

NOTES

On Critical Concentrations in Micellar Solutions

INTRODUCTION

In an earlier paper (1) it was shown that the total concentration of single amphiphiles in a micellar solution possesses a critical value below which the size distribution of micellar aggregates is a monotonic decreasing function of size and above which the size distribution exhibits two extrema. The objective of this note is to clarify the relation between that critical concentration and the usually reported critical micelle concentration. Computations have been carried out on the basis of both the empirical thermodynamic equations of Tanford (2) and the relations of statistical thermodynamics (3).

DEFINITION OF C_{crit}

Micelle formation was treated in our earlier paper (1) assuming that aggregates of all sizes are formed. The total free energy of the system, consisting of the solvent molecules, single amphiphiles and aggregates of all sizes, is given by

$$\Phi = N_S \mu_S^0 + N_A \mu_A^0 + \sum_{g=2}^{\infty} N_g (\mu_B^0 g + \mu_g^0) + kT \left[N_S \ln \frac{N_S}{F} + N_A \ln \frac{N_A}{F} + \sum_{g=2}^{\infty} N_g \ln \frac{N_g}{F} \right] \quad [1]$$

where the total number of molecules F , is given by

$$F = N_S + N_A + \sum_{g=2}^{\infty} N_g \quad [2]$$

N_S , N_A , and N_g are the number of molecules of the solvent, single amphiphiles, and aggregates of size g , respectively; μ_S^0 and μ_A^0 are the standard chemical potentials per molecule of the solvent and single amphiphile, μ_B^0 is the size independent part of the standard chemical potential per single amphiphile for the aggregate and μ_g^0 is the size dependent part of the standard chemical potential for the aggregate as a whole. For a constant total amphiphilic concentration, the equilibrium condition yields the following size distribution function:

$$\frac{N_g}{F} = \left(\frac{N_A}{F} \right)^g \exp - \frac{1}{kT} \{ (\mu_B^0 - \mu_A^0) g + \mu_g^0 \}. \quad [3]$$

For small values of the monomer concentration N_A/F , the size distribution function is a monotonic decreasing function of g . For sufficiently high values of N_A/F , the size distribution function can have a maximum and a minimum. Therefore, a critical value of N_A/F exists, for which the size distribution has an inflection point, separating two kinds of shapes of the size distribution function. The total amphiphile concentration corresponding to this critical point was defined (1) as the critical concentration C_{crit} .

DEFINITION OF THE CRITICAL MICELLE CONCENTRATION (CMC)

Usually the CMC is determined on the basis of a sharp change in one of the physicochemical properties of the surfactant system accompanying an increase in the amphiphilic concentration. Some of these properties depend on the total number of molecules ($N_A + \sum_{g=2}^{\infty} N_g$). Examples are osmotic pressure, vapor pressure and freezing point depression. Some others, such as light scattering, depend on the weight average aggregation $(N_A + \sum_{g=2}^{\infty} g^2 N_g) / (N_A + \sum_{g=2}^{\infty} g N_g)$. Experimental results show that sharp changes in physical properties do not occur at a single amphiphilic concentration, but rather over a narrow range of concentrations. In practice, the CMC is determined as the point of intersection of two lines extrapolating the measured properties of the solution from below and from above the region in which the change of slope is observed.

RELATION BETWEEN C_{crit} AND CMC

The concentration C_{crit} at which a transition in the size distribution function occurs refers to a surfactant system which is almost completely dispersed as single amphiphiles. Sharp changes in physical properties can occur only when the concentration of the aggregates becomes significant. Hence C_{crit} is a lower bound of the CMC. With the size distribution function given by Eq. [3] any of the size dependent physical properties can be calculated. With the values of the parameters used in our earlier paper for amphiphiles with an octyl hydrocarbon chain and the hexoxyethylene glycol monoether head group, the different size dependent quantities, viz., the mole fraction $(N_A + \sum_{g=2}^{\infty} N_g) / F$

of single amphiphiles and aggregates, the total concentration $\sum_{\sigma=2}^{\infty} gN_{\sigma}/F$ of amphiphiles present as dimers and higher aggregates, the number average aggregation $(N_A + \sum_{\sigma=2}^{\infty} gN_{\sigma})/(N_A + \sum_{\sigma=2}^{\infty} N_{\sigma})$ and the weight average aggregation $(N_A + \sum_{\sigma=2}^{\infty} g^2N_{\sigma})/(N_A + \sum_{\sigma=2}^{\infty} gN_{\sigma})$ have been computed as a function of the total amphiphilic concentration $(N_A + \sum_{\sigma=2}^{\infty} gN_{\sigma})/F$. The intersection of the extrapolated lines in the two concentration regions determined as shown in Fig. 1 is the calculated CMC. For the different size dependent quantities the intersection points occur at different amphiphilic concentrations. Hence, the calculated and the measured CMC depend on the particular size dependent quantity used.

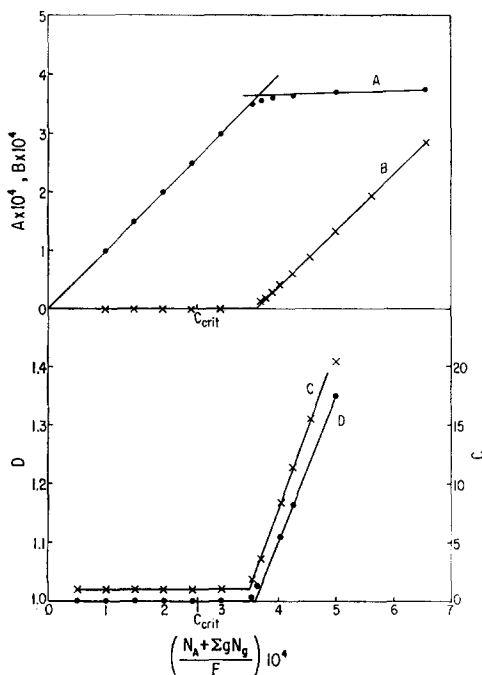


FIG. 1. Dependence of some size dependent quantities on total amphiphilic concentration for octyl hydrocarbon chain with hexoxyethylene glycol monoether head group.

- A. $(N_A + \sum_2^{\infty} N_{\sigma})/F$
- B. $\sum_2^{\infty} gN_{\sigma}/F$
- C. $(N_A + \sum_2^{\infty} g^2N_{\sigma})/(N_A + \sum_2^{\infty} gN_{\sigma})$
- D. $(N_A + \sum_2^{\infty} gN_{\sigma})/(N_A + \sum_2^{\infty} N_{\sigma})$.

TABLE I

Dependence of the Critical Concentration on the Length of Hydrocarbon Chain for Amphiphiles^a

n_{σ}	Calcd C_{crit}	Calcd CMC	Experimental CMC
	(in molar fraction units)		
			(2a)
6	2.64×10^{-3}	3.72×10^{-3}	2.76×10^{-3}
8	2.61×10^{-4}	3.65×10^{-4}	2.59×10^{-4}
10	2.58×10^{-5}	3.60×10^{-5}	2.44×10^{-5}
12	2.52×10^{-6}	3.51×10^{-6}	2.30×10^{-6}
14	2.49×10^{-7}	3.40×10^{-7}	2.16×10^{-7}
16	2.45×10^{-8}	3.25×10^{-8}	2.04×10^{-8}

^a With hexoxyethylene glycol monoether head-groups. Based on empirical expressions for the free energy with $\delta = 3\text{\AA}$ and $\alpha = 8 \times 10^4 \text{ cal } \text{\AA}^2/\text{mol}$.

The CMC values based on changes in the size dependent quantity $(N_A + \sum_{\sigma=2}^{\infty} N_{\sigma})/F$ are computed for amphiphiles of different chainlengths. The calculated CMC values are reported in Table I along with values of C_{crit} and the experimentally measured values of the CMC. The computed values are based on an arbitrary choice of one of the parameters (the parameter α in the empirical thermodynamic equation, for which only a range of values is indicated). For this reason, computations based on statistical thermodynamics have also been carried out.

RESULTS FROM STATISTICAL THERMODYNAMIC TREATMENT

The micellization process has also been treated using statistical thermodynamics (3). The total partition function of the system is given by

$$Q = \frac{Q_S^{N_S}}{N_S!} \frac{Q_A^{N_A}}{N_A!} \prod_{\sigma=2}^{\infty} \frac{Q_{\sigma}^{N_{\sigma}}}{N_{\sigma}!} \quad [4]$$

where Q_S , Q_A , and Q_{σ} refer to the partition functions of solvent molecule, single amphiphile, and aggregate of

TABLE II

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

n_{σ}	Calcd C_{crit}	Calcd CMC	Experimental CMC
	(in units of moles/liter)		
			(4)
8	1.87×10^{-2}	2.95×10^{-2}	2.51×10^{-2}
10	1.75×10^{-3}	3.50×10^{-3}	2.19×10^{-3}
12	1.42×10^{-4}	2.64×10^{-4}	1.92×10^{-4}
14	1.04×10^{-5}	2.05×10^{-5}	1.67×10^{-5}
16	0.72×10^{-6}	1.45×10^{-6}	1.45×10^{-6}

^a Based on statistical thermodynamical treatment.

TABLE III

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

n_c	Calcd C_{crit} (in units of moles/liter)	Calcd CMC	Experimental CMC (4)
8	1.01×10^{-1}	1.22×10^{-1}	1.15×10^{-1}
10	2.67×10^{-2}	3.35×10^{-2}	2.95×10^{-2}
12	6.21×10^{-3}	8.24×10^{-3}	7.60×10^{-3}
14	1.15×10^{-3}	1.79×10^{-3}	1.95×10^{-3}
16	1.80×10^{-4}	2.99×10^{-4}	5.00×10^{-4}

^a Based on statistical thermodynamical treatment.

size g , respectively. The equilibrium condition yields the size distribution function

$$\ln N_g = g \ln N_A + \ln (Q_g/Q_A^g). \quad [5]$$

With explicit expressions for the partition functions Q_g and Q_A incorporating various degrees of freedom of motion and various kinds of interactions, the size distribution and the critical concentrations can be calculated (3).

The size distribution functions have been calculated for alkyl glucosides and sodium alkyl sulfates at 25°C. For different alkyl chain lengths, the calculated values of C_{crit} and CMC (based on sharp changes in the total number of single amphiphiles and aggregates) are presented for alkyl glucosides in Table II and sodium alkyl sulfates in Table III. The values of C_{crit} are lower bounds on the experimental CMC's. The computed CMC compares very well with the experimental one.

CONCLUSIONS

C_{crit} corresponds to a transition in the structure of the amphiphilar system, because the size distribution has at this point a qualitative change in shape. The

transition in the size distribution function occurs at total amphiphilar concentrations lower than those corresponding to the transitions in any other physical property. This explains why C_{crit} is a lower bound of the calculated and experimental CMC.

The values of the CMC when the various experimental techniques mentioned earlier are applied to the same amphiphilar species differ from one another. Clearly, the parameter C_{crit} as defined by us is the one unique characteristic of the aggregation of a micellar system. A calculation similar to that resulting in Fig. 1 can be used to relate the various CMC's to one another and to C_{crit} . The experimental observation of the sharp change in a particular physical property can thus determine C_{crit} .

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