

# Critical Micelle Concentration: A Transition Point for Micellar Size Distribution

## A Statistical Thermodynamical Approach

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The size distribution of aggregates in amphiphilic systems are computed on the basis of statistical thermodynamics. Numerical calculations have been carried out for alkyl glucosides and sodium alkyl sulfates. In these cases the computations show that the amphiphilic solution consists of single amphiphiles and only a narrow size range of aggregates. A critical concentration, defined earlier, corresponding to a transition in the shape of the micellar size distribution from a monotonic decreasing function to a function exhibiting extrema, is calculated. This critical concentration is a lower bound of the CMC's determined from sharp changes in the physical properties of the amphiphilic systems.

### I. INTRODUCTION

In an earlier paper (1), a critical micelle concentration which separates two kinds of behavior of the size distribution of micellar aggregates of surfactant molecules was introduced. Below this critical concentration the size distribution is a monotonic decreasing function of size; above this concentration the size distribution is a function exhibiting two extrema. Empirical expressions provided by Tanford (2) for the free-energy terms were used to obtain the aggregate size distribution as well as the critical concentration. In this paper a statistical thermodynamical approach is used to calculate the free energy of the system in order to obtain the equilibrium micellar size distribution and the critical concentration.

Hoeve and Benson (3) treated the micellar system using the canonical ensemble of aggregates of all possible sizes. In the absence of

detailed information, only qualitative results concerning the size distribution function for nonionic micelles could be obtained and the problem of the critical concentration was not treated. They concluded that the micellar size and the single amphiphile concentration were not constant above the CMC.

Poland and Scheraga (4) developed a quantitative treatment of micellization of non-ionic amphiphiles, assuming that the system is composed only of solvent molecules and aggregates of a single size. To obtain a stable aggregate, two conditions have to be fulfilled: The free energy per amphiphile of the aggregate has to be a minimum at a large degree of aggregation, and this minimum has to be smaller than that of a single amphiphile in the solution. They defined the CMC as the concentration where the free energy per amphiphile of the aggregate and the free energy of the monomer are equal. This approach was extended (5) to ionic micelles by including the electrostatic repulsion between the ionic head groups.

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In the present work, we consider instead a system consisting of solvent molecules, single amphiphiles, and polydispersed aggregates, i.e., aggregates of all possible sizes. From the condition of equilibrium the size distribution of micelles is obtained. A critical concentration is evaluated as the total amphiphile concentration corresponding to the transition in the shape of the size distribution function. Using the size distribution function, any size-dependent property of the amphiphilic system can be calculated. This permitted evaluation of CMC values based on a sharp change in slope of any size-dependent property of the system (6).

The main contribution of the present work lies in the computation, on the basis of statistical thermodynamics, of the size distribution and of the critical concentration defined earlier. Compared to the treatment of Poland and Scheraga, the present approach takes into account the size distribution of the aggregates. Compared to the treatment of Hoeve and Benson, the present treatment identifies clearly all the contributions to the total free energy of the system and thus quantitative estimation of the micellar size distribution is made possible.

In the following section, the total free energy of the system is written in terms of the partition functions of the ensemble of aggregates of the single amphiphiles and of the molecules of solvent. The equilibrium condition, corresponding to the minimum of the free energy of the system, gives the size distribution of the aggregates. In Section III, explicit expressions for different terms contributing to the partition function for both nonionic and ionic micelles are derived, and the equilibrium size distribution is obtained in Sections IV and V. In Section VI, values for different parameters are evaluated and illustrative numerical results for the size distribution of aggregates and for the critical concentration are calculated for both nonionic and ionic surfactants.

## II. STATISTICAL THERMODYNAMICAL FORMULATION

*Ensemble partition function.* A dilute surfactant solution is considered, containing  $N_s$  molecules of solvent and a total of  $N$  surfactant molecules which are present as  $N_1, N_2, \dots, N_g, \dots$  number of aggregates containing 1, 2,  $\dots, g, \dots$  monomers each, respectively. Hence

$$\sum_{g=1}^{\infty} gN_g = N. \quad [1]$$

If  $Q_g$  denotes the partition function of an aggregate of size  $g$ ,  $Q_1$  the partition function of a single amphiphile, and  $Q_s$  the partition function of a solvent molecule, then the partition function of the system is

$$Q = \frac{Q_s^{N_s} \cdot Q_1^{N_1}}{N_s! \cdot N_1!} \cdot \prod_{g=2}^{\infty} \frac{Q_g^{N_g}}{N_g!}. \quad [2]$$

The partition functions  $Q_1$  and  $Q_g$  include the interactions with the solvent while  $Q_s$  is the partition function of the pure solvent.

*Equilibrium aggregate size distribution.* The free energy of the system is given by

$$F = -kT \ln Q, \quad [3]$$

where  $k$  is Boltzmann's constant and  $T$  the absolute temperature. The equilibrium condition subject to constraint [1] is

$$\frac{\partial}{\partial N_g} \left[ \ln Q + \lambda \left( \sum_{g=1}^{\infty} gN_g - N \right) \right] = 0, \quad [4]$$

for  $g = 1, \dots, \infty,$

where  $\lambda$  is a Lagrangian multiplier. Using Stirling's approximation in Eq. [2] and introducing the result into Eq. [4] yields

$$\ln N_1 = \ln Q_1 + \sum_{g=2}^{\infty} N_g \frac{\partial \ln Q_g}{\partial N_1} + \lambda \quad [5]$$

and

$$\ln N_g = \ln Q_g + \lambda g. \quad [6]$$

Eliminating  $\lambda$  between Eqs. [5] and [6], the size distribution of aggregates at equilibrium

is obtained as

$$\ln N_g = \ln \left( \frac{Q_g}{Q_1^g} \right) + g \ln N_1 - g \sum_{g=2}^{\infty} N_g \times \frac{\partial \ln Q_g}{\partial N_1}. \quad [7]$$

### III. EXPLICIT EXPRESSIONS FOR THE PARTITION FUNCTION

*Form of  $Q_g$ .* It is assumed that  $Q_g$  can be represented as the product of partition functions representing contributions from the external degrees of freedom of the aggregate, the internal degrees of freedom of amphiphiles within the aggregate, the interactions between monomers within the aggregate, the interfacial interactions of the head groups with the solvent, and the interfacial free energy between the hydrocarbon core and the solvent. In the case of ionic micelles, the free-energy term accounting for the electrostatic repulsion between the ionic head groups is also included in  $Q_g$ . Therefore

$$Q_g = Q_g^{\text{external}} Q_g^{\text{internal}} Q_g^{\text{internal interactions}} \times Q_g^{\text{interface}} Q_g^{\text{electrical}}. \quad [8]$$

*External partition function.* The external contribution is the product of the partition functions for the translation and rotation of the aggregate as a whole:

$$Q_g^{\text{external}} = Q_{\text{agg}}^{\text{trans}} Q_{\text{agg}}^{\text{rot}}, \quad [9]$$

where

$$Q_{\text{agg}}^{\text{trans}} = [2\pi m g k T / h^2]^{3/2} V f_1 \quad [10]$$

and

$$Q_{\text{agg}}^{\text{rot}} = [2\pi \bar{I}_g k T / h^2]^{3/2} 8\pi^2. \quad [11]$$

In these expressions,  $m$  is the mass of a monomer unit,  $V$  is the total volume of the system,  $f_1$  is the ratio of the free volume available for translation to the total volume,  $\bar{I}_g$  is the moment of inertia of the aggregate, and  $h$  is Planck's constant. Since the system is very dilute in surfactant,  $f_1$  is approximately equal to the ratio of free volume to total volume of solvent.

For the sake of simplicity, it is assumed that the aggregates have spherical shapes. This assumption is not a restrictive one and it is possible, in principle, to incorporate changes in shape occurring, in particular, above a critical radius of the aggregate of the order of the extended length of the amphiphile. For spherical micelles, the moment of inertia is given by

$$\bar{I}_g = \frac{2}{5} m g r_g^2, \quad [12]$$

where  $r_g$  is the radius of the aggregate. The volume of the hydrophobic core of an aggregate of amphiphiles with  $n_c$  carbon atoms in the hydrocarbon chain is given by [2]

$$g v_0 = g [27.4 + 26.9(n_c - 1)], \quad [13]$$

where  $v_0$  is the volume of the hydrocarbon tail of a single amphiphile in cubic angstroms. The radius  $r_g$  of the aggregate is obtained by increasing the radius  $r_{0g}$  of the hydrophobic core by a thickness  $\delta$ , which accounts for the surface roughness due to the head groups (2). Hence

$$r_g = r_{0g} + \delta, \quad [14]$$

where

$$r_{0g} = (3v_0/4\pi)^{1/3} g^{1/3}. \quad [15]$$

*Internal partition function.* The internal contribution to the partition function arises from the translational, rotational, and vibrational contributions of the monomers within the aggregate:

$$Q_g^{\text{internal}} = (1/g!) Q_g^{\text{trans}} Q_g^{\text{rot}} Q_g^{\text{vib}}. \quad [16]$$

The translational contribution of amphiphiles that are free to move without any constraint within an aggregate of size  $g$  is given by

$$Q_g^{\text{trans}} = [(2\pi m k T / h^2)^{3/2} g v_0 f_2]^{g-1}, \quad [17]$$

where  $f_2$  is the ratio of the free volume to the total volume of the bulk amphiphilic phase. The exponent is reduced by unity because the translation of the aggregate as a whole has already been considered. Since the head groups are constrained to move on the surface, the actual free volume available for translation is smaller than that in the absence of any con-

straint. The motion of each of the head groups is hindered sterically and by the interactions with other head groups. The ratio of the free volume available in the presence of constraints to the free volume available in their absence is equal to the nonexcluded fraction  $(A_g - ga_p)/A_g$  of the aggregate surface area. Here  $A_g$  is the surface area of the aggregate and  $a_p$  the effective area of a polar head group. The translational partition function is consequently given by

$$Q_g^{\text{trans}} = \left[ \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} g v_0 f_2 \left( \frac{A_g - ga_p}{A_g} \right) \right]^{g-1}, \quad [18]$$

where

$$A_g = 4\pi r_g^2, \quad [19]$$

and  $r_g$  is given by Eq. [14].

The micellar core is considered to be liquid-like (2, 3). The vibrational partition functions of monomers within the aggregate are considered to be the same as those in a bulk amphiphilic phase. The orientation of the monomers in the aggregates, however, prevents their free rotation. The monomers are free to rotate about their long axis, while rotation about the other two short axes is restricted. We assume here that they are totally restricted. The rotational and vibrational contributions are then given by

$$Q_g^{\text{rot}} = [Q_{1z}^{\text{rot}}]^{g-1} \quad [20]$$

and

$$Q_g^{\text{vib}} = [Q_1^{\text{vib}}]^g, \quad [21]$$

where  $Q_{1z}^{\text{rot}}$  and  $Q_1^{\text{vib}}$  are the partition functions for rotation about the long axis and the vibration of a single molecule in the pure liquid. The rotational term is calculated from

$$Q_{1z}^{\text{rot}} = (2\pi I_{1z} kT / h^2)^{\frac{1}{2}} 2\pi, \quad [22]$$

where  $I_{1z}$  is the moment of inertia of the monomer about the long axis. The monomer has a rodlike shape with length  $l$  and radius  $R$  of the hydrocarbon tail (both in angstroms)

given by (2)

$$l = 1.5 + 1.265(n_c - 1) \quad [23]$$

and

$$R = (v_0 / \pi l)^{\frac{1}{2}}. \quad [24]$$

The value of  $I_{1z}$  is given by

$$I_{1z} = m v_0 / 2\pi l. \quad [25]$$

*Interaction partition function-internal interactions.* The van der Waals interactions between the hydrocarbon tails within the micellar core are proportional to the total number of  $\text{CH}_2$  (and  $\text{CH}_3$ ) groups not exposed to the aqueous medium. The  $\text{CH}_2$  group adjacent to the polar head group is in the sphere of hydration of the head group and, therefore, does not contribute to the van der Waals interactions. The total number of  $\text{CH}_2$  (and  $\text{CH}_3$ ) groups mutually interacting is then given by

$$N^{\text{vw}} = g(n_c - 1). \quad [26]$$

If  $-F^{\text{vw}}$  denotes the free energy per  $\text{CH}_2$  group due to the van der Waals interaction between the hydrocarbon chains, then their contribution to the total free energy is

$$-\ln Q_g^{\text{internal interactions}} = -\frac{F^{\text{vw}}}{kT} g(n_c - 1). \quad [27]$$

*Interaction partition function-interfacial interactions.* The polar head groups at the micellar surface interact with the aqueous medium. Also, there is an interfacial free energy between the hydrocarbon core and the aqueous medium. The corresponding partition function can be written as the product

$$Q_g^{\text{interface}} = Q_{gp}^{\text{solvent}} Q_{gh}^{\text{solvent}}, \quad [28]$$

where the subscripts p and h refer to the polar head group and to the hydrocarbon core, respectively. The polar head-solvent interaction energy for aggregates is the same as that for single amphiphilic molecules. Since it vanishes in the final expressions for the size distribution of aggregates, it is not explicitly calculated but is written as

$$Q_{gp}^{\text{solvent}} = [Q_p^{\text{solvent}}]^g, \quad [29]$$

where  $Q_p^{\text{solvent}}$  refers to the polar head-solvent interaction contribution for a single polar head. The hydrocarbon-solvent interfacial free-energy term is proportional to the interfacial area of contact between the hydrocarbon core and the aqueous medium. Denoting by  $\sigma$  the hydrocarbon-aqueous medium interfacial free energy per unit area, one can write

$$-\ln Q_{ph}^{\text{solvent}} = (\sigma/kT)(A_{0g} - ga_0), \quad [30]$$

where  $A_{0g}$  denotes the surface area of the hydrocarbon core and  $a_0$  is the actual cross-sectional area per amphiphile covered by the polar head group. The core surface area  $A_{0g}$  is calculated from

$$A_{0g} = 4\pi r_{0g}^2,$$

where  $r_{0g}$  is given by Eq. [15]. The interfacial energy  $\sigma$  is related to  $r_{0g}$  through the equation

$$\sigma = \sigma_0[1 - (\alpha/r_{0g})] \quad (\alpha \approx 1 \sim 2 \text{ \AA}), \quad [31]$$

where  $\sigma_0$  and  $\alpha$  are constants.

*Electrostatic free-energy partition function.* In the case of ionic micelles the contribution of repulsive interactions between ionic head groups can be evaluated (2b) from the work required to charge a sphere of radius  $r_g$ . Using Debye-Hückel approximations, one obtains the free energy per charge as

$$W_g = \frac{2\pi\epsilon^2 r_g(1 + \kappa a_i)}{(DA_g/\beta g)(1 + \kappa r_g + \kappa a_i)}, \quad [32]$$

where  $\epsilon$  is the electronic charge,  $\kappa$  is the reciprocal Debye length,  $a_i$  is the average radius of the counterions in the electrolyte medium,  $\beta$  is the fraction of the dissociated ionic groups of the surface, and  $D$  is the dielectric constant of the medium. The reciprocal Debye length for an aqueous 1-1 electrolyte solution at 25°C is defined by (8)

$$\kappa = \frac{C^{\frac{1}{2}}}{3.04 \times 10^{-8}} \text{ cm}^{-1}, \quad [33]$$

where the ionic strength  $C$ , expressed in moles/liter, is

$$C = \beta(N_1/N_0V) + C_s. \quad [34]$$

Here  $N_1/N_0V$  is the molar concentration of the single amphiphile,  $N_0$  is Avogadro's number, and  $C_s$  is the molar concentration of the added salt. The free-energy contribution due to the electrostatic repulsion between univalent head groups is given by

$$-\ln Q_g^{\text{electrical}} = (W_g/kT)g\beta. \quad [35]$$

*Partition function of the single amphiphile.*

The partition function of the single amphiphile in solution is the product of the translational, rotational, and vibrational contributions of the single molecule, the contributions due to interactions of the head group and of the hydrocarbon tail with the solvent, and the contributions due to intramolecular van der Waals interactions.

The translational contribution is

$$Q_1^{\text{trans}} = [2\pi mkT/h^2]^{\frac{3}{2}} V f_1. \quad [36]$$

In the pure liquid phase the hydrocarbon tails have a rodlike conformation with a consequent restriction on rotation. In an aqueous solution, the hydrocarbon chain is coiled up and, although there is a restriction on rotation, the number of possible configurations is larger than that for stretched rods in the pure liquid. Introducing a configurational term  $Q_1^{\text{config}}$  to account for this difference, the internal degrees of freedom of an amphiphile in solution can be represented by (7)

$$Q^{\text{internal}} = Q_1^{\text{rot}} Q_1^{\text{config}} Q_1^{\text{vib}}, \quad [37]$$

where  $Q_1^{\text{rot}}$  and  $Q_1^{\text{vib}}$  are the same as for the pure amphiphilic phase. The rotational partition function in the pure liquid  $Q_1^{\text{rot}}$  is given by

$$Q_1^{\text{rot}} = (2\pi \bar{I}_1 kT/h^2)^{\frac{1}{2}} 8\pi^2, \quad [38]$$

where  $\bar{I}_1$  is the moment of inertia of the monomer. For a monomer with a rodlike conformation

$$\bar{I}_1 = (I_{1x} I_{1y} I_{1z})^{\frac{1}{3}} = \left(\frac{1}{32}\right)^{\frac{1}{3}} \frac{mv_0}{\pi l}. \quad [39]$$

If the configurational entropy change per molecule is denoted by  $\Delta S^{\text{config}}$ , then the contribution to the partition function of this

term is

$$\ln Q_1^{\text{config}} = \Delta S^{\text{config}}/k. \quad [40]$$

The polar head-solvent interaction term has already been mentioned and is denoted by  $Q_p^{\text{solvent}}$ . The hydrocarbon-solvent interaction energy arises because of the changes in the structure of water in the neighborhood of the hydrocarbon tails of the amphiphiles and because of the van der Waals interactions between the hydrocarbon tails and the solvent. Denoting by  $C_h$  the hydrocarbon-solvent interaction energy per  $\text{CH}_2$  group, one can write

$$-\ln Q_h^{\text{solvent}} = (C_h/kT)n_c. \quad [41]$$

The single molecules in the aqueous medium are coiled and hence some intramolecular van der Waals interactions exist between the  $\text{CH}_2$  groups of the same hydrocarbon tail. If the number of  $\text{CH}_2$  groups participating in the intramolecular contacts is denoted by  $n^{\text{vW}}$ , then the free-energy contribution of intramolecular van der Waals interactions is given by

$$-\ln Q_1^{\text{vW}} = - (F^{\text{vWs}}/kT) \cdot n^{\text{vW}}. \quad [42]$$

Here  $F^{\text{vWs}}$  denotes the van der Waals interaction energy per  $\text{CH}_2$  group when the groups are not in the bulk hydrocarbon, but in the aqueous solution. It has been estimated (7) that about 20 to 30% of the  $\text{CH}_2$  groups in the hydrocarbon tail are involved in the intramolecular van der Waals interactions. Hence as an approximation

$$n^{\text{vW}} = 0.25n_c. \quad [43]$$

The single amphiphile partition function is thus

$$Q_1 = Q_1^{\text{trans}} Q_1^{\text{rot}} Q_1^{\text{config}} Q_1^{\text{vib}} \times Q_p^{\text{solvent}} Q_h^{\text{solvent}} Q_1^{\text{vW}}. \quad [44]$$

#### IV. SIZE DISTRIBUTION OF NONIONIC MICELLES

For nonionic micelles, the aggregate partition function  $Q_g$  is independent of the number  $N_1$  of single amphiphiles. The size distribution

function is obtained by substituting the partition function of the aggregate (Eq. [8]) and the single amphiphile partition function (Eq. [44]) in Eq. [7] to get

$$\begin{aligned} \ln N_g = & \ln \left( \frac{2\pi m g k T}{h^2} \right)^{\frac{3}{2}} V f_1 + \ln \left( \frac{2\pi \bar{I}_g k T}{h^2} \right)^{\frac{3}{2}} 8\pi^2 \\ & + (g-1) \ln \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} g v_0 \cdot f_2 \left( \frac{A_g - g a_p}{A_g} \right) \\ & + (g-1) \ln \left( \frac{2\pi I_{1z} k T}{h^2} \right)^{\frac{1}{2}} 2\pi - g \ln g + g \\ & + \frac{F^{\text{vW}}}{kT} g(n_c - 1) - \frac{\sigma}{kT} (4\pi r_{0g}^2 - g a_0) \\ & - g \ln \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \cdot V \cdot f_1 - g \ln \left( \frac{2\pi \bar{I}_1 k T}{h^2} \right)^{\frac{3}{2}} 8\pi^2 \\ & + \frac{C_h}{kT} g n_c - \frac{F^{\text{vWs}}}{kT} g n^{\text{vW}} + g \ln N_1 \\ & - g \frac{\Delta S^{\text{config}}}{k}. \quad [45] \end{aligned}$$

After some rearrangement, Eq. [45] becomes

$$\begin{aligned} \ln \frac{N_g}{N_0 V} = & \left\{ \frac{3}{2} \ln g - \ln N_0 v_0 + \ln \left( \frac{2\pi \bar{I}_g k T}{h^2} \right)^{\frac{3}{2}} 8\pi^2 \right. \\ & + (g-1) \ln g \left( 1 - \frac{g a_p}{A_g} \right) \frac{f_2}{f_1} - g \ln g \\ & + g \left[ \ln N_0 v_0 + \ln \left( \frac{N_1}{N_0 V} \right) + 1 - \frac{\Delta S^{\text{config}}}{k} \right] \\ & + (g-1) \ln \left( \frac{2\pi I_{1z} k T}{h^2} \right)^{\frac{1}{2}} \cdot 2\pi \\ & \left. - g \ln \left( \frac{2\pi \bar{I}_1 k T}{h^2} \right)^{\frac{3}{2}} 8\pi^2 \right\} + \left\{ \frac{F^{\text{vW}}}{kT} g(n_c - 1) \right. \\ & - \frac{\sigma}{kT} (4\pi r_{0g}^2 - g a_0) + \frac{C_h}{kT} g n_c \\ & \left. - \frac{F^{\text{vWs}}}{kT} g n^{\text{vW}} \right\}. \quad [46] \end{aligned}$$



The van der Waals interaction energy between  $\text{CH}_2$  groups has been estimated (7) as  $-150$  cal/mole of  $\text{CH}_2$  for pairwise interactions. For a hexagonal packing of hydrocarbon molecules in the liquid, the total interaction energy based on the above value is  $-900$  cal/mole of  $\text{CH}_2$ . Hence  $F^{vW}$  is equal to  $6.3 \times 10^{-14}$  ergs/ $\text{CH}_2$  group. The van der Waals interactions between  $\text{CH}_2$  groups which are in close contact with the aqueous medium are expected to be small compared to  $F^{vW}$ . Correspondingly, we assign an arbitrary value to  $F^{vW_s}$  equal to  $0.5 F^{vW}$ .

The water-hydrocarbon interaction energy  $C_h$  includes the contributions of the van der Waals interactions between the hydrocarbon tails and the solvent, as well as the changes in the water structure in the layers adjacent to the hydrocarbon tails of the amphiphiles. These contributions to  $C_h$  have been evaluated for aliphatic hydrocarbons with up to eight carbon atoms in the hydrocarbon chain (7). The estimate of  $C_h$  is based on calculations carried out for octane.

Taking into account the number of interacting solvent molecules in the layer adjacent to the hydrocarbon, the van der Waals interaction energy for octane was estimated by Nemethy and Scheraga (7) to be about  $-870$  cal/mole of octane. The estimation was made by modifying the theoretical dispersion energy so as to fit the experimental measurements of the free energy of transfer of a hydrocarbon chain from an aqueous phase to the bulk hydrocarbon phase. The contribution to  $C_h$  due to the disruption of the water structure was calculated using the model proposed by Nemethy and Scheraga (9) and is estimated as  $3400$  cal/mole of octane. Based on these values, the water-hydrocarbon interaction energy is estimated to be about  $2500$  cal/mole of octane. This corresponds to a value of about  $315$  cal/mole of  $\text{CH}_2$  group; that is,  $C_h = 2.25 \times 10^{-14}$  ergs/ $\text{CH}_2$  group. The interfacial free energy  $\sigma_0$  for hydrocarbon-aqueous medium is estimated to be about  $50$  ergs/ $\text{cm}^2$ .

The configurational entropy change due to the coiling of a single amphiphile in the aqueous medium from its rodlike conformation in the hydrocarbon medium has been estimated by Nemethy and Scheraga (7) as

$$\Delta S^{\text{config}} = 0.6(n_c - 4) \text{ cal/mole degree.} \quad [50]$$

From this one obtains

$$\frac{\Delta S^{\text{config}}}{k} = 0.3(n_c - 4)$$

per single amphiphile molecule. [51]

The free volume available for a molecule is dependent both on the size of the molecule and on the nature of intermolecular interactions and is normally a fraction of the molar volume in the case of liquids. For water, a free volume value of about  $4.4 \times 10^{-25}$   $\text{cm}^3$  per molecule was adopted by Nemethy and Scheraga (9) as the best fit in their model for the structure of water. Taking the molar

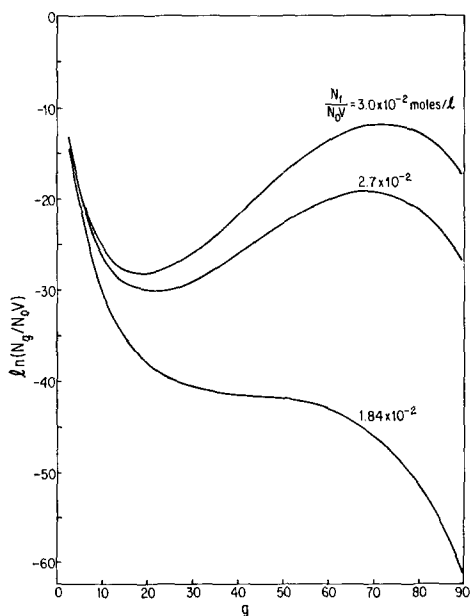


Fig. 1. Dependence of size distribution on concentration of single amphiphiles for octyl glucoside at  $25^\circ\text{C}$ . Both  $N_g/N_0V$  and  $N_1/N_0V$  are expressed in moles per liter.



TABLE I

Dependence of Aggregate Concentration on the Concentration of Single Amphiphile for Dodecyl Glucoside at 25°C.

$\frac{N_1}{N_0V}$ (moles/liter)	$\sum_{g=2}^{\infty} g \frac{N_g}{N_0V}$ (moles/liter)	$\frac{N_1}{N_0V} + \sum_{g=2}^{\infty} g \frac{N_g}{N_0V}$ (moles/liter)
$2.4 \times 10^{-4}$	$1.65 \times 10^{-11}$	$2.40 \times 10^{-4}$
$2.5 \times 10^{-4}$	$6.27 \times 10^{-9}$	$2.50 \times 10^{-4}$
$2.6 \times 10^{-4}$	$2.06 \times 10^{-6}$	$2.621 \times 10^{-4}$
$2.65 \times 10^{-4}$	$3.54 \times 10^{-5}$	$3.004 \times 10^{-4}$
$2.70 \times 10^{-4}$	$5.88 \times 10^{-4}$	$8.580 \times 10^{-4}$
$2.75 \times 10^{-4}$	$9.43 \times 10^{-3}$	$9.708 \times 10^{-3}$

volume of water as 18 cm<sup>3</sup>, one obtains

$$f_1 = \frac{4.4 \times 10^{-25} \times N_0}{18} = 0.01467. \quad [52]$$

Methods of estimation of the free volume from either the thermal expansion and compressibility data or the vapor pressure data have been discussed by Fowler and Guggenheim (10). The computation of the ratio  $f_2$  (free volume to total volume of bulk amphiphilic phase) was carried out using the expressions developed by Fowler and Guggenheim (10) for nonpolar liquids to obtain

$$f_2 = \frac{v_{\text{amphiphile}}}{V_{\text{amphiphile}}} = \left( \frac{14}{V_{\text{amphiphile}}} \right)^3, \quad [53]$$

where  $v$  denotes the free molar volume and  $V$  the total molar volume. Since (3)

$$V_{\text{amphiphile}} = 16.2n_c \text{ cm}^3/\text{mole}, \quad [54]$$

TABLE II

Dependence of Critical Concentration on the Length of the Hydrocarbon Chain for Alkyl Glucosides at 25°C.

$n_c$	$C_{\text{critical, calcd}}$ (moles/liter)	CMC, exptl (11) (moles/liter)
8	$1.865 \times 10^{-2}$	$2.51 \times 10^{-2}$
10	$1.750 \times 10^{-3}$	$2.19 \times 10^{-3}$
12	$1.420 \times 10^{-4}$	$1.92 \times 10^{-4}$
14	$1.040 \times 10^{-5}$	$1.67 \times 10^{-5}$
16	$0.715 \times 10^{-6}$	$1.45 \times 10^{-6}$

the ratio  $f_2/f_1$  is obtained as

$$\frac{f_2}{f_1} = \left( \frac{14}{16.2n_c} \right)^3 \frac{1}{0.01467}. \quad [55]$$

*Results for nonionic micelles.* The aggregate size distribution function is calculated for alkyl glucosides [ROCH(CHOH)<sub>5</sub>]. The effective cross-sectional area,  $a_p$ , of the polar head is taken (3) as 40 Å<sup>2</sup>. The increment  $\delta$  of the core radius, used to approximate the real surface area of the aggregate, is taken as 2 Å. The cross-sectional area covered by the polar head group,  $a_0$ , is taken as 22 Å<sup>2</sup> per amphiphile.

The size distribution function for a monomer with  $n_c = 8$  carbon atoms in the hydrocarbon chain is shown in Fig. 1 for different single amphiphile concentrations. The concentration of aggregates remains significant only in a narrow size range around the maximum in the size distribution. The size distribution index calculated as the ratio of the true weight average aggregation  $\sum_{2}^{\infty} g^2 N_g / \sum_{2}^{\infty} g N_g$  to the true number average aggregation  $\sum_{2}^{\infty} g N_g /$

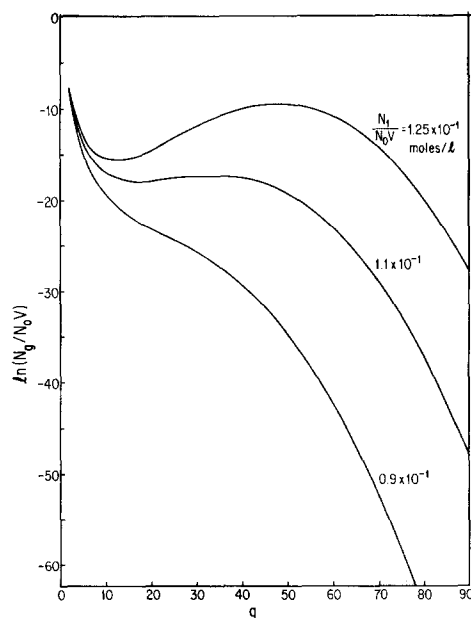


FIG. 2. Dependence of size distribution on concentration of single amphiphiles for sodium octyl sulfate at 25°C. Both  $N_g/N_0V$  and  $N_1/N_0V$  are expressed in moles per liter.

TABLE III

Dependence of Critical Concentration on the Chain Length of Hydrocarbon for Sodium Alkyl Sulfates at 25°C.

$n_c$	$C_{\text{critical, calcd}}$ (moles/liter)	CMC, exptl (11) (moles/liter)
8	$1.010 \times 10^{-1}$	$1.15 \times 10^{-1}$
10	$2.67 \times 10^{-2}$	$2.95 \times 10^{-2}$
12	$6.21 \times 10^{-3}$	$7.6 \times 10^{-3}$
14	$1.150 \times 10^{-3}$	$1.95 \times 10^{-3}$
16	$1.80 \times 10^{-4}$	$5.0 \times 10^{-4}$

$\sum z^{\infty} N_z$  is close to unity (smaller than 1.03). The critical concentration is evaluated as the total amphiphile concentration for which a transition in the behavior of the size distribution occurs. At this point the total amphiphile concentration is virtually equal to that of unaggregated single amphiphiles. The dependence of the total amphiphile concentration on the concentration of single amphiphiles is presented in Table I. The region where a sharp rise in aggregate concentration occurs is usually identified as the CMC. The transition in the shape of the size distribution function, used to define the critical concentration, occurs at somewhat lower amphiphilic concentrations. Hence, the critical concentration calculated here is a lower bound on the CMC normally determined.

The values of the critical concentration for amphiphiles with different hydrocarbon chain lengths and the same head group are calculated for alkyl glucosides and are given in Table II. The calculated critical concentrations are compared with the experimental measurements of CMC (11). A change of the head group will introduce changes in the values of the parameters  $m$  and  $a_p$  which depend on the size and the shape of the head group and, hence, changes in the size distribution and critical concentration.

*Results for ionic micelles.* Computations of the size distributions and critical concentrations are carried out for ionic amphiphiles with  $-\text{SO}_3\text{Na}$  head groups. The effective area of the head group  $a_p$  is taken as  $30 \text{ \AA}^2$ , and the incre-

ment  $\delta$  of the core radius as  $2 \text{ \AA}$ . The cross-sectional area covered by the polar head group  $a_0$  is taken as  $22 \text{ \AA}^2$  per amphiphile. The dielectric constant  $D$  of the solvent is taken as 80 and the electronic charge  $e$  has a value of  $4.8 \times 10^{-10}$  esu. The dissociated fraction of the surface charge depends upon pH, ionic strengths, and the density of the head groups. For illustrative purposes a constant value of 0.67 is taken for  $\beta$ .

The aggregate size distribution function for sodium octyl sulfate is shown in Fig. 2, for different concentrations of single amphiphiles. The critical concentrations have been computed for amphiphiles with the same ionic head and different alkyl chain lengths and are given in Table III. The calculated values of the critical concentration are compared with the experimental measurements of the CMC's from Ref. (11).

The effect of ionic strength on the critical concentration is calculated for sodium dodecyl sulfate at 25°C. The calculated values are compared in Table IV with the experimental values of Williams *et al.* (12).

The size distribution function shows that only over a narrow size range is the number of aggregates significant. The size distribution index calculated as the ratio of the weight average aggregation to the number average aggregation is close to unity (smaller than 1.03) (6). This suggests that a model assuming single amphiphiles in equilibrium with aggregates of a single size can in some cases represent amphiphilic solutions.

TABLE IV

Dependence of Critical Concentration on Ionic Strength for Sodium Dodecyl Sulfate at 25°C.

$C_s$ (moles/liter)	$C_{\text{critical, calcd}}$ (moles/liter)	CMC, exptl (12) (moles/liter)
0.00	$6.21 \times 10^{-3}$	$8.12 \times 10^{-3}$
0.01	$4.23 \times 10^{-3}$	$5.29 \times 10^{-3}$
0.03	$2.60 \times 10^{-3}$	$3.13 \times 10^{-3}$
0.05	$1.88 \times 10^{-3}$	$2.27 \times 10^{-3}$
0.10	$1.13 \times 10^{-3}$	$1.46 \times 10^{-3}$

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