Comments

On Interpreting Fluorescence Measurements: What Does Thermodynamics Have To Say about Change in Micellar Aggregation Number versus Change in Size Distribution Induced by Increasing Concentration of the Surfactant in Solution?

Fluorescence techniques have been widely used for the determination of micellar aggregation numbers.[1] However, the interpretation of the fluorescence data and the consequent estimates for the micellar aggregation numbers are not always unambiguous. The results usually depend on both the type of experiments performed and the micellar models invoked for the data analysis. In an interesting recent study, Reekmans et al.[2] employed dynamic fluorescence quenching to examine whether an increase in the concentration of the surfactant in solution will cause a growth in the size of the micellar aggregates or only a change in the size distribution and polydispersity of the micelles. Fluorescence decay measurements were made on the cationic surfactant cetyltrimethylammonium chloride (CTAC) using 1-methylpyrene as the fluorescence probe and cetylpyridinium chloride (C(Pyr)C) as the quencher. Eight different decay curves were obtained corresponding to differing values of quencher concentration, and all the decay curves were simultaneously analyzed using modified versions of the Infelta–Tachia model. Reference 2 provides the details of the experimental measurements as well as the methods of data interpretation. In carrying out the analysis, two different descriptions of the micelles were employed. In the first case, the micellar solution was assumed to be made up of aggregates of a single size. In the second case, the micelles were assumed to be polydispersed. For a given total surfactant concentration, a global fitting of the eight decay curves (each corresponding to a different quencher concentration) yielded the aggregation numbers and indices of size polydispersity for the two micellar models considered. A part of the results, obtained at 20 °C (summarized in Table II of ref 2), is shown in Table 1.

The tabulated data (see results for either sample I or II) reveal that when a monodispersed micellar model was assumed, the fluorescence decay curves were consistent with the interpretation that an increasing concentration of the surfactant causes an increase in the aggregation number. By definition, the size dispersion index is 0 for this case. When a polydispersed micellar model was assumed, the fluorescence decay measurements were consistent with the interpretation than an increasing concentration of the surfactant causes a decrease in the size polydispersity index while the weight-average aggregation number of the micelle remains practically a constant.

In this paper, we show that the above interpretations of experimental measurements are not consistent with the general thermodynamic principles of self-assembly for both nonionic and ionic surfactants. In particular, if the micelles are all of a single size, then their size cannot increase significantly with increasing surfactant concentration. On the other hand, if the micelles are polydispersed, then the

Table 1. Aggregation Numbers and Size Dispersion Indices for CTAC Solutions at 20 °C: Estimates Based on Fitting of Fluorescence Decay Data (from Reference 2)[a]

	7 mM		10 mM		20 mM		40 mM
	I	II	I	II	I	II	I
	Monodispersed Micellar Model						
g_w	68.6	69.1	73.4	74.8	80.8	82.5	92.6
σ/g_w	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Polydispersed Micellar Model						
g_w	94.7	103.8	93.1	99.6	88.4	99.7	96.2
σ/g_w	0.71	0.76	0.63	0.71	0.41	0.59	0.22

[a] The molar concentrations refer to the total amount of surfactant CTAC in solution. At each surfactant concentration, I and II refer to identical samples measured at two different time increments of 0.8 ns/channel (I) and 1.7 ns/channel (II), respectively. σ^2 refers to the variance of the size distribution as defined by eq 29 (which is eq 6 of ref 2). g_w refers to the aggregation number of micelles of a single size in the case of the monodispersed micellar model and to the weight-average aggregation number in the case of the polydispersed micellar model. The cmc was estimated to be 1.3 mM in ref 2.

weight-average aggregation number cannot remain a constant with increasing surfactant concentration, but must necessarily increase.

Thermodynamics of Self-Assembly of Nonionic Surfactants

Thermodynamic principles of self-assembly have been widely discussed in the literature, and the main results to be shown here are already well-known.[3-5] Let us consider a nonionic surfactant solution consisting of micelles of aggregation numbers g coexisting with singly dispersed surfactant molecules. The aggregation number g is a single-valued variable in the case of a monodispersed micellar system, whereas g assumes all possible values from 2 to ∞ in the case of a polydispersed micellar system. The condition of thermodynamic equilibrium requires that the chemical potential of the singly dispersed surfactant molecule be equal to the chemical potential per molecule of a micelle.

$$(1/g)(\mu_g^\circ + kT \ln X_g) = (\mu_1^\circ + kT \ln X_1) \qquad (1)$$

In this equation, μ_1° is the standard chemical potential of the singly dispersed surfactant, μ_g° is the standard chemical potential of the micelle of aggregation number g, X_1 is the concentration of the singly dispersed surfactant in solution, and X_g is the concentration of micelles whose aggregation number is g. In writing this relation, we have assumed that the solution is dilute and that intermicellar interactions are not important. Indeed, even when intermicellar interactions are significant, the above relation remains valid for certain functional forms of the interaction energy.[6-8]

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The equivalence of chemical potentials given in eq 1 can be rewritten in the form of the size distribution equation:

$$X_g = X_1{}^g \exp\left[-\frac{\mu_g{}^\circ - g\mu_1{}^\circ}{kT}\right] \quad (2)$$

For a given value of the monomer concentration X_1, eq 2 allows the calculation of the concentration of micelles of a single size g in the case of a monodispersed micellar system and the size distribution of micelles in the case of a polydispersed micellar solution. From the size distribution equation, all the size-dependent properties of the micellar solution can be readily calculated. For example, the number-average, the weight-average, and the z-average aggregation numbers which are measured by different experimental techniques are obtainable, respectively, from the relations

$$g_n = \frac{\sum g X_g}{\sum X_g}, \quad g_w = \frac{\sum g^2 X_g}{\sum g X_g}, \quad g_z = \frac{\sum g^3 X_g}{\sum g^2 X_g} \quad (3)$$

The total concentration of the surfactant in solution, denoted by S_t, can be calculated from

$$S_t = X_1 + \sum g X_g \quad (4)$$

In the above equations (and also everywhere else in the following discussion), the summation extends over all possible aggregation numbers, if a polydispersed micellar model is considered. On the other hand, if all of the micelles are considered as being of a single size, then no summation is necessary and g will refer to the aggregation number of the single-sized micelles. Evidently, the various average aggregation numbers g_n, g_w, and g_z have no special relevance to this case and can all be considered identical to g.

The standard chemical potentials appearing in eq 2 are defined as those corresponding to the isolated species in the solution, at infinitely dilute conditions. Thus, for nonionic surfactants, the exponential factor in eq 2 is not dependent on the concentration of the singly-dispersed surfactant or on the total concentration of the surfactant. From eq 2, we can write the following derivatives:

$$\partial \ln \sum X_g = \frac{1}{\sum X_g}\left[\sum g X_g \,\partial \ln X_1\right] = g_n \,\partial \ln X_1 \quad (5)$$

$$\partial \ln \sum g X_g = \frac{1}{\sum g X_g}\left[\sum g^2 X_g \,\partial \ln X_1\right] = g_w \,\partial \ln X_1 \quad (6)$$

$$\partial \ln \sum g^2 X_g = \frac{1}{\sum g^2 X_g}\left[\sum g^3 X_g \,\partial \ln X_1\right] = g_z \,\partial \ln X_1 \quad (7)$$

Equations 6 and 7 show that the weight-average aggregation number defined in eq 3 depends on the concentration of the micellized surfactant (i.e., $\sum g X_g = S_t - X_1$) in the form

$$\partial \ln g_w = [g_z/g_w - 1]\,\partial \ln \sum g X_g \quad (8)$$

The size dispersion of micelles is measured by the variance σ^2 defined as

$$\sigma^2 = \frac{\sum (g - g_w)^2 g X_g}{\sum g X_g} = g_w{}^2\left(\frac{g_z}{g_w} - 1\right) \quad (9)$$

where we have used the fraction of surfactant present in aggregates of size g (i.e., $g X_g / \sum g X_g$) as the probability density associated with the occurrence of micelles of size g. The expression for the variance of the size distribution function can be rewritten using eq 8 in the form

$$\left[\frac{\sigma}{g_w}\right]^2 = \frac{g_z}{g_w} - 1 = \frac{\partial \ln g_w}{\partial \ln \sum g X_g} = \frac{\partial \ln g_w}{\partial \ln(S_t - X_1)} \quad (10)$$

This equation clearly states that the weight-average aggregation number g_w must increase appreciably with increasing concentration of the micellized surfactant ($S_t - X_1$), if σ/g_w is large. On the other hand, the aggregation number must be virtually independent of the total surfactant concentration if σ/g_w is small, close to zero. Equation 10 is a general thermodynamic result applicable to any self-assembling system and is not dependent on one or another microscopic model of micellization. Therefore, in interpreting any experimental data pertaining to self-assembling systems, one must ensure that eq 10 is not violated.

Thermodynamics of Self-Assembly of Ionic Surfactants

The size distribution of ionic micelles can also be represented by eq 2 provided that the ionic interactions involving the surfactant head groups are properly taken into account in the analysis. The most common approach is to incorporate an ionic interaction energy contribution within the standard chemical potential difference term in eq 2. The Deybe-Hückel equation and approximate and/or numerical solutions to the Poisson–Boltzmann equation have been employed for this purpose in the literature.[4,9-11] An alternate approach visualizing the micellar solution as consisting of a collection of cells and treating the electrostatic interactions between the charged molecules on the basis of the Poisson–Boltzmann equation has also been presented in the literature.[12] We could develop our analysis below, by following any one of these treatments available in the literature. However, it becomes difficult to discern whether our conclusions originate from the particularity of the microscopic model of electrostatic interactions employed or whether they are completely model-independent. Consequently, in this paper, we will follow the purely thermodynamic analysis pioneered by Hall[13,14] which does not invoke one or another specific model for the computation of the ionic interaction energies. Although Hall's analysis is more than a decade old and predicts all the important features of ionic surfactant solutions, it has unfortunately been overlooked in the literature. The analysis below is essentially due to Hall except for the notations employed, and all the conclusions reached here have been explicitly stated by Hall.[13] The reader is referred to the original paper for details omitted here.

The basis of the approach developed by Hall is an equation describing the Donnan equilibrium between a micellar solution and a solution that is micelle-free but contains electrolytes. This equation is obtained from purely thermodynamic arguments, and from this equation, the necessary expressions for the chemical potentials of the micelle and the electrolyte are readily derived. We will consider an ionic micellar solution in the presence of

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an electrolyte in which there is only one counterion species (denoted by c). We donote by θ_1 and θ_g the quantities

$$\theta_1 = \mu_1 + \mu_c, \quad \theta_g = \mu_g + g\beta_g\mu_c \qquad (11)$$

where μ_1 is the chemical potential of the singly-dispersed surfactant ion, μ_g is the chemical potential of the micelle of aggregation number g having $g(1 - \beta_g)$ associated counterions on the surface, and μ_c is the chemical potential of the singly-dispersed counterion. Thus, θ_1 is the chemical potential of the electrically neutral surfactant molecule consisting of one surfactant ion and one counterion necessary to neutralize its charge, while θ_g is the chemical potential of the electrically neutral micelle consisting of the charged micelle of aggregation number g along with the $g\beta_g$ counterions necessary to neutralize the micellar charge. One may view β_g as the degree of dissociation of the surfactants constituting the micelle of aggregation number g. Expressions for the chemical potential θ_1 of the electrically neutral monomeric surfactant 1 and θ_g of the electrically neutral micelle of aggregation number g are obtained from a consideration of the Donnan equilibrium between the micellar solution and a micelle-free solution containing the electrolyte. The detailed thermodynamic development has been discussed by Hall,[13] and only the final results relevant to the following analysis are given here. One obtains the following relations for the chemical potentials:

$$\theta_1 = \theta_1{}^\circ(T,p) + kT\ln X_1 + kT\ln X_c + kT\ln\gamma^2 \qquad (12)$$

$$\theta_g = \theta_g{}^\circ(T,p) + kT\ln X_g + g\beta_g kT\ln X_c \qquad (13)$$

Here, $\theta_1{}^\circ$ and $\theta_g{}^\circ$ are the standard-state chemical potentials of the electrically neutral species whose concentrations in solution are X_1 and X_g, respectively. X_c denotes the total concentration of the counterions and includes contributions from the singly-dispersed surfactant molecules, micelles, and electrolytes present and is given by

$$X_c = X_1 + \sum \beta_g g X_g + X_s \qquad (14)$$

where X_s is the concentration of the added electrolyte. The summation extends over all values of g, thus accounting for micelles of all possible aggregation numbers. The ionic activity coefficients of the surfactant ion, the co-ion in the electrolyte, and the counterion are all take to be equal (an assumption not essential for the treatment), and γ is used to denote the mean ionic activity coefficient.

The equilibrium condition of equality of chemical potentials $\theta_g = g\theta_1$ gives rise to the size distribution equation

$$X_g = X_1{}^g X_c{}^{g(1-\beta_g)} \gamma^{2g} \exp\left[-\frac{\theta_g{}^\circ - g\theta_1{}^\circ}{kT}\right] \qquad (15)$$

This equation for ionic surfactants is the analog of eq 2 discussed earlier for the nonionic surfactants. The last factor appearing in eq 15 involves the standard-state chemical potentials of the electrically neutral species. Consequently, this factor is independent of the total concentration of the surfactant and also the concentrations of the singly-dispersed surfactant and the electrolyte. Starting from eq 15, one can obtain important relations between various measurable quantities describing the micellar system without having to propose any detailed models for the electrostatic interactions involving the surfactant head groups. Thus, the results to be obtained

below are based solely on thermodynamic considerations summarized in eq 15.

As in the case of the nonionic surfactants, the various average aggregation numbers are defined via eq 3 and the total concentration of the surfactant is that given by eq 4. We will define for notational convenience the number-average, the weight-average, and the z-average degrees of micelle dissociation to be

$$\beta_n = \frac{\sum \beta_g g X_g}{\sum g X_g}, \quad \beta_w = \frac{\sum \beta_g g^2 X_g}{\sum g^2 X_g}, \quad \beta_z = \frac{\sum \beta_g g^3 X_g}{\sum g^3 X_g} \qquad (16)$$

Similar to the derivatives, eqs 5–7, obtained from the size distribution equation for the nonionic surfactants, from eq 15 we can write the following derivatives for the case of ionic surfactants:

$$\partial\ln\sum X_g = \frac{1}{\sum X_g}[\sum g X_g \, \partial\ln(X_1\gamma^2) +$$

$$\sum g(1 - \beta_g)X_g \, \partial\ln X_c]$$
$$= g_n[\partial\ln(X_1\gamma^2) + (1 - \beta_n) \, \partial\ln X_c] \qquad (17)$$

$$\partial\ln\sum g X_g = \frac{1}{\sum g X_g}[\sum g^2 X_g \, \partial\ln(X_1\gamma^2) +$$

$$\sum g^2(1 - \beta_g)X_g \, \partial\ln X_c]$$
$$= g_w[\partial\ln(X_1\gamma^2) + (1 - \beta_w) \, \partial\ln X_c] \qquad (18)$$

$$\partial\ln\sum g^2 X_g = \frac{1}{\sum g^2 X_g}[\sum g^3 X_g \, \partial\ln(X_1\gamma^2) +$$

$$\sum g^3(1 - \beta_g)X_g \, \partial\ln X_c]$$
$$= g_z[\partial\ln(X_1\gamma^2) + (1 - \beta_z) \, \partial\ln X_c] \qquad (19)$$

In writing the above equations, we have incorporated the definitions of the various average degrees of dissociation given by eq 16. Another derivative needed for the analysis involves the degree of dissociation and is written as

$$\partial\ln\sum\beta_g g X_g = \frac{1}{\sum\beta_g g X_g}[\sum\beta_g g^2 X_g \, \partial\ln(X_1\gamma^2) +$$

$$\sum\beta_g g^2(1 - \beta_g)X_g \, \partial\ln X_c]$$
$$= \frac{g_w}{\beta_n}\left[\beta_w \, \partial\ln(X_1\gamma^2) + \right.$$

$$\left. \left(\beta_w - \frac{\sum g^2\beta_g{}^2 X_g}{\sum g^2 X_g}\right)\partial\ln X_c\right] \qquad (20)$$

The factor $\partial\ln(X_1\gamma^2)$ appearing in the above equations can be expressed in terms of the total surfactant concentration $\sum g X_g$ and the total counterion concentration X_c using eq 18. One obtains

$$\partial\ln(X_1\gamma^2) = (1/g_w) \, \partial\ln\sum g X_g - (1 - \beta_w) \, \partial\ln X_c \qquad (21)$$

The derivative of the weight-average aggregation number g_w defined in eq 3 can now be obtained by combining eqs 18, 19, and 21.

$$\partial\ln g_w = [g_z/g_w - 1] \, \partial\ln\sum g X_g +$$

$$g_z(\beta_w - \beta_z) \, \partial\ln X_c \qquad (22)$$

This equation summarizes the main result for ionic surfactants pertinent to the present study. One may observe its analogy to eq 8 developed before for the nonionic surfactants. Equation 22 clearly shows that if the micelles are monodispersed (i.e., $g_w = g_z$ and $\beta_w = \beta_z$), the weight-average aggregation number g_w of ionic micelles is invariant with the total surfactant concentration and also the total counterion concentration. In contrast, when the micelles are polydispersed, g_w must increase with the total surfactant concentration. This conclusion is similar to that arrived at earlier for nonionic surfactants and contradicts the interpretation of the fluorescence data presented in ref 2.

Many other important features of ionic surfactant solutions can also be predicted from the present thermodynamic analysis. The derivative of the number-average degree of dissociation β_n defined in eq 15 is obtained by combining eqs 18, 20, and 21.

$$\partial\beta_n = (\beta_w - \beta_n)\,\partial\ln\sum gX_g +$$
$$\left(g_w\beta_w{}^2 - \frac{\sum\beta_g{}^2 g^2 X_g}{\sum gX_g}\beta_n\right)\partial\ln X_c \quad (23)$$

One may note that the degree of dissociation (which is a fraction) is of the order of 1 whereas the aggregation number of the micelles is of the order of 100. Using these orders of magnitude, eq 23 shows that

$$\left[\frac{\partial\beta_n}{\partial\ln X_c}\right]_{\Sigma gX_g} \gg \left[\frac{\partial\beta_n}{\partial\ln\sum gX_g}\right]_{\Sigma X_c} \quad (24)$$

This implies that the degree of dissociation depends much less on the total surfactant concentration when compared to its dependence on the total counterion concentration (or total ionic strength). Further, from eqs 22 and 23 we find that the two quantities

$$\left[\frac{\partial\ln g_w}{\partial\ln X_c}\right]^2_{\Sigma gX_g} \quad\text{and}\quad \left[g_w\frac{\partial\beta_n}{\partial\ln X_c}\right]_{\Sigma gX_g}$$

are of the same order of magnitude. This implies that if

$$\left[\frac{\partial\ln g_w}{\partial\ln X_c}\right]_{\Sigma gX_g} \approx 1, \quad\text{then}\quad \left[\frac{\partial\beta_n}{\partial\ln X_c}\right]_{\Sigma gX_g} \approx \frac{1}{g_w}$$

Since the micellar aggregation numbers are large (of the order of 100), the above order of magnitude analysis shows that, as long as the change in the aggregation number g_w due to a change in X_c (or the total ionic strength) is *not enormous*, the average degree of dissociation β_n does not depend to any significant extent on X_c. Moreover, as we have already noted in eq 24, the effect of total surfactant concentration on β_n is even smaller than the effect of the total counterion concentration X_c. Hence, we can conclude that the average degree of dissociation β_n is practically a constant independent of both the total surfactant concentration and the added salt concentration, as long as g_w does not change *dramatically* with X_c. This conclusion from purely thermodynamic arguments has been experimentally validated, and this conclusion has also been arrived at on the basis of the cell model calculations for the electrostatic interactions.[12,15] A constant value for β_n implies that $\Sigma\beta_g gX_g$ is proportional to ΣgX_g. This condition is satisfied if β_g is a constant, independent of

the micelle aggregation number g. Consequently, we can write $\beta_n = \beta_w = \beta_z = \beta_g = $ constant.

Considering that the degree of dissociation does not depend on the aggregation number of the micelles and can be treated as a constant, we find that eq 22 simplifies to

$$\partial\ln g_w = [g_z/g_w - 1]\,\partial\ln\sum gX_g \quad (25)$$

Consequently, the variance in the size dispersion of ionic micelles can be written as

$$\left[\frac{\sigma}{g_w}\right]^2 = \frac{g_z}{g_w} - 1 = \frac{\partial\ln g_w}{\partial\ln\sum gX_g} = \frac{\partial\ln g_w}{\partial\ln(S_t - X_1)} \quad (26)$$

One may observe that the results for ionic surfactants contained in the above two equations (assuming a constant value for the degree of dissociation) are identical to those derived earlier for nonionic surfactants.

Another important feature of the solution behavior of ionic surfactants follows from eq 17 when it is rewritten in the form

$$(1/g_n)\,\partial\ln\sum X_g = \partial\ln(X_1\gamma^2) + (1 - \beta_n)\,\partial\ln X_c \quad (27)$$

Since the micelle aggregation numbers are large, of the order of 100, the left-hand side of eq 27 can be approximated to 0. Noting that β_n is practically a constant and that the total counterion concentration is given by eq 14, we find that eq 27 reduces to

$$\ln(X_1\gamma^2) + (1 - \beta_n)\ln(X_1 + \beta_n\sum gX_g + X_s) =$$
$$\text{constant} \quad (28)$$

This result clearly shows that (i) the concentration of the singly-dispersed surfactant ion X_1 decreases as the total surfactant concentration is increased, (ii) a plot of $\ln(X_1\gamma^2)$ against $\ln(X_c)$ will be a straight line with the slope $-(1 - \beta_n)$, and (iii) the mean ionic activity $(X_1 X_c\gamma^2)^{1/2}$ will increase slightly with increasing total surfactant concentration and the total added salt concentration. All these results which follow from the purely thermodynamic analysis have been experimentally observed[15-18] and are well-known in the literature.

To summarize, eqs 22–28 represent the principal results from the thermodynamic analysis of ionic surfactant solutions. Equation 22 stipulates that, for monodispersed micellar systems, the weight-average aggregation number should be invariant with the total surfactant concentration. Equation 26 clearly states that the weight-average aggregation number g_w of ionic surfactant micelles must increase appreciably with increasing concentration of the micellized surfactant $(S_t - X_1)$, if σ/g_w is large as in polydispersed micellar solutions. Equation 26 is a general thermodynamic result and is not dependent on one or another microscopic model of micellization. Therefore, in interpreting any experimental data for ionic surfactant systems, one must ensure that eq 26 is not violated.

Approach to Interpreting the Fluorescence Data

Figure 1 shows the relation between g_w and $S_t - X_1$ obtained in ref 2 by fitting fluorescence data to the monodispersed and the polydispersed micellar models. For the monodispersed micellar model, the interpretation of fluorescence data suggests an increasing micelle ag-

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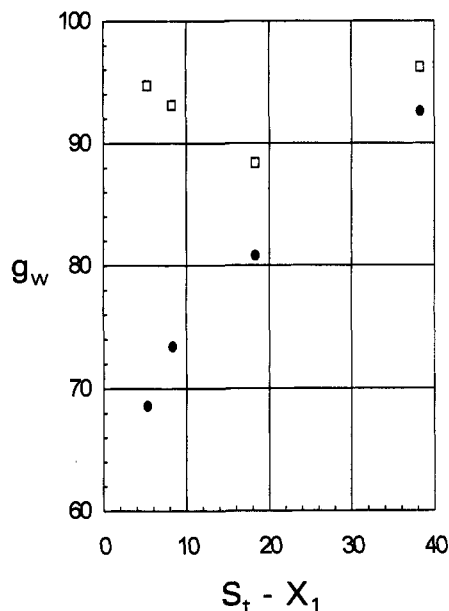(18) Shinoda, K.; Hutchinson, E. *J. Phys. Chem.* **1962**, *66*, 577.

Figure 1. Weight-average aggregation number of micelles estimated in ref 2 as a function of the total concentration of surfactant present as micelles. Filled circles denote the fitted estimates for the monodispersed micellar model. In this case, g_w refers to the single micelle size. Open squares denote the fitted estimates for the polydispersed micelle model. The data plotted are from ref 2, obtained at 20 °C and designated as corresponding to sample I.

gregation number. This violates eq 26 which requires the aggregation number to be constant and independent of surfactant concentration if the variance of the size dispersion is 0. For the polydispersed micellar model, the interpretation of the fluorescence data suggests a practically constant average aggregation number. This violates eq 26 which requires the weight-average aggregation number to increase with increasing surfactant concentration. Thus, in interpreting the fluorescence data in ref 2, the need for maintaining thermodynamic consistency was overlooked. This oversight is not uncommon in the literature since information on the average aggregation number of the micelles and the micellar polydispersity is often sought independently from experimental measurements. It is essential that, in invoking a model of micellization for data analysis, the concentration dependence of the micelle size and the size polydispersity should be treated as two factors connected to one another by the thermodynamic relation in eq 26.

The interpretation of the fluorescence decay data consistent with thermodynamic principles can be achieved by adopting the following approach. One starts with eq 6 of ref 2 where the quencher-average aggregation number g_q is related to the weight-average aggregation number g_w by the expression

$$g_q = g_w - (1/2)\sigma^2\eta + (1/6)\kappa\eta^2 \ldots \qquad (29)$$

Here, η is the ratio between the concentration of the micelle-bound quencher and the total amount of the micellized surfactant, σ^2 is the variance, and κ is the third cumulant giving the skewness of the size distribution. In ref 2, eq 29 was fitted independently, at each total surfactant concentration, in order to determine values for g_w and σ^2 at that total surfactant concentration. The appropriate data fitting procedure would be to use all the experimental measurements obtained at various total surfactant concentrations to fit eq 29 simultaneously,

consistent with eq 26. Thus, one can ensure that the resulting values for the aggregation number and the size polydispersity as a function of the total surfactant concentration will be consistent with the general principles of thermodynamics.

We describe below a possible approach to the fitting of the fluorescence data and the determination of the average size and the size dispersion of the micelles. Let us postulate an empirical dependence of the weight-average aggregation number on the concentration of the micellized surfactant as follows:

$$g_w = a + b(\sum g X_g)^c \qquad (30)$$

where a, b, and c are constants. This functional form represents exactly the theoretical[5] dependence of the micelle size on the surfactant concentration when spherical micelles transform into spherocylindrical micelles. This functional form is versatile enough to be used as an empirical expression. All variables of interest governing the size dispersion of micelles can now be related to the concentration of the micellized surfactant and the constants a, b, and c using eq 30. The z-average aggregation number is obtained by introducing eq 30 into eq 26.

$$g_z = g_w\left[1 + \frac{\partial \ln g_w}{\partial \ln \sum g X_g}\right] = a + b(\sum g X_g)^c + bc$$
$$(\sum g X_g)^c \qquad (31)$$

The variance σ^2 is obtained by combining eq 26 with eq 30.

$$\sigma^2 = g_w^2[g_z/g_w - 1] = [a + b(\sum g X_g)^c][bc(\sum g X_g)^c] \qquad (32)$$

The third cumulant κ is defined as

$$\kappa = \frac{\sum(g - g_w)^3 g X_g}{\sum g X_g} = g_z g_w \frac{\sum g^4 X_g}{\sum g^3 X_g} - 3g_z g_w^2 + 2g_w^3 \qquad (33)$$

The ratio present in the first term of the above equation can be rewritten by considering the differential relations in eqs 17–19 as well as an analogous expression for $\partial \ln(\sum g^3 X_g)$:

$$\frac{\sum g^4 X_g}{\sum g^3 X_g} = g_w \frac{\partial \ln \sum g^3 X_g}{\partial \ln \sum g X_g} = g_w \frac{\partial \ln(g_z g_w \sum g X_g)}{\partial \ln \sum g X_g} \qquad (34)$$

The combination of eqs 30–34 yields the following expression for the third cumulant as a function of the concentration of the micellized surfactant:

$$\kappa = [a + b(\sum g X_g)^c][bc(\sum g X_g)^c]^2 + [a + b(\sum g X_g)^c]^2[bc^2(\sum g X_g)^c] \qquad (35)$$

We can now introduce the expressions for g_w from eq 30, σ^2 from eq 32, and κ from eq 35 into eq 29 which describes the quencher-average aggregation number obtained from the fluorescence data at various values of η. The three constants a, b, and c can be determined by the simultaneous fit of all the values of g_q versus η obtained at various quencher concentrations and at various surfactant concentrations.

We have fitted the 30 data points listed in Table 1 of ref 2 to eq 29 as explained above, and the constants are found to be $a = 51.2$, $b = 719$, and $c = 0.363$. Using these three constants, we can calculate the values for the weight-
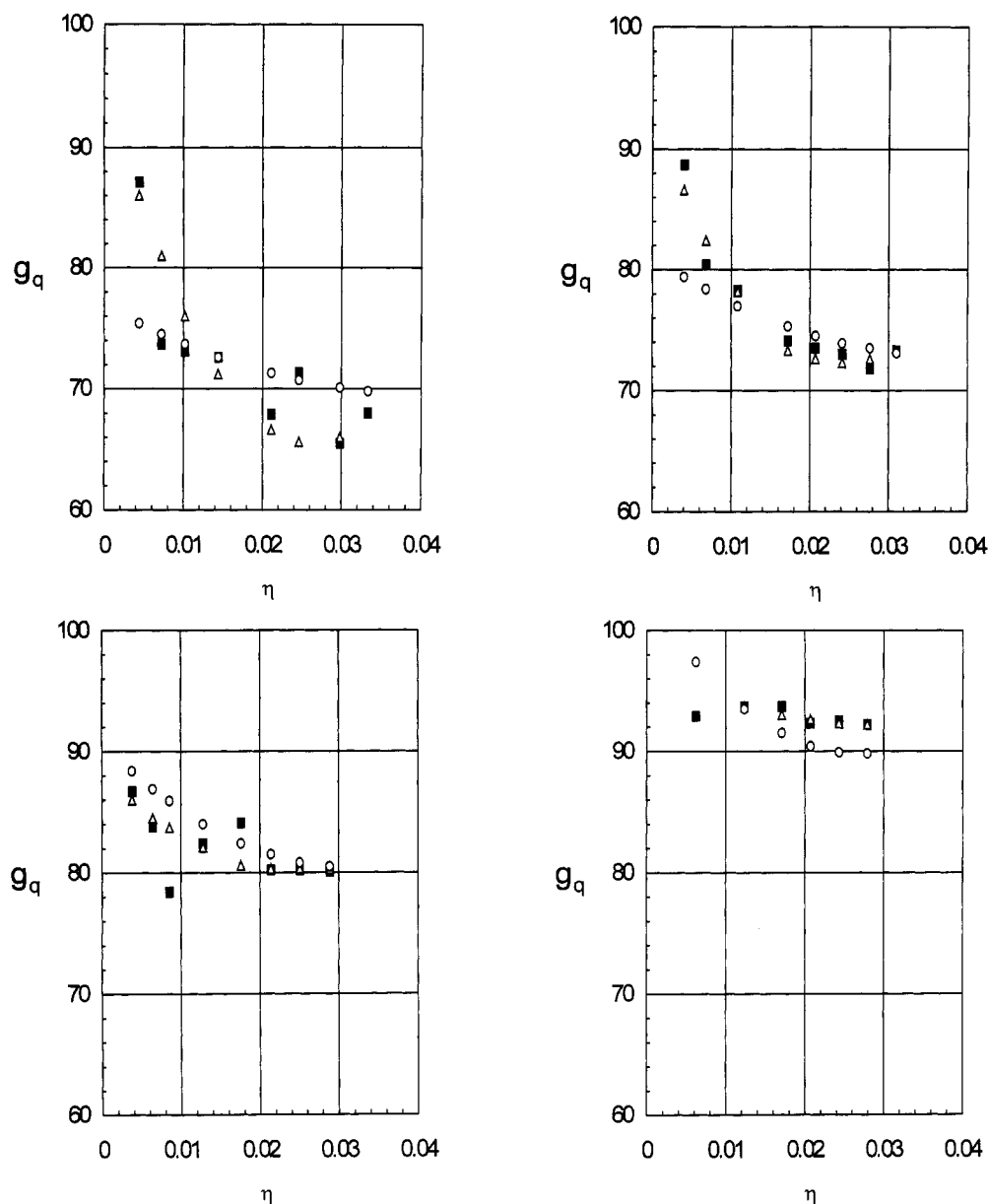
Figure 2. Quencher-average aggregation number of micelles g_q as a function of the molar ratio of the quencher to the surfactant in the micelle, η. The total surfactant concentrations are (a, top left) 7 mM CTAC, (b, top right) 10 mM CTAC, (c, bottom left) 20 mM CTAC, and (d, bottom right) 40 mM CTAC. The filled squares are the values deduced from the fluorescence experiments. The standard deviation associated with these aggregation numbers is stated to be ±8% in ref 2. The open triangles are the fits obtained in ref 2 to the experimental data while the open circles are the fits obtained in this paper. See discussion in the text.

average aggregation number, the variance, and the third moment of the size dispersion at each of the four total surfactant concentrations, and the results are summarized in Table 2. Figure 2 shows the quencher-average aggregationnumbers as fitted in this work (open circles) and the fitted values of ref 2 (open triangles) as well as the values determined from the fluorescence quenching experiments (filled squares) at each of the four surfactant concentrations investigated. The quencher-average aggregation numbers deduced from the experiments deviate to a similar degree from both the fitted aggregation numbers of this work and the fitted aggregation numbers of ref 2. The fitted values for the aggregation numbers in this work are obtained by satisfying not only eq 29 but also the thermodynamic requirement imposed by eq 26, whereas the fitted values of ref 2 are the best fits obtained at each total surfactant concentration without accounting for eq 26. Obviously, the fits obtained in this work based on a total of three parameters (the constants a, b, and c) cannot be as good as the fits obtained in ref 2 based on

Table 2. Moments of Size Distribution for CTAC Micelles at 20 °C: Estimates Based on Fitting of Fluorescence Decay Data to Eqs 29, 30, 32, and 35[a]

	7 mM I	10 mM I	20 mM I	40 mM I
g_w	76.9	81.1	90.7	103
σ/g_w	0.348	0.366	0.397	0.427
κ/g_w^3	0.0587	0.0665	0.0824	0.0991

[a] The molar concentrations refer to the total amount of surfactant CTAC in solution. At each surfactant concentration, I refers to the samples measured at time increments of 0.8 ns/channel. The first moment of the size distribution g_w is the weight-average aggregation number, σ^2 refers to the variance or the second moment of the size distribution about the mean, and κ is the third moment of the size distribution about the mean. The cmc was estimated to be 1.3 mM in ref 2.

a total of eight parameters (g_w and σ^2 at each of the four surfactant concentrations). It is evident from the scatter of the experimental aggregation numbers that there is appreciable uncertainty in the estimates. The standard

deviation on the quencher-average aggregation numbers is stated to be ±8% in ref 2. If one takes this into account, the fits obtained in this paper are statistically as good as the fits obtained in ref 2 while also meeting the thermodynamic consistency requirement.

Conclusions

We have examined the interpretation of dynamic fluorescence quenching data on micellar solutions in the recent literature as to their thermodynamic consistency. We show that the general thermodynamic principles of self-assembly for nonionic as well as ionic surfactants rule out the possibility that monodispersed micelles could increase in their size as the total surfactant concentration is increased. They also rule out the possibility that the weight-average aggregation number could remain unaffected by increasing surfactant concentration when the micelles are polydispersed. Thus, the interpretation of the fluorescence data on CTAC solutions, referred to earlier, is not consistent with model-independent thermodynamic principles. In general, while interpreting experimental results on micellar solutions, the concentration dependence of the micellar aggregation number and the micelle polydispersity should be viewed not as independent of one another but as factors linked together by the thermodynamic result contained in eq 8 for the nonionics and eqs 22 and 26 for the ionics. A method of data interpretation consistent with the thermodynamic requirements is suggested, and the experimental data of ref 2 are reinterpreted on that basis.

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