression for the standard free energy change on aggregation. Using this free energy expression and the geometrical relations for aggregates, he was able to explain why surfactant aggregates form in aqueous solutions, why they grow, why they do not keep growing but are finite in size, and why they assume a given shape. Israelachvili, Mitchell, and Ninham proposed the concept of molecular packing parameter and demonstrated how the size and
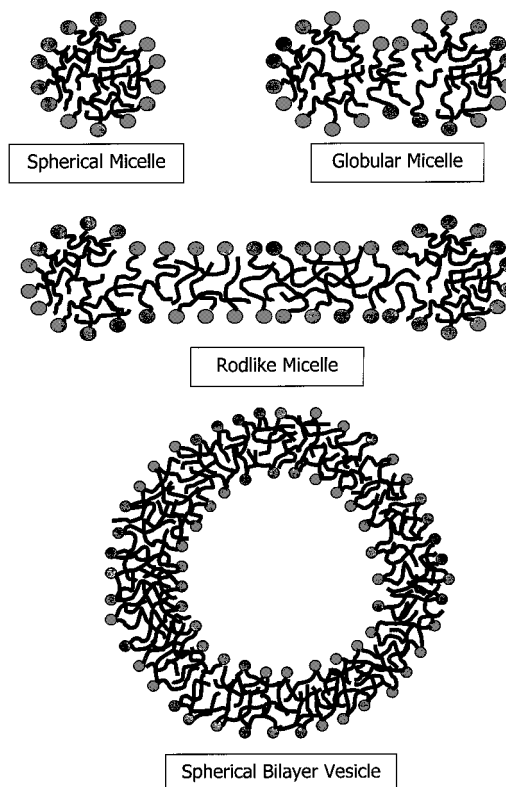
Figure 1. Schematic representation of surfactant aggregates in dilute aqueous solutions.

the shape of the aggregate at equilibrium can be predicted from a combination of molecular packing considerations and general thermodynamic principles. Without any doubt, the contributions of Tanford and of Israelachvili et al. have had a lasting impact on the surfactant literature over the past 25 years.

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(1) Tanford, C. *The Hydrophobic Effect*; Wiley-Interscience: New York, 1973.
(2) Israelachvili, J.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525.

Table 1. Geometrical Relations for Spherical, Cylindrical, and Bilayer Aggregates[a]

variable	sphere	cylinder	bilayer
volume of core $V = g v_0$	$4\pi R^3/3$	πR^2	$2R$
surface area of core $A = ga$	$4\pi R^2$	$2\pi R$	2
area per molecule a	$3v_0/R$	$2v_0/R$	v_0/R
packing parameter v_0/al_0	$v_0/al_0 \leq {}^1/_3$	$v_0/al_0 \leq 1/2$	$v_0/al_0 \leq 1$
largest aggregation number g_{max}	$4\pi l_0^3/3v_0$	$\pi l_0^2/v_0$	$2l_0/v_0$
aggregation number g	$g_{max}(3v_0/al_0)^3$	$g_{max}(2v_0/al_0)^2$	$g_{max}(v_0/al_0)$

[a] Variables V, A, g, and g_{max} refer to the entire spherical aggregate, unit length of a cylinder or unit area of a bilayer. R is the radius of spherical or cylindrical micelle or the half-bilayer thickness of the spherical vesicle. v_0 and l_0 are the volume and extended length of the surfactant tail. g_{max} is the largest aggregation number possible for the given geometry based on the constraint that the aggregate core is filled and the tail cannot stretch beyond its extended length.

Molecular Packing Parameter

The concept of molecular packing parameter has been widely cited in the chemistry, physics, and biology literature because it allows a simple and intuitive insight into the self-assembly phenomenon. The molecular packing parameter is defined as v_0/al_0, where v_0 and l_0 are the volume and the length of the surfactant tail and a is the surface area of the hydrophobic core of the aggregate expressed per molecule in the aggregate (hereafter referred to as the area per molecule). If we consider a spherical micelle with a core radius R, made up of g molecules, then the volume of the core $V = g v_0 = 4\pi R^3/3$, the surface area of the core $A = ga = 4\pi R^2$, and hence $R = 3v_0/a$, from simple geometrical relations. If the micelle core is packed with surfactant tails without any empty space, then the radius R cannot exceed the extended length l_0 of the tail. Introducing this constraint in the expression for R, one obtains $0 \leq v_0/al_0 \leq {}^1/_3$, for spherical micelles.

For spherical, cylindrical or bilayer aggregates made up of g surfactant molecules, the geometrical relations for the volume V and the surface area A are given in Table 1. The variables V, A, and g in the table refer to the entire spherical aggregate, unit length of a cylindrical aggregate, or unit area of a bilayer aggregate, respectively, for the three shapes. These geometrical relations, together with the constraint that at least one dimension of the aggregate (the radius of the sphere or the cylinder, or the half-bilayer thickness, all denoted by R) cannot exceed l_0, lead to the following well-known[2] connection between the molecular packing parameter and the aggregate shape: $0 \leq v_0/al_0 \leq {}^1/_3$ for sphere, ${}^1/_3 \leq v_0/al_0 \leq {}^1/_2$ for cylinder, and ${}^1/_2 \leq v_0/al_0 \leq 1$ for bilayer. Therefore, if we know the molecular packing parameter, the shape and size of the equilibrium aggregate can be readily identified as shown above. This is the predictive sense in which the molecular packing parameter of Israelachvili et al.[2] has found significant use in the literature.

The notion of molecular packing into various aggregate shapes was recognized even in the earlier work of Tartar[3] and Tanford,[1] as can be seen, for example, from Figure 9.1 of Tanford's classic monograph. However, only after this concept was explored thoroughly in the work of Israelachvili et al.[2] taking the form of the packing parameter, has it evoked wide appreciation in the literature.

(3) Tartar, H. V. *J. Phys. Chem.* **1955**, *55*, 1195.

For common surfactants, the ratio v_0/l_0 is a constant independent of tail length, equal to 21 Å^2 for single tail and 42 Å^2 for double tail.[1] Consequently, only the area a_e reflects the specificity of the surfactant in the packing parameter $v_0/a_e l_0$. The area a_e is influenced directly by the headgroup interactions, in the framework of Tanford's free energy model to be discussed in the following section. Hence, the accepted notion in the surfactant literature is, given a headgroup, a_e is fixed, which, then, determines the packing parameter $v_0/a_e l_0$; thus, the headgroup controls the equilibrium aggregate structure.

In this view, the surfactant tail has no recognizable role in determining the shape and size of the self-assembled structure. Here, we show this is contrary to fact, by exploring the neglected role of the surfactant tail. For this purpose, we do not seek to introduce new physical features such as the aggregate surface being rough rather than be molecularly smooth (as implied by the molecular packing descriptions). Instead, we show that, keeping in tact the common assumptions of the molecular packing model, one still obtains results contrary to conventional understanding and interpretation.

Estimating Equilibrium Area From Tanford's Free Energy Model

The area per molecule a$_e$ is a *thermodynamic quantity obtained from equilibrium considerations of minimum free energy* and is *not a simple variable connected to the geometrical shape and size of the surfactant headgroup*. To estimate a_e, Israelachvili et al.[2] invoked the model for the standard free energy change on aggregation pioneered by Tanford.[1] Although more detailed free energy models have since been formulated[4–6] and have been shown to predict accurately experimental results, we will use the simple framework provided by Tanford for the purposes of this analysis.

In his phenomenological model, Tanford suggested that the standard free energy change associated with the transfer of a surfactant from its infinitely dilute state in water to an aggregate of size g (aggregation number) has three contributions:

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right) = \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{Transfer} + \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{Interface} + \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{Head} \quad (1)$$

The first term $(\Delta\mu_g^\circ/kT)_{Transfer}$ is a negative free energy contribution arising from the transfer of the tail from its unfavorable contact with water to the hydrocarbon-like environment of the aggregate core. The transfer free energy contribution depends on the surfactant tail but not on the aggregate shape or size. The second term $(\Delta\mu_g^\circ/kT)_{Interface}$ provides a positive contribution to account for the fact that the entire surface area of the tail is not removed from water but there is still residual contact with water at the surface of the aggregate core. This is represented as the product of a contact free energy per unit area σ (or an interfacial free energy) and the surface area per molecule of the aggregate core a. The third term $(\Delta\mu_g^\circ/kT)_{Head}$ provides another positive contribution representing the repulsive interactions between the headgroups that crowd at the aggregate surface. The repul-

(4) Nagarajan, R.; Ruckenstein, E. *Langmuir* **1991**, *7*, 2934.

(5) Nagarajan, R. In *Structure-Performance Relationships in Surfactants*; Esumi, K., Ueno, M., Eds., Marcel Dekker: New York, 1997; Chapter 1, pp 1–89.

(6) Nagarajan, R.; Ruckenstein, E. In *Equations of State for Fluids and Fluid Mixtures*; Sengers, J. V., Kayser, R. F., Peters, C. J., White, H. J., Jr., Eds.; Elsevier Science: Amsterdam, 2000; Chapter 15, pp 589–749.

sions may be due to steric interactions (for all types of headgroups) and also electrostatic interactions (dipole–dipole interactions for zwitterionic headgroups and ion–ion repulsions for ionic headgroups). Since the repulsion would increase if the headgroups come close to one another, Tanford proposed an expression with an inverse dependence on a. Thus, the standard free energy change per molecule on aggregation, proposed by Tanford has the form:

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right) = \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{\text{Transfer}} + \left(\frac{\sigma}{kT}\right)a + \left(\frac{\alpha}{kT}\right)\frac{1}{a} \quad (2)$$

where α is the headgroup repulsion parameter, k the Boltzmann constant, and T the temperature.

Starting from the free energy model of Tanford, the equilibrium aggregation behavior can be examined either by treating the surfactant solution as consisting of aggregates with a distribution of sizes or by treating the aggregate as constituting a pseudophase.[1,4-6] If the aggregate is viewed as a pseudophase, in the sense of small systems thermodynamics, the equilibrium condition corresponds to a minimum in the standard free energy change ($\Delta\mu_g^\circ/kT$). The minimization can be done with respect to either the aggregation number g or the area per molecule a, since they are dependent on one another through the geometrical relations given in Table 1. One obtains in this manner, the equilibrium condition:

$$\frac{\partial}{\partial a}\left(\frac{\Delta\mu_g^\circ}{kT}\right) = 0 \Rightarrow \left(\frac{\sigma}{kT}\right) - \left(\frac{\alpha}{kT}\right)\frac{1}{a^2} = 0 \text{ at } a = a_e \Rightarrow$$

$$a_e = \left(\frac{\alpha}{\sigma}\right)^{1/2} \quad (3)$$

The critical micelle concentration (cmc, denoted as X_{cmc} in mole fraction units), in the pseudophase approximation, is obtained from the relation,

$$\ln X_{\text{cmc}} = \left(\frac{\Delta\mu_g^\circ}{kT}\right) = \left(\frac{\Delta\mu_g^\circ}{kT}\right)_{\text{Transfer}} + \left(\frac{\sigma}{kT}\right)a_e + \left(\frac{\alpha}{kT}\right)\frac{1}{a_e} \quad (4)$$

In Tanford's free energy expression (eq 2), the first contribution, the tail transfer free energy, is negative. Hence, this contribution is responsible for the aggregation to occur. It affects only the cmc (as shown by eq 4) but not the equilibrium area a_e (as shown by eq 3) or the size and shape of the aggregate. The second contribution, the free energy of residual contact between the aggregate core and water, is positive and decreases in magnitude as the area a decreases. A decrease in the area a, corresponds to an increase in the aggregation number g, for all aggregate shapes, as shown in Table 1. Hence, this contribution promotes the growth of the aggregate. The third contribution, the free energy due to headgroup repulsions, is also positive and increases in magnitude if the area a decreases or the aggregation number g increases. Hence, this contribution is responsible for limiting the growth of aggregates to a finite size. Thus, Tanford's model clearly identifies why aggregates form, why they grow and why they do not keep growing but remain finite in size.

Predicting Self-assembly from Molecular Packing Parameter

The packing parameter $v_0/a_e l_0$ can be estimated using the area a_e obtained from eq 3. One can observe that a_e will be small and the packing parameter will be large if the headgroup interaction parameter α is small. The area a_e will increase and the packing parameter will decrease,

if the interfacial free energy per unit area σ decreases. These simple considerations allow one to predict many features of surfactant self-assembly as summarized below.

(i) For nonionic surfactants with ethylene oxide units as the headgroup, the headgroup parameter α can be expected to increase in magnitude if the number of ethylene oxide units in the headgroup increases. Therefore, when the number of ethylene oxide units is small, α is small, a_e is small, $v_0/a_e l_0$ is large, and bilayer aggregates (lamellae) are favored. For larger number of ethylene oxide units, α increases, a_e increases, $v_0/a_e l_0$ decreases, and cylindrical micelles become possible. When the number of ethylene oxide units is further increased, $v_0/a_e l_0$ becomes small enough so that spherical micelles will form with their aggregation number g decreasing with increasing ethylene oxide chain length.

(ii) Comparing nonionic and ionic surfactants, the headgroup interaction parameter α will be smaller for nonionics than for ionics, because one has to also consider ionic repulsions in the latter case. Therefore, a_e will be smaller and $v_0/a_e l_0$ will be larger for the nonionics compared to the ionics. As a result, nonionic surfactants would form aggregates of larger aggregation number compared to ionic surfactants of the same tail length.

(iii) For a given surfactant molecule, the headgroup repulsion can be decreased, by modifying the solution conditions. For example, adding salt to an ionic surfactant solution decreases ionic repulsions; increasing the temperature for a nonionic surfactant molecule with ethylene oxide headgroup decreases steric repulsions. Because α decreases, a_e will decrease and $v_0/a_e l_0$ will increase. Thus, one can achieve a transition from spherical micelles to rodlike micelles and possibly to bilayer aggregates, by modifying solution conditions that control headgroup repulsions.

(iv) If single tail and double tail surfactant molecules are compared, for the same equilibrium area a_e, the double tail molecule will have a packing parameter $v_0/a_e l_0$ twice as large as that of the single tail molecule. Therefore, the double tail molecule can self-assemble to form bilayer vesicles while the corresponding single tail molecule aggregates into only spherical or globular micelles.

(v) If the solvent is changed from water to a mixed aqueous–organic solvent, then the interfacial tension parameter σ decreases. For a given surfactant, this would lead to an increase in the equilibrium area per molecule a_e, and hence, a decrease in $v_0/a_e l_0$. Therefore, upon the addition of a polar organic solvent to an aqueous surfactant solution, bilayers will transform into micelles, rodlike micelles into spherical micelles, and spherical micelles into those of smaller aggregation numbers including only small molecular clusters.

All of the above predictions are in agreement with numerous experiments and are by now well established in the literature (see papers cited in refs 1, 2, and 4–6). One can thus see the evidence for the predictive power of the molecular packing parameter model and its dramatic simplicity.

Neglected Role of the Surfactant Tail

From the discussion so far, it is obvious that the equilibrium area a_e has become closely identified with the headgroup of the surfactant because of its dependence on the headgroup interaction parameter α. Indeed, a_e is often referred to as the "headgroup area" in the literature. *This has even led to the erroneous identification of a_e as a simple geometrical area based on the chemical structure of the headgroup in many papers, in contrast to the actuality*

that a_e is an equilibrium parameter derived from thermodynamic considerations. Needless to say, that for the same surfactant molecule, the area a_e can assume widely different values depending on the solution conditions such as temperature, salt concentration, additives present, etc.; hence, it is meaningless to associate one specific area with a given headgroup.

Regardless of whether a_e is recognized correctly as the result of equilibrium free energy minimum considerations or erroneously as a simple geometrical property of the headgroup, the role of the surfactant headgroup in controlling self-assembly is appreciated in the literature. In contrast, the role of the surfactant tail has been virtually neglected. This is because, the ratio v_0/l_0 appearing in the molecular packing parameter is independent of the chain length for common surfactants and the area a_e depends only on the headgroup interaction parameter α (eq 3).

To illustrate the significant role surfactant tail plays in governing the equilibrium aggregate structures, we present below three illustrations relating to spherical micelles, rodlike micelles and bilayer vesicles, all in the framework of Tanford's free energy expression. In these examples, the equilibrium area a_e, given by eq 3, is directly dependent on the headgroup interaction parameter α. We will show that the surfactant tail can, nevertheless, control the nature of aggregates formed. This can be an explicit control, through modification of a_e and hence of the packing parameter; alternatively, it can be an implicit control by other means, without changing a_e or the packing parameter.

Finally, we will discuss an extension to Tanford's free energy expression to account for the packing entropy of the surfactant tail in the aggregates. The need for such a contribution had already been recognized by Tanford[1] through an empirical correction to the magnitude of the tail transfer free energy. However, only later, detailed chain packing models to estimate this free energy contribution were developed following different approaches, such as those by Gruen,[7] Dill and Flory,[8] Ben-Shaul and Gelbart,[9] Puvvada and Blankschtein,[10] and Nagarajan and Ruckenstein.[4] This contribution has been shown to be important for quantitative predictions of a wide range of self-assembly phenomena, such as micelles, mixed micelles, and solubilization.[4−6,10] The inclusion of this free energy contribution obviously leads to the surfactant tail directly influencing a_e, and hence the packing parameter, size, and shape of the equilibrium aggregate.

Example 1: Spherical Micelles of Ionic Surfactants

Let us look at solution conditions for which the molecular packing parameter is in the range $0 \leq v_0/a_e l_0 \leq {}^1\!/_3$. The packing parameter model predicts that spherical micelles should form, and further, that the aggregation number of the micelle should be proportional to the square of the tail length (as discussed below).

Consider a family of nonionic or zwitterionic surfactants with identical headgroup but differing tail lengths. The headgroup repulsion parameter α is a constant for this homologous family of molecules. Therefore, a_e calculated

(7) Gruen, D. W. R. *Biochim. Biophys. Acta* **1980**, *595*, 161; *J. Colloid Interface Sci.* **1981**, *84*, 281; *J. Phys. Chem.* **1985**, *89*, 146.
(8) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3115; *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *78*, 676.
(9) Ben-Shaul. A.; Szleifer, I.; Gelbart, W. M. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 4601; *J. Chem. Phys.* **1985**, *3*, 3597. Ben-Shaul, A.; Gelbart, W. M. *Rev. Phys. Chem.* **1985**, *36*, 179.
(10) Puvvada, S.; Blankschtein, D. *J. Chem. Phys.* **1990**, *92*, 3710; *J. Phys. Chem.* **1992**, *96*, 5567.

from eq 3, and the packing parameter $v_0/a_e l_0$ are both independent of the tail length. The aggregation number of the resulting spherical micelles (from Table 1) is given by

$$g = g_{max}\left(\frac{3v_0}{a_e l_0}\right)^3 = \left(\frac{4\pi l_0^3}{3v_0}\right)\left(\frac{3v_0}{a_e l_0}\right)^3 \propto n_C^2 \qquad (5)$$

One may note that because of the proportionality of v_0 and l_0 to the number of carbon atoms n_C in an aliphatic tail, g_{max} is proportional to n_C^2, and the molecular packing parameter is a constant. The packing parameter model thus predicts that the aggregation number will be proportional to n_C^2, or the square of the surfactant tail length.

Now consider a family of ionic surfactants, with identical headgroup but differing tail lengths. At first sight, it appears that the previous analysis should hold and the aggregation number of spherical micelles of ionic surfactants should also be proportional to n_C^2 just as for nonionic and zwitterionic surfactants. However, this is not true because of the role played by the surfactant tail.

The influence of the tail is exerted as follows. The equilibrium area a_e depends on the headgroup repulsion parameter α, which in this case, accounts for electrostatic interactions between ionic headgroups. These interactions depend on the ionic strength of the solution. In the absence of any added electrolyte, near the cmc, the ionic strength is determined primarily by the concentration of the singly dispersed surfactant in solution, which is practically equivalent to the cmc. The cmc is strongly dependent on the transfer free energy of the tail, which is directly dependent on n_C or the length of the tail. Thus, the headgroup interaction parameter α and hence, the equilibrium area a_e, for ionic surfactants, in the absence of added electrolytes, has a strong dependence on the tail length. Therefore, the aggregation number of spherical ionic micelles at the cmc will not be proportional to n_C^2. Instead, as the chain length increases, the cmc will decrease, the ionic strength will decrease, the headgroup interaction parameter α will increase, equilibrium area a_e will increase, and the micelle size g will become smaller than what is predicted by the molecular packing model.

A simple numerical illustration is presented here assuming the Debye−Hückel form of the electrostatic interaction energy between headgroups[1,2] and making some simplifications for illustrative purposes. The headgroup repulsion term α/a in eq 2 can be written as

$$\frac{\alpha}{a} = \frac{2\pi e^2 d}{\epsilon a}\left(\frac{1}{1 + \kappa R}\right) \approx \frac{2\pi e^2 d}{\epsilon a}\left(\frac{1}{1 + \kappa l_0}\right) \Rightarrow$$

$$\alpha = \frac{2\pi e^2 d}{\epsilon}\left(\frac{1}{1 + \kappa l_0}\right) \quad (6)$$

where the bracketed term is the electrical double layer correction term[1] that accounts for ionic strength effects and the approximation $R \approx l_0$ is made in this term. Here, e is the electronic charge (4.8×10^{-10} esu), ϵ is the dielectric constant of the solvent medium (80 for water), κ is the inverse Debye length that depends on the ionic strength, and d is the capacitor thickness in the double layer model. For uni-univalent ionic systems, such as sulfate coion and sodium counterion for the anionic sodium alkyl sulfate surfactants, κ is given by

$$\kappa = \left[\frac{8\pi n_0 e^2}{\epsilon kT}\right]^{1/2} = \left[\frac{8\pi e^2}{\epsilon kT}\frac{cmc}{1000}N_{Avo}\right]^{1/2} \qquad (7)$$

Table 2. Spherical Micelles of Ionic Surfactants: Tail Length Dependence of Aggregation Number[a]

n_C	l_o (Å)	cmc (M)	κ^{-1} (Å)	κl_o	$1/(1 + \kappa l_o)^{1/2}$	a_e (Å^2)	$v_o/a_e l_o$	g
8	11.5	0.032	17.22	0.668	0.774	63.5	0.331	$0.979 g_{max}$
10	14	0.016	24.35	0.575	0.797	65.4	0.321	$0.893 g_{max}$
12	16.5	0.008	34.43	0.479	0.822	67.4	0.312	$0.820 g_{max}$
14	19	0.004	48.7	0.390	0.848	69.5	0.302	$0.744 g_{max}$
16	21.5	0.002	68.9	0.312	0.873	71.6	0.293	$0.679 g_{max}$

[a] The cmc values approximate those for sodium alkyl sulfates. The calculated values of the packing parameter is fitted to the chain length and shows the dependence, $v_o/a_e l_o \propto n_C^{-1/6}$. This leads to $g \propto n_C^{3/2}$, because $g_{max} \propto n_C^2$. See text for discussion.

where n_0 is the number of counterions in solution per cm^3 which has been related to the cmc in mol/L. Here N_{Avo} is the Avogadro number and the factor 1000 converts concentration per liter to that per cm^3 of solution. Introducing α from eq 6 into eq 3, the equilibrium area per molecule is

$$a_e = \left[\frac{2\pi e^2 d}{\epsilon \sigma} \frac{1}{1 + \kappa l_o}\right]^{1/2} \tag{8}$$

For numerical illustration, one can calculate a_e as a function of the tail length (using eq 8), taking for example purposes, $(2\pi e^2 d/\epsilon\sigma)^{1/2} = 82$ Å^2. The results are summarized in Table 2 along with the cmc values (typical of sodium alkyl sulfates) and tail lengths l_o used for estimating κ (from eq 7). The results show that the packing parameter $v_o/a_e l_o$ is not a constant, but is approximately proportional to $n_C^{-1/6}$. Noting that g_{max} is proportional to n_C^2, we conclude that the aggregation number g of spherical micelles of ionic surfactants is proportional to $n_C^{3/2}$. Thus, the influence of the surfactant tail operating through the parameter κ has led to a different prediction for g in the case of ionic surfactants. Detailed numerical calculations in ref 4 for sodium alkyl sulfates show even a stronger influence of the tail than that suggested by the simplified model calculations here.

This is an example where the surfactant tail plays an explicit role in controlling the aggregate size. The role is explicit in the sense that the surfactant tail directly influences the equilibrium area a_e and the molecular packing parameter. The pathway through which the surfactant tail exerts its influence is. however, indirect, and not obvious at first sight.

Example 2: Transition from Spherical to Rodlike Micelles

We will now consider solution conditions when the molecular packing parameter is in the range $^1/_3 \le v_o/a_e l_o \le ^1/_2$. The packing parameter model predicts the formation of rodlike micelles.

The thermodynamics of transition from spherical micelles to rodlike micelles is well established in the literature based on the pioneering analysis by Mukerjee.[11] Alternate but equivalent versions of the model have also been presented.[2,4,12,13] The rodlike aggregates can be visualized as having a cylindrical middle part with two spherical endcaps as shown in Figure 1. The standard chemical potential of a rodlike aggregate of size g containing g_{cap} molecules in the two spherical endcaps

and $(g - g_{cap})$ molecules in the cylindrical middle can be written as

$$\frac{\mu_g^\circ}{kT} = (g - g_{cap})\frac{\mu_{cyl}^\circ}{kT} + g_{cap}\frac{\mu_{cap}^\circ}{kT} \tag{9}$$

where μ_{cyl}° and μ_{cap}° are the standard chemical potentials of the molecules in the two regions of the spherocylindrical aggregate, respectively. Introducing the above relation in the aggregate size distribution equation,[1-3]

$$X_g = \left[X_1 \exp\left(-\frac{\Delta\mu_g^\circ}{kT}\right)\right]^g \tag{10}$$

we obtain

$$X_g = \frac{1}{K} Y^g, \quad Y = X_1 \exp\left(-\frac{\Delta\mu_{cyl}^\circ}{kT}\right),$$
$$\ln K = g_{cap}\left(\frac{\Delta\mu_{cap}^\circ - \Delta\mu_{cyl}^\circ}{kT}\right) \tag{11}$$

where $\Delta\mu_{cyl}^\circ$ and $\Delta\mu_{cap}^\circ$ are the differences in the standard chemical potentials between the surfactant molecules in the cylindrical middle or the endcaps of the rodlike micelle and the singly dispersed surfactant molecule. The concentration X_1 refers to the singly dispersed molecules and is practically equal to X_{cmc}. The variable K is a measure of the free energy cost of having g_{cap} molecules in the spherical endcaps compared to the energetically favored cylindrical portion. The parameter Y indicates the possibility of occurrence of rodlike aggregates at a given concentration of the singly dispersed surfactant molecules. The number and weight average aggregation numbers g_n and g_w can be computed on the basis of the size distribution[2,4,11-13] as a function of the total surfactant concentration X_{tot}:

$$g_n = g_{cap} + [K(X_{tot} - X_1)^{1/2}];$$
$$g_w = g_{cap} + 2[K(X_{tot} - X_1)^{1/2}] \tag{12}$$

The aggregation number of the micelle depends on the sphere-to-rod transition parameter K as shown above. For large rodlike micelles to form at reasonable surfactant concentrations, K has to be in the range $10^7 - 10^{12}$.[2,11] K depends on two factors as shown by eq 11: (i) g_{cap}, which is influenced by the length of the tail and (ii) $\Delta\mu_{cap}^\circ - \Delta\mu_{cyl}^\circ$, the standard free energy difference between a molecule in the cylindrical part and one in the endcap, which is determined by the molecular packing parameter. For a given molecular packing parameter, K increases with increasing g_{cap}. Therefore, it is obvious that, for the same magnitude of the packing parameter, K will increase with increasing tail length making the formation of rodlike micelles more favorable for longer tail lengths than for shorter tail lengths.

The above conclusions are quantitatively illustrated below. Let us calculate the sphere-to-rod transition

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Table 3. Formation of Rodlike Micelles: Tail Length Dependence of K and Aggregation Number[a]

n_C	l_o (Å)	g_{cap}	K	$[K(X_{tot} - X_1)]^{1/2}$	g_w
		For $v_o/a_e l_o = 0.42$, $K = \exp(0.322 g_{cap})$			
8	11.5	27	6×10^3	2.4	32
10	14	40	3.9×10^5	19.7	79
12	16.5	55	6.8×10^7	261	577
14	19	72	1.2×10^{10}	3464	7000
16	21.5	92	7.3×10^{12}	85440	170972
		For $v_o/a_e l_o = 0.45$, $K = \exp(0.508 g_{cap})$			
8	11.5	27	9.1×10^5	30	87
10	14	40	6.7×10^8	818	1676
12	16.5	55	2.3×10^{12}	47958	95971

[a] The weight average aggregation numbers have been calculated at $X_{tot} - X_1 = 10^{-3}$, which corresponds to 55 mM surfactant in aggregated state. K must be in the range $10^7 - 10^{12}$ for large rodlike micelles to form at physically meaningful surfactant concentrations.

parameter K in the framework of Tanford's model, taking the endcaps to be the largest hemispheres possible. A more detailed description of the endcap has been used in the predictive theory developed by us previously,[4] but for the illustrative calculations intended in this paper, the simplified view of largest hemispheres is adequate. One can write

$$\ln K = g_{cap}\left[\left(\frac{\Delta\mu^\circ_{cap}}{kT}\right) - \left(\frac{\Delta\mu^\circ_{cyl}}{kT}\right)\right] = g_{cap}\left[\left(\frac{\sigma}{kT}\right)(a_{cap} - a_{cyl}) + \left(\frac{\alpha}{kT}\right)\left(\frac{1}{a_{cap}} - \frac{1}{a_{cyl}}\right)\right] \quad (13)$$

For endcaps treated as the largest hemispheres, $a_{cap} = 3v_o/l_o = 63$ Å^2 and $g_{cap} = g_{max}$ for the spherical micelles (given in Table 1). For illustrative purposes, two different values of the molecular packing parameter $v_o/a_e l_o = 0.42$ and 0.45 are considered, both of which would predict that cylindrical micelles should form.

For $v_o/a_e l_o = 0.42$, $a_{cyl} = 50$ Å^2 since $v_o/l_o = 21$ Å^2 for a single tail surfactant. The corresponding headgroup interaction parameter is found from eq 3, given $\sigma = 50$ dyn/cm^2 or $(\sigma/kT) = 0.12$ Å^{-2}. We obtain $\alpha/kT = 300$ Å^2. Introducing these values in eq 13, the sphere to rod transition parameter K is computed.

$$\ln K = g_{cap}\left[\left(\frac{\Delta\mu^\circ_{cap}}{kT}\right) - \left(\frac{\Delta\mu^\circ_{cyl}}{kT}\right)\right] = 0.322\, g_{cap} \quad (14)$$

Similarly, for $v_o/a_e l_o = 0.45$, $a_{cyl} = 46.67$ Å^2, and from eq 3, $\alpha/kT = 261.4$ Å^2. Correspondingly,

$$\ln K = g_{cap}\left[\left(\frac{\Delta\mu^\circ_{cap}}{kT}\right) - \left(\frac{\Delta\mu^\circ_{cyl}}{kT}\right)\right] = 0.508 g_{cap} \quad (15)$$

Using these values, we estimate the magnitude of K and the weight-average aggregation number g_w of the micelle for surfactants of varying tail lengths. The weight average aggregation numbers are calculated (eq 12) at a concentration of $X_{tot} - X_1 = 10^{-3}$ (which is equal to approximately 55 mM) for the surfactant in aggregated form. The illustrative results are summarized in Table 3.

For both values of $v_o/a_e l_o$, the packing parameter model would predict the formation of cylindrical micelles. However, we observe from Table 3, that for a given packing parameter, K is small for short tail lengths and increases with increasing tail lengths. The entry g_{cap} gives the aggregation number of the largest spherical micelle and this can be compared with the equilibrium aggregation number g_w. For example, when $v_o/a_e l_o = 0.42$, g_w for $n_C =$

8 is practically the same as for the spherical micelle; for $n_C = 10$, g_w is only twice as large as that of the sphere, suggesting a globular micelle. Only for longer tail lengths g_w is large enough representing rodlike micelles. Thus, although the molecular packing parameter permits the formation of rodlike micelles, the surfactant tail plays a role to prevent the formation of rods and favor spheres or globular aggregates for $n_C = 8$ and 10 when $v_o/a_e l_o = 0.42$. The same observations are valid for $n_C = 8$ when $v_o/a_e l_o = 0.45$.

This is an example of the implicit role played by the surfactant tail in controlling the equilibrium aggregate structure. The role is implicit in the sense that the tail does not affect the equilibrium area a_e, and hence, the packing parameter. Rather, the tail length influences g_{cap}, which in turn affects the magnitude of the sphere-to-rod transition parameter K, thereby controlling whether rodlike micelles can form or not, even under conditions when the packing parameter allows rods.

Example 3: Formation of Spherical Bilayer Vesicles

Let us now consider solution conditions when the molecular packing parameter is in the range $^1/_2 \leq v_o/a_e l_o \leq 1$. The packing parameter model would predict the formation of spherical bilayer vesicle.

When bilayer vesicles form with an enclosed aqueous cavity, the headgroups of the surfactants in the inner layer of the bilayer are located within this inner aqueous cavity. Therefore, for bilayer vesicles to form, the volume of this inner aqueous cavity per molecule must be larger than the volume of the headgroup. This is an additional constraint beyond what has been implied by the molecular packing parameter. We will show that the surfactant tail plays an implicit role in controlling whether vesicular structures can form, even when the molecular packing parameter allows it, through this constraint on the inner aqueous cavity volume.

Consider a vesicle (schematically shown in Figure 1) whose hydrophobic domain has an outer radius R_o and the half-bilayer thickness is R. The inner radius of the hydrophobic domain is thus $R_o - 2R$. Israelachvili et al.[2] have shown that, in order to satisfy packing within aggregates everywhere locally with uniform density, and not simply on the average, it is necessary to satisfy the local packing criterion

$$\frac{v_o}{a} = l\left[1 - \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{l^2}{3R_1 R_2}\right] \quad (16)$$

where R_1 and R_2 are the local radii of curvature and l is the length of the hydrocarbon region of the amphiphiles. Applying this packing criterion to the outer layer of the bilayer, they obtained

$$R_o = \frac{l[3 + \sqrt{3(4v_o/a_o l - 1)}]}{6(1 - v_o/a_o l)} \quad (17)$$

where a_o refers to the equilibrium area per molecule at the outer surface. If we denote the equilibrium area per molecule at the inner surface of the vesicle by a_i, then the number of surfactant molecules g_i in the inner layer of the bilayer and the volume per molecule of the inner aqueous cavity V_{cavity} are given by

$$g_i = \frac{4\pi(R_o - 2R)^2}{a_i},$$

$$V_{cavity} = \frac{4\pi}{3}\frac{(R_o - 2R)^3}{g_i} = \frac{(R_o - 2R)a_i}{3} \quad (18)$$

We will now perform illustrative calculations assuming that a_o and a_i are equal and that R is equal to the extended length l_o of the surfactant tail. Detailed predictive calculations[5,6] show that, in actuality, a_o and a_i are different from one another. Also, the thickness of the inner and the outer layers differ and they both will be smaller than the extended length of the tail. But inclusion of these details is not necessary for the present purposes, since they do not affect the main arguments and conclusions.

Let us consider two values for the molecular packing parameter $v_o/a_e l_o = 0.75$ and 0.8 and assume that they are associated with double chain amphiphiles such as phospholipids for which $v_o/l_o = 42$ Å². The packing parameter model predicts the formation of spherical bilayer vesicles in both cases. For $v_o/a_e l_o = 0.75$, $a_e = 56$ Å² since $v_o/l_o = 42$ Å² and the vesicle radius is $R_o = 3.63\, l_o$ from eq 17. Taking $R = l_o$, we find from eq 18, the volume per molecule of the inner cavity, $V_{cavity} = (3.63\, l_o - 2\, l_o)\,a_e/3$. Similarly, for $v_o/a_e l_o = 0.80$, $a_e = 52.5$ Å² and vesicle radius is $R_o = 4.64\, l_o$, and $V_{cavity} = (4.64\, l_o - 2\, l_o)a_e/3$. Note that vesicles have small radii in these illustrations; their radii can be an order of magnitude larger than l_o if the packing parameter assumes values closer to unity. For mixtures of phospholipids of short and long chain lengths, radii in the range of 100−300 Å have been experimentally determined.[14]

Numerical estimates of V_{cavity} are summarized in Table 4 for the two values of the molecular packing parameter, and for varying tail lengths. The aqueous cavity volume per molecule increases as the tail length increases. For phospholipids, the headgroup volume is about 400−500 Å³ depending upon the specificity of the headgroup. Therefore, one can see from Table 4, that the short chain dialkyl surfactants cannot aggregate into spherical bilayer vesicles even though the molecular packing parameter allows it. With increasing tail length, spherical bilayer vesicles become possible. Indeed, the experimental studies of Tausk et al.[13] on synthetic phosphotidylcholines showed that for tail lengths of $n_C = 5$, 6, or 7, only micelles form, but when $n_C = 8$, spherical vesicles form.

In this example, the surfactant tail plays an implicit role in controlling self-assembly. The role is implicit in the sense that the tail does not affect the equilibrium area a_e and the packing parameter, but the tail length influences the volume of the aqueous cavity. The tail exerts its controlling influence on the aggregate structure through its effect on the aqueous core volume of the vesicle.

Tail Packing Free Energy and Explicit Importance of Tail

In the previous three examples, the equilibrium area a_e given by eq 3 was directly dependent on the headgroup interaction parameter α but not on the tail length. Equation 3 for the equilibrium area is based on the free energy model of Tanford (eq 2). In formulating and evaluating his free energy expression, Tanford had already noted[1] that the transfer free energy of the tail $(\Delta\mu_g^\circ/kT)_{Transfer}$ has a magnitude different from the free energy for transferring the corresponding hydrocarbon chain from aqueous solution to a pure hydrocarbon phase.

Table 4. Formation of Spherical Bilayer Vesicles: Tail Length Dependence of Aqueous Cavity Volume[a]

n_C	l_o (Å)	V_{cavity} (Å³) $v_o/a_e l_o = 0.75$	V_{cavity} (Å³) $v_o/a_e l_o = 0.80$
6	9	272	416
7	10.25	310	474
8	11.5	348	531
10	14	423	647
12	16.5	499	762
14	19	575	878
16	21.5	650	993

[a] R is taken equal to l_o. For $v_o/a_e l_o = 0.75$, $a_e = 56$ Å², $V_{cavity} = 30.24\, l_o$; for $v_o/a_e l_o = 0.80$, $a_e = 52.5$ Å², $V_{cavity} = 46.2\, l_o$. If the headgroup area of the surfactant is larger than the calculated V_{cavity}, then the formation of the bilayer vesicle is not possible.

He had correctly surmised that the difference arises from the packing constraints inside the aggregates that are absent in the case of a bulk hydrocarbon liquid phase. He took account of this factor empirically, as a correction to the transfer free energy, independent of the aggregate size and shape.

Later studies have shown[4,7−10] that the packing free energy contribution $(\Delta\mu_g^\circ/kT)_{Packing}$ is dependent on the aggregate shape and size and methods for estimating this contribution have been developed by adopting different approaches. Of these, we follow our previous work[4] here, because of the analytical nature and simplicity of the free energy expression formulated. This expression is based on the analysis carried out by Semenov[15] for block copolymer systems, and takes into account the fact that the tail has to deform nonuniformly along its length to fill the aggregate core with uniform density. The packing free energy contribution has the form

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{Packing} = \left(\frac{3\pi^2}{80}\right)\frac{R^2}{NL^2}, \quad \left(\frac{5\pi^2}{80}\right)\frac{R^2}{NL^2}, \quad \left(\frac{10\pi^2}{80}\right)\frac{R^2}{NL^2} \quad (19)$$

for spheres, cylinders, and bilayers. In the above equation, L is a characteristic segment length that is taken to be 4.6 Å (see ref 4 for details) and N is the number of segments in a tail such that $NL^3 = v_o$. Since $R = 3v_o/a$, $2v_o/a$, and v_o/a for the three geometries (Table 1), the packing free energy contribution can be rewritten as

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{Packing} = \frac{Q}{a^2}, \quad Q_{sph} = \left(\frac{27}{8}\right)v_o L, \quad Q_{cyl} = \left(\frac{20}{8}\right)v_o L,$$

$$Q_{bilayer} = \left(\frac{10}{8}\right)v_o L \quad (20)$$

where the symbol Q is used to denote the coefficient of $1/a^2$ in the free energy expression and it stands for Q_{sph}, Q_{cyl}, or $Q_{bilayer}$, depending upon the aggregate shape. The equilibrium area a_e given before by eq 3 is now obtained from

$$\frac{\partial}{\partial a}\left(\frac{\Delta\mu_g^\circ}{kT}\right) = 0 \Rightarrow \left(\frac{\sigma}{kT}\right) - \left(\frac{\alpha}{kT}\right)\frac{1}{a^2} - \frac{2Q}{a^3} = 0$$

$$\text{at } a = a_e \Rightarrow a_e = \left(\frac{\alpha}{\sigma} + \frac{2Q/a_e}{\sigma/kT}\right)^{1/2} \quad (21)$$

Since the variable Q is dependent on the tail, the tail has direct influence over the equilibrium area a_e and the packing parameter. The consequence is the direct control exerted by the tail over the size and shape of the equilibrium aggregate.

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Table 5. Formation of Spherical and Rodlike Micelles and Spherical Vesicles: Consequences of Incorporating Tail Packing Free Energy[a]

	from eq 3		spheres (eq 21)		cylinder (eq 21)		bilayers (eq 21)	
n_C	a_e (Å²)	$v_o/a_e l_o$	a_e (Å²)	$v_o/a_e l_o$	a_e (Å²)	$v_o/a_e l_o$	a_e (Å²)	$v_o/a_e l_o$
	For $\sigma/kT = 0.12$ Å⁻², $\alpha/kT = 120$ Å²							
8	31.6	0.664	(48.1)	(0.437)	45.1	0.466	39.9	0.527
12	31.6	0.664	(52.1)	(0.403)	48.8	0.43	(42.3)	(0.496)
16	31.6	0.664	(55.9)	(0.391)	51.9	0.404	(44.6)	(0.471)
	For $\sigma/kT = 0.12$ Å⁻², $\alpha/kT = 240$ Å²							
8	44.7	0.47	(55.9)	(0.375)	53.6	0.392	(49.7)	(0.423)
12	44.7	0.47	(59.4)	(0.354)	56.5	0.372	(51.5)	(0.408)
16	44.7	0.47	62.45	0.336	59.1	0.356	(53.1)	(0.395)
	For $\sigma/kT = 0.12$ Å⁻², $\alpha/kT = 300$ Å²							
8	50	0.42	(59.6)	(0.352)	57.5	0.365	(54.1)	(0.388)
12	50	0.42	62.9	0.334	60.1	0.349	(55.7)	(0.377)
16	50	0.42	65.7	0.320	62.5	0.336	(57.2)	(0.367)

[a] Although the results in parentheses are solutions to eq 21, they are invalid for physical reasons. This is because, in calculating the area using eq 21 in which eq 20 is incorporated, a shape is assumed, but the resulting estimate for the area is physically inconsistent with that shape. Only the results without the parenthesis are physically attainable and hence, relevant. See text for details.

Illustrative numerical calculations have been carried out taking into account this packing free energy contribution. For this purpose, we have chosen three different values for the headgroup interaction parameter (α/kT) keeping $\sigma/kT = 0.12$ Å⁻², consistent with σ being 50 dyn/cm. Q depends on the tail length and the shape of the aggregate as shown in eq 20. A summary of the calculated results for three tail lengths of single tail surfactants is given in Table 5. Shown in the table are the equilibrium area a_e and the molecular packing parameter $v_o/a_e l_o$ calculated based on eq 3 ignoring the packing free energy contribution and those based on eq 21 accounting for this contribution.

When using eq 21 to calculate a_e, the expression for Q_{sph}, Q_{cyl}, or $Q_{bilayer}$ is introduced while calculating the area corresponding to the sphere, cylinder or the bilayer, respectively. In each case, a numerical solution is obtained and all three solutions corresponding to the three shapes are listed in the table. However, not all three of the solutions are valid. A solution is not valid if the calculated area is not consistent with the aggregate shape assumed for the calculation. For example, in the first entry, the area per molecule calculated assuming a spherical shape turns out to be 48.1 Å², but such an area is not consistent with a spherical structure since the smallest area per molecule attainable for a sphere is 63 Å². Hence, this solution is not valid. In Table 5, the physically invalid results are shown within parentheses.

One can now compare the predictions of a_e and $v_o/a_e l_o$ obtained by ignoring the packing free energy and by accounting for the packing free energy. The inclusion of the packing free energy (eq 21) results in the equilibrium area a_e being larger than that estimated from eq 3 neglecting this contribution. For $\alpha/kT = 120$ Å², $a_e = 31.6$ Å² from eq 3; hence, $v_o/a_e l_o = 0.664$, and correspondingly, bilayer structures are predicted, independent of the tail length. However, when eq 21 is applied, one obtains for

$n_C = 8$, $a_e = 45.1$ Å², and $v_o/a_e l_o = 0.466$, implying a cylindrical aggregate. In this case, there is also another solution: $a_e = 39.9$ Å² and $v_o/a_e l_o = 0.527$, implying a bilayer aggregate. For $n_C = 12$ or 16, only one valid solution exists corresponding to the formation of cylindrical aggregates. Similarly, for $\alpha/kT = 240$ Å², eq 3 predicts $v_o/a_e l_o = 0.47$ and, correspondingly, large rodlike micelles for all three tail lengths. However, eq 21 predicts $v_o/a_e l_o$ in the range of 0.33–0.39 depending upon the tail length, indicating the formation of only smaller cylinders or near-spherical aggregates. For $\alpha/kT = 300$ Å², when eq 3 is used, we obtain $v_o/a_e l_o = 0.42$ consistent with cylindrical micelles, for all three tail lengths. But eq 21 for the same conditions predicts $v_o/a_e l_o$ to be in the range 0.32–0.365 depending upon the tail length, suggesting only spherical or small globular aggregates. In all cases, the predictions are significantly modified by the incorporation of the tail packing free energy contribution. The surfactant tail exerts a direct influence over the equilibrium area per molecule a_e, hence on the packing parameter and the size and shape of the equilibrium aggregate.

Conclusions

The molecular packing parameter concept emphasizes the importance of the surfactant headgroup in predicting the shape and size of equilibrium aggregates. In this paper, we have shown though illustrative numerical examples, that the surfactant tail also has a controlling role. In the framework of the free energy model of Tanford, the equilibrium area is directly dependent on the headgroup interaction parameter but not on the tail; nevertheless, the tail still exerts a strong influence over the formation of spherical micelles, rodlike micelles and spherical bilayer vesicles. In the case of spherical ionic micelles, the tail influences the ionic strength and thereby modifies the equilibrium area and the packing parameter, and thus, the aggregate size. In the case of cylindrical aggregates, the tail does not affect the equilibrium area and the packing parameter, but affects the sphere-to-rod transition parameter by influencing the number of molecules in the endcaps of rodlike micelle. Consequently, even when the molecular packing parameter allows their formation, rodlike micelles are not formed in some cases. In the case of bilayer vesicles, the tail again does not affect the equilibrium area and the packing parameter but influences the volume of the aqueous cavity inside the vesicle. If the volume of the aqueous cavity cannot accommodate the surfactant headgroups, then vesicles are not realizable. Consequently, even when the molecular packing parameter allows their formation, spherical bilayer vesicles are not formed in some cases. Finally, we consider an extension of Tanford's free energy expression to account for the packing entropy of tails inside aggregates. Obviously, in this case, the tail directly influences the equilibrium area and the packing parameter, and therefore, the size and shape of the equilibrium aggregates formed. Therefore, while predicting the structure of equilibrium surfactant aggregates on the basis of the molecular packing parameter, one should not neglect the role of the tail and focus only on the headgroup.