

Relation between the Transition Point in Micellar Size Distribution, the CMC, and the Cooperativity of Micellization

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The critical micelle concentration C_{crit} , defined by us as the concentration at which a transition in the shape of the micellar size distribution occurs, and the conventional critical micelle concentration CMC are related to the stepwise association equilibrium constant which reflects the cooperative nature of micellization. It is shown (i) that the horizontal inflection point in the micellar size distribution corresponding to C_{crit} as well as the maximum in the stepwise association constant occur at the same aggregation number g_{crit} and (ii) that the inverse of C_{crit} is equal to the maximum value of the stepwise association constant at g_{crit} . The inverse of the conventional CMC is also equal to the stepwise association constant but at an aggregation number g^* where both a maximum in the micellar size distribution and a maximum in the free energy of micellization per surfactant molecule ($-\Delta G_g^0$) occur. One thus demonstrates, in a direct and simple way, that the theoretically defined C_{crit} is a close lower bound of the practical CMC.

INTRODUCTION

A theoretical definition of the critical micelle concentration (C_{crit}) was proposed by us (1) as the concentration at which a transition in the shape of the micellar size distribution occurs from a monotonic decreasing function to one possessing a minimum and a maximum. In practice, the critical micelle concentration (CMC) is determined as the concentration at which a sharp change occurs in any of a wide variety of properties of the surfactant solution. For a number of surfactant systems, it has been shown, using phenomenological and statistical thermodynamic expressions for the free energy of micellization, that the calculated C_{crit} , the calculated CMC, and the experimentally determined CMC agree well with one another

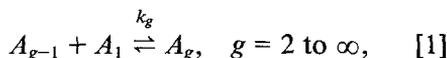
(1-3). Such agreement implies an intimate connection between the two quantities C_{crit} and CMC. Of course, one obvious connection is in terms of the size distribution since the CMC is determined by measuring properties of the surfactant solution which depend on the micellar size distribution and C_{crit} is determined as the concentration at which a transition in shape of the size distribution occurs. A more meaningful connection between C_{crit} and CMC is established in this paper on the basis of the general thermodynamic relation for the size distribution of micelles. We show that both C_{crit} and CMC are explicitly related to the stepwise association equilibrium constant, which reflects the cooperative nature of micellization. This general result, independent of any specific model for the free energies of micellization, permits one to explain why C_{crit} is always a close lower bound of the CMC. Finally, we

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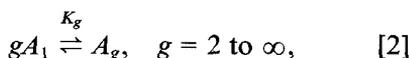
illustrate the relation between C_{crit} , CMC, and cooperativity of micelle formation using Tanford's phenomenological expression (4, 5) for the free energy of micellization.

GENERAL THERMODYNAMIC RELATIONS FOR MICELLIZATION

The self-assembly of surfactant molecules in dilute aqueous solutions can be represented by the multiple equilibria



where A_1 refers to the singly dispersed surfactant molecule, A_g refers to a micelle of aggregation number g , and k_g is the stepwise association equilibrium constant for the "reaction" in which a g -mer results from the combination of a $(g - 1)$ -mer with a monomer. The aggregation number g is allowed to assume all the values starting from that of a dimer. An alternate representation of micellization is provided by the monomer-micelle equilibria



where K_g is the overall association equilibrium constant for the "reaction" in which a g -mer forms from g singly dispersed surfactant molecules. The stepwise and the overall association equilibrium constants are related by

$$K_g = \prod_{j=2}^g k_j, \quad g = 2 \text{ to } \infty, \quad [3]$$

and

$$k_g = K_g/K_{g-1}, \quad g = 2 \text{ to } \infty. \quad [4]$$

The size distribution of micelles can be written on the basis of Eq. [2], as

$$X_g = K_g X_1^g = X_1^g \exp\left(-\frac{g\Delta G_g^0}{kT}\right), \quad [5]$$

where X_1 and X_g are the mole fractions of singly dispersed surfactant and micelles of size g , respectively, and ΔG_g^0 is the change in the standard free energy per surfactant molecule associated with the formation of

micelles of size g . The overall association constant K_g and the stepwise association constant k_g are related to ΔG_g^0 via the expressions

$$K_g = \exp[-g\Delta G_g^0/kT] \quad [6]$$

and

$$k_g = \exp\left[-\frac{g\Delta G_g^0}{kT} - \frac{(g-1)\Delta G_{g-1}^0}{kT}\right]. \quad [7]$$

The variation of k_g with the aggregation number g determines the detailed patterns of aggregation, namely, whether the aggregates are small or large and whether they are monodispersed or polydispersed. Of course, if $k_g X_1 > 1$ for all values of g above a certain aggregation number, then infinitely large aggregates form implying the occurrence of a phase separation. This situation is not discussed in the following.

A lucid explanation of how micelle formation is influenced by the dependence of k_g on g has been presented by Mukerjee (6-8). When k_g is independent of g , the association is said to be continuous and noncooperative. In this case, polydispersed aggregates form and their size distribution is monotonically decreasing. Consequently, all the properties of the surfactant solution vary only gradually and a CMC is absent. If k_g increases with g , then the larger aggregates are favored over the smaller ones and the system is considered to exhibit positive cooperativity. If k_g decreases with g , then the formation of larger aggregates is increasingly disfavored and the system is said to exhibit negative or anti-cooperativity (6-9).

In typical micellar systems, the shielding of the hydrophobic part of the micellar core from water becomes more and more effective with every incremental addition of a surfactant to the micelle. Thus the incremental change in free energy due to the van der Waals interactions between the hydrocarbon chains and to the structural changes in water (hydrophobic interactions) becomes more negative with increasing size of the micelles. This has the tendency to increase k_g with increasing g . However, as g increases, the mi-

cellar surface becomes increasingly crowded with the polar head groups of the surfactants. Consequently, for every incremental addition of a surfactant to the micelle, the repulsion between the polar head groups increases. Because this head group repulsion is unfavorable to the formation of large aggregates, it has the tendency to decrease k_g with increasing g . At the initial stages of aggregation, hence for relatively small values of g , the incremental change in the hydrophobic interactions is greater than that in the head group repulsions. Hence there is an initial region of positive cooperativity in which k_g increases with increasing g . Beyond some critical aggregation number, the incremental change in the head group repulsions exceeds that in the hydrophobic interactions. Therefore beyond a maximum value corresponding to a critical aggregation number, k_g begins to decrease with g signalling a region of negative cooperativity. When large cylindrical micelles begin to form, the surface area of the micelle per amphiphile becomes a constant. As a result, the incremental addition of a surfactant molecule to the micelle does not alter the incremental changes in the attractive hydrophobic interactions and in the repulsive head group interactions. Consequently, k_g becomes independent of g indicating a final region of noncooperativity. Thus, the stepwise association constant k_g provides a quantitative description of the cooperative nature of micellization. On the basis of the general thermodynamic relations governing micellization, one can relate explicitly C_{crit} and CMC to k_g .

RELATION BETWEEN C_{crit} AND k_g

The critical concentration C_{crit} represents the concentration at which a transition in the shape of the micellar size distribution occurs. At this transition point, the size distribution has a horizontal inflection point and therefore

$$\frac{dX_g}{dg} = 0 \quad \text{at} \quad g = g_{\text{crit}} \quad [8]$$

and

$$\frac{d^2X_g}{dg^2} = 0 \quad \text{at} \quad g = g_{\text{crit}} \quad [9]$$

Combining Eqs. [5], [8], and [9], one obtains

$$\frac{d^2}{dg^2} \left(\frac{g\Delta G_g^0}{kT} \right) = 0 \quad \text{at} \quad g = g_{\text{crit}} \quad [10]$$

and

$$\ln (X_1)_{\text{crit}} = \frac{d}{dg} \left(\frac{g\Delta G_g^0}{kT} \right) \quad \text{at} \quad g = g_{\text{crit}} \quad [11]$$

Replacing the difference $[g\Delta G_g^0 - (g-1) \times \Delta G_{g-1}^0]$ by the derivative $(d/dg)(g\Delta G_g^0)$, Eq. [7] becomes

$$\ln k_g = - \frac{d}{dg} \left(\frac{g\Delta G_g^0}{kT} \right) \quad [12]$$

Combining Eqs. [11] and [12], one obtains a simple and interesting relation between the critical concentration C_{crit} and the cooperativity of micellization reflected in k_g :

$$(X_1)_{\text{crit}} = 1/k_g \quad \text{at} \quad g = g_{\text{crit}} \quad [13]$$

Further, Eqs. [10] and [12] lead to

$$\frac{d}{dg} (\ln k_g) = 0 \quad \text{at} \quad g = g_{\text{crit}} \quad [14]$$

Consequently, the aggregation number g_{crit} at which the size distribution exhibits an inflection point is also the aggregation number at which the stepwise association constant has its maximum value; further, the inverse of $(X_1)_{\text{crit}}$ is equal to the maximum of k_g . Therefore, g_{crit} has an interesting physical meaning since it represents the aggregation number at which the incremental increase in k_g due to hydrophobic interactions is balanced by the incremental decrease in k_g due to head group repulsions.

RELATION BETWEEN CMC AND k_g

In order to relate the conventional CMC to the stepwise association constant k_g , one can take into account the fact that near the CMC, the size distribution exhibits a minimum and a maximum. At the peak of this

micellar size distribution which occurs at an aggregation number g^* , one can write (7),

$$X_g \approx X_{g-1} \text{ at } g = g^* \quad [15]$$

Combining Eqs. [5] and [15], one obtains

$$\ln (X_1)_{\text{CMC}} = \left[\frac{g\Delta G_g^0}{kT} - \frac{(g-1)\Delta G_{g-1}^0}{kT} \right] \text{ at } g = g^* \quad [16]$$

which because of Eq. [7] reduces to

$$(X_1)_{\text{CMC}} = 1/k_g \text{ at } g = g^* \quad [17]$$

An upper bound of the aggregation number g^* corresponding to the most populous micelle at CMC is usually estimated as equal to the aggregation number at which $(-\Delta G_g^0/kT)$ or $K_g^{1/g}$ has a maximum (6-8). Therefore,

$$\frac{d}{dg} \left(\frac{\Delta G_g^0}{kT} \right) = 0 \text{ at } g = g^* \quad [18]$$

Consequently,

$$\frac{d}{dg} \left(\frac{g\Delta G_g^0}{kT} \right) = \left(\frac{\Delta G_g^0}{kT} \right) \text{ at } g = g^* \quad [19]$$

and Eq. [17] thus reduces to

$$(X_1)_{\text{CMC}} = 1/k_g = 1/K_g^{1/g} \text{ at } g = g^* \quad [20]$$

One may note that Eq. [20] provides an upper bound for $(X_1)_{\text{CMC}}$ because an upper bound of g^* is used in its estimation.

Alternate expressions for the conventional CMC such as those proposed by Hartley (10) and Phillips (11, 12) can also be used to estimate $(X_1)_{\text{CMC}}$. Hartley (10) has considered the equilibrium between monomers and micelles of a single size g^* and has suggested that the conventional CMC can be estimated as equal to X_1 when the amount of surfactant present as micelles (i.e., gX_g) is equal to X_1 . Therefore, using Eq. [5] one can write,

$$X_1 = gX_g = g[K_g X_1^{g^*}] \text{ at } g = g^* \quad [21]$$

Correspondingly, one obtains

$$(X_1)_{\text{CMC}} = \left[\frac{1}{gK_g} \right]^{1/(g-1)} \text{ at } g = g^* \quad [22]$$

Phillips (11) has proposed that the conventional CMC can be estimated as the concentration at which an ideal colligative property of the surfactant solution when plotted against the total surfactant concentration shows maximum curvature. Based on this suggestion, for a solution consisting of monomers and micelles of a single size g^* , $(X_1)_{\text{CMC}}$ can be calculated (12-14) from the equation

$$\begin{aligned} \ln (X_1)_{\text{CMC}} &= -\frac{1}{(g-1)} \ln K_g - \frac{1}{(g-1)} \\ &\times \ln \left[\frac{g^2(2g-1)}{(g-2)} \right] - \ln \left[\frac{g(2g-1)}{2(g^2-1)} \right] \\ &\text{at } g = g^* \quad [23] \end{aligned}$$

Additional methods for estimating the conventional CMC have been suggested by Corrin (15) and Hall and Pethica (13). It may be noted that the values of $(X_1)_{\text{CMC}}$ estimated based on any of the above suggestions are smaller than the value of $(X_1)_{\text{CMC}}$ calculated from Eq. [20].

We thus obtain on the basis of general thermodynamic considerations (Eqs. [13] and [17]), the following relation between $(X_1)_{\text{crit}}$ and $(X_1)_{\text{CMC}}$:

$$\frac{(X_1)_{\text{CMC}}}{(X_1)_{\text{crit}}} = \frac{(k_g)_{g=g^{\text{crit}}}}{(k_g)_{g=g^*}} = \frac{(k_g)_{g=g^{\text{crit}}}}{(K_g^{1/g})_{g=g^*}} \quad [24]$$

We emphasize again that g_{crit} corresponds to the horizontal inflection point in the micellar size distribution as well as to the maximum in the stepwise association constant k_g , while g^* corresponds to the maximum in the micellar size distribution as well as to the maximum in $K_g^{1/g}$. Both $(X_1)_{\text{crit}}$ and $(X_1)_{\text{CMC}}$ are equal to the inverse of the stepwise association constant k_g but at aggregation numbers g_{crit} and g^* , respectively. In the next section explicit expressions are obtained for the size dependencies of k_g and $K_g^{1/g}$ using for illustrative purposes the simple phenomenological expression developed by Tanford for the free energy of micellization. The resulting

expressions are used to estimate the typical magnitude of the ratio $(X_1)_{\text{CMC}}/(X_1)_{\text{crit}}$.

ILLUSTRATION BASED ON TANFORD'S EXPRESSION

The phenomenological expression for the free energy change associated with micellization developed by Tanford (4, 5) has the form

$$\left(\frac{g\Delta G_g^0}{kT}\right) = \eta g^{4/3} - \beta g + \xi g^{2/3}, \quad [25]$$

where η , β , and ξ are positive constants (see Appendix). The first term represents the head group repulsions at the micellar surface and the remaining two terms account for the hydrophobic interactions. The stepwise association constant k_g is given, in this case by the equation

$$\ln k_g = -\frac{d}{dg} \left(\frac{g\Delta G_g^0}{kT}\right) = -\frac{4}{3} \eta g^{1/3} + \beta - \frac{2}{3} \xi g^{-1/3}, \quad [26]$$

while the overall association constant is obtained as

$$\ln K_g^{1/g} = \left(-\frac{\Delta G_g^0}{kT}\right) = -\eta g^{1/3} + \beta - \xi g^{-1/3}. \quad [27]$$

The quantities $\ln k_g$ and $\ln K_g^{1/g}$ are plotted in Fig. 1 as functions of the aggregation number g , by choosing the following typical values for the model parameters: $\beta = 17$, $\xi = 9$, and $\eta = 0.6$. As mentioned in Appendix, these values correspond to a typical non-ionic surfactant. One can observe in Fig. 1 the initial region of positive cooperativity followed by a region of negative cooperativity. The stepwise association constant k_g varies only slowly in the entire region of aggregation. Such a dependence of k_g on g is capable of generating practically monodispersed micelles of average aggregation number of about 58.

The inflection point in the size distribution and the maximum in the stepwise association

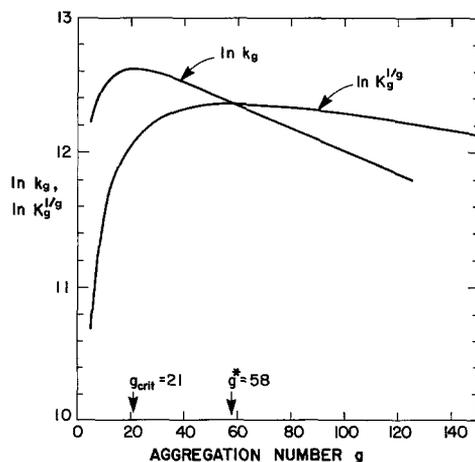


FIG. 1. Dependence of k_g and $K_g^{1/g}$ on the micellar aggregation number g . k_g is the stepwise association equilibrium constant and K_g is the overall association equilibrium constant. The values of k_g and $K_g^{1/g}$ are calculated using Eqs. [26] and [27], respectively.

constant occur at g_{crit} . Combining Eqs. [10] and [25] (or, Eqs. [14] and [26]), one obtains

$$g_{\text{crit}} = \left[\frac{\xi}{2\eta}\right]^{3/2} = 21. \quad [28]$$

The corresponding critical concentration results by combining Eqs. [26] and [28]:

$$\ln (X_1)_{\text{crit}} = \frac{4\sqrt{2}}{3} (\xi\eta)^{1/2} - \beta = -12.62. \quad [29]$$

The maxima in $K_g^{1/g}$ and in micellar size distribution occur at g^* . From Eq. [27], one obtains

$$g^* = \left[\frac{\xi\eta}{\eta}\right]^{3/2} = 58. \quad [30]$$

Correspondingly the CMC is obtained from Eqs. [20], [27], and [30] as

$$\ln (X_1)_{\text{CMC}} = 2(\xi\eta)^{1/2} - \beta = -12.35. \quad [31]$$

The ratio between $(X_1)_{\text{CMC}}$ and $(X_1)_{\text{crit}}$ is thus given by

$$\begin{aligned} (X_1)_{\text{CMC}}/(X_1)_{\text{crit}} &= \exp\left[\left(2 - \frac{4\sqrt{2}}{3}\right)(\xi\eta)^{1/2}\right] \\ &= \exp[0.27]. \end{aligned} \quad [32]$$

This ratio equals 1.31 for the values of the parameters used to generate Fig. 1. The re-

sults presented in our earlier paper (1-3) show that indeed there is only a small difference between the CMC and the C_{crit} . Further in Eq. [32], η is proportional to $n_c^{-2/3}$ while ξ is proportional to $n_c^{2/3}$ (n_c being the total number of CH_2 and CH_3 groups in the hydrocarbon tail of the surfactant). Therefore, the ratio in Eq. [32] remains independent of n_c . This fact was already pointed out in our earlier calculations (1, 3) for the homologous series of alkyl hexoxyethylene glycol monoethers with hydrocarbon tail lengths varying from $n_c = 8$ to $n_c = 16$. As mentioned earlier, the estimate of $(X_1)_{\text{CMC}}$ obtained using Eq. [20] is an upper bound. If Hartley's suggestion for $(X_1)_{\text{CMC}}$ is adopted, then using Eq. [22] at $g^* = 58$, one obtains $(X_1)_{\text{CMC}} / (X_1)_{\text{crit}} = 0.98$. If Phillips' proposal is used to estimate $(X_1)_{\text{CMC}}$, then using Eq. [23] at $g^* = 58$, one gets $(X_1)_{\text{CMC}} / (X_1)_{\text{crit}} = 0.90$.

CONCLUSIONS

There are simple connections between the transition point at which a change in shape of the micellar size distribution occurs, the conventional critical micelle concentration, and the cooperative nature of micelle formation as reflected in the stepwise association equilibrium constant k_g . Specifically we have shown that:

(i) The inflection point in micellar size distribution occurs at an aggregation number g_{crit} at which the stepwise association constant k_g has its maximum. At this aggregation number, the incremental increase in k_g due to hydrophobic interactions is balanced by the incremental decrease in k_g due to head group repulsions.

(ii) The critical concentration corresponding to the transition in shape of the size distribution is equal to the inverse of the stepwise association constant k_g at its maximum.

(iii) The conventional CMC is also equal to the inverse of the stepwise association constant k_g but for an aggregation number g^* somewhat larger than g_{crit} . At g^* , k_g is also equal to $K_g^{1/g}$, where K_g is the overall asso-

ciation constant. Further, both the micellar size distribution and $K_g^{1/g}$ have their maxima at g^* .

(iv) The explicit relation between $(X_1)_{\text{crit}}$, $(X_1)_{\text{CMC}}$, and the stepwise association constant k_g indicates that C_{crit} is always less than CMC, but close to it.

APPENDIX: TANFORD'S FREE ENERGY EXPRESSION

Tanford's expression (4, 5) for the free energy change associated with micelle formation, consists of the following three parts:

$$\left[\frac{g\Delta G_g^0}{kT} \right] = \left[\frac{S + I(n_c - 1)}{RT} \right] g + \left[\frac{25(A - 21)}{RT} \right] g + \left[\frac{\alpha g}{ART} \right]. \quad [\text{A.1}]$$

Here n_c is the length of the hydrocarbon chain of the amphiphile, R is the gas constant, T is the temperature, A is the area per molecule of the micellar surface (in \AA^2), S depends upon the specificity of the head group and is of the order of -2000 cal/mole, and I depends upon the nature of the surfactant and is about -700 cal/mole for non-ionics and -420 cal/mole for ionic surfactants. The first two terms in Eq. [A.1] represent the hydrophobic interactions (the second term accounting for the incomplete shielding of the micellar core from water). The last term accounts for the repulsive interactions between the polar head groups of the surfactants at the micellar surface (the quantity α is a measure of the magnitude of this repulsive interaction).

For spherical micelles the surface area per molecule at the micellar core-water interface is given by

$$A = \frac{1}{g} (4\pi r_0^2) = \frac{1}{g} \left[4\pi \left(\frac{3g v_0}{4\pi} \right)^{2/3} \right], \quad [\text{A.2}]$$

where r_0 is the radius of the hydrocarbon core, v_0 is the volume of the hydrocarbon tail of the surfactant, and g is the aggregation number of the micelle. The following expression is valid for v_0 :

$$v_0 = (27.4 + 26.9 n_c) \quad (\text{in } \text{\AA}^3). \quad [\text{A.3}]$$

Introducing Eqs. [A.2] and [A.3] in [A.1], one obtains

$$\left[\frac{g\Delta G_g^0}{kT} \right] = \eta g^{4/3} - \beta g + \xi g^{2/3}, \quad [\text{A.4}]$$

where

$$\eta = \left(\frac{\alpha}{RT} \right) \frac{1}{4\pi} \left(\frac{3v_0}{4\pi} \right)^{-2/3}, \quad [\text{A.5}]$$

$$\xi = \left(\frac{25}{RT} \right) 4\pi \left(\frac{3v_0}{4\pi} \right)^{2/3}, \quad [\text{A.6}]$$

$$\beta = - \left[\frac{S + I(n_c - 1)}{RT} \right] + \left[\frac{25 \times 21}{RT} \right]. \quad [\text{A.7}]$$

The quantities η , ξ , and β defined above are all positive constants. For a nonionic surfactant with $n_c = 12$, choosing $\alpha = 8 \times 10^3$ cal $\text{\AA}^2/\text{mole}$, one obtains $\eta = 0.6$, $\beta = 17$, and $\xi = 9$.

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