

# Theoretical Study of the Role of Head-group Interactions in the Micellization of Non-ionic Surfactants

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The critical micelle concentration (c.m.c.) and various properties of amphiphiles in solution have been simulated for a simple parametrization of the free energy of formation of micelles in terms of their aggregation numbers. A simple expression for the dependence of the c.m.c. on the energy parameters is obtained empirically from the numerical determinations of the c.m.c. The criterion used for the c.m.c. is that the rate of change of monomer concentration with respect to total amphiphile concentration is at a maximum. This is compared with the results of an alternative expression based on a horizontal inflection point in the micelle size distribution (the Ruckenstein-Nagarajan criterion).

Numerical results are scaled to highlight the effect of headgroup interactions, and experimental light-scattering results are simulated for a variety of systems.

The problem of self-assembly of amphiphilic molecules into micelles and lamellar structures has been treated theoretically with an increasing amount of success over the past decade. The general 'principle of opposing forces' propounded by Tanford<sup>1</sup> has been expanded upon and applied to a multitude of situations involving self-assembly.<sup>2–6</sup> According to ideal-solution theory the relationship defining the distribution of aggregates in solution is given in general by

$$X_i = X_1^i \exp(-\Delta G_i^\circ) \quad (1)$$

where  $X_i$  is the mole fraction of aggregates of aggregation number  $i$  and  $\Delta G_i^\circ$  is the free energy (per  $kT$ ) of transfer of  $i$  amphiphiles to a micelle of size  $i$ . This equation assumes only that there is no interaction between micelles and usually forms the basis of a thermodynamic analysis of micellar solutions.

While eqn (1) is applicable to any amphiphilic solute, the parametrization of  $\Delta G_i^\circ$  is dependent to a large degree upon the geometry of the aggregate.<sup>2</sup> Once the general form of  $\Delta G_i^\circ$  is established, in principle any property of the solution may be determined. We will be concerned in subsequent sections with parameters derived from the colligative properties of the solution: specifically the number-average and weight-average aggregation numbers

$$\langle i \rangle' = \sum_{i=2}^{\infty} i X_i / \sum_{i=2}^{\infty} X_i \quad (2)$$

$$\langle i \rangle'_w = \sum_{i=2}^{\infty} i^2 X_i / \sum_{i=2}^{\infty} i X_i \quad (3)$$

where primes denote that the summations are carried out excluding the monomer concentration ( $i = 1$ ) term.

From the total amphiphile mole fraction and a mass balance of the amphiphile, it is also possible to determine properties related to the monomer concentration, *viz.*

$$X_1 = X - \sum_{i=2}^{\infty} iX_i \quad (4)$$

A convenient and physically realistic parametrization of  $\Delta G_i^\circ$  for spherical micelles, which has been used by several workers,<sup>1-3</sup> is

$$\Delta G_i^\circ = -ai + bi^{2/3} + ci^{4/3} - (-a + b + c) \quad (5)$$

where  $a$ ,  $b$  and  $c$  are dimensionless coefficients and  $\Delta G_i^\circ$  goes to zero at  $i = 1$  as required by eqn (1).

The coefficient  $a$  is a bulk free-energy term for transfer of an alkyl chain from water into the micellar core,  $b$  is the surface free energy per amphiphile at the micelle/solution interface, the total surface free energy of the micelle being proportional to surface area, and  $c$  is a term for repulsions *etc.* between the headgroups in the micelle and is proportional to surface area squared per micelle.<sup>1,2</sup>

For computational simplicity we have chosen a slightly modified form of eqn (5) for the free-energy parametrization:

$$\Delta G_i^\circ = -a(i-1) + b(i-1)^{2/3} + c(i-1)^{4/3}. \quad (6)$$

This form is essentially the same as eqn (5) far from  $i = 1$  where the formulation is realistic. For  $i$  close to 1 spherical micelles are geometrically prohibited, so the exact form of  $\Delta G_i^\circ$  is not important in what follows.

Eqn (5) and (6) are only suitable for spherically shaped aggregates, and to describe more realistic aggregate free energies when non-spherical shapes are expected to occur (*e.g.* at very large and very small values of  $i$ ) significantly more complicated expressions are needed. Provided the polydispersity of the micellar aggregate is not too great, simple parametrizations, as are used here, will provide a satisfactory description of the behaviour investigated. This is because contributions from the  $X_i$  for small  $i$  to any colligative property which exhibits the sharp break indicative of c.m.c. behaviour are not significant. Thus errors in  $\Delta G_i^\circ$  for small  $i$ , which lead to errors in the corresponding  $X_i$ , do not alter the conclusions outlined below.

All that is necessary, then, is reasonable parametrization in the neighbourhood of  $i = \langle i \rangle$ . Eqn (5) and (6) are suitable parametrizations in that they contain the correct physical properties (of negative bulk energy, positive surface energy and repulsive headgroup interactions) and lead to aggregate distributions in which  $X_2$ ,  $X_3$  *etc.* are negligibly small. The fact that the actual values of  $X_2$ ,  $X_3$  *etc.* may be in error is immaterial if they do not contribute significantly to the total colligative property being investigated.

Ruckenstein and Nagarajan<sup>1</sup> (RN) have used eqn (5) to exemplify their criterion for the critical micelle concentration (c.m.c.). Their definition of the c.m.c. was based on the appearance of a horizontal inflection point in the micelle size distribution function. From eqn (1) it follows that

$$\frac{\partial \ln X_i}{\partial i} = \ln X_1 - \frac{\partial \Delta G_i^\circ}{\partial i} \quad (7a)$$

$$\frac{\partial^2 \ln X_i}{\partial i^2} = -\frac{\partial^2 \Delta G_i^\circ}{\partial i^2}. \quad (7b)$$

A horizontal inflection point thus occurs when  $\ln X_1 = \partial \Delta G_i^\circ / \partial i$  and  $\partial^2 \Delta G_i^\circ / \partial i^2$  is zero for some value of  $i$ . Using eqn (5) for  $\Delta G_i^\circ$  leads to a value for both the c.m.c. and the aggregation number at the c.m.c., viz.

$$X_{\text{cmc}} = X_1^{\text{cmc}}$$

where

$$\ln (X_1^{\text{cmc}}) = -a + (2^{5/2}/3)(bc)^{1/2} \quad (8a)$$

$$i_{\text{RN}} = (b/2c)^{3/2}. \quad (8b)$$

If eqn (6) is used then  $i_{\text{RN}} = (b/2c)^{3/2} + 1$ .  $i_{\text{RN}}$  is determined to be the aggregation number at the inflection point and not an average such as that defined in eqn (2) and (3). This means that it is not necessarily a parameter which can easily be related to any experimental quantity. Note also that c.m.c.<sub>RN</sub> is determined to be the concentration of monomer at the horizontal inflection point and not the total surfactant concentration. These two values should be very close together for most systems, but this need not always be the case.

It has been shown that while the value of c.m.c.<sub>RN</sub> is a good approximation (in fact a close lower bound) to the c.m.c. of several systems,<sup>3</sup> an alternative parametrization for  $\Delta G_i^\circ$  can lead to discrepancies of an order of magnitude between c.m.c.<sub>RN</sub> and the true c.m.c.<sup>4</sup> Also there is no *a priori* reason to suppose that  $i_{\text{RN}}$  is the same aggregation number as that determined experimentally, especially since such determinations are usually performed far from the c.m.c. It is the definition of the true c.m.c. and the nature of  $\langle i \rangle'$  and  $\langle i \rangle'_w$  for the free-energy parametrization described above with which we are concerned here.

If  $P$  is some property (e.g. surface tension, conductivity) which is a function of  $X_1$ , then experimentally the conventionally defined c.m.c. may be determined by extrapolation of the two linear portions of the graph of  $P$  against  $X$  to their intersection. The curve  $P(X)$  is in reality a smoothly varying curve but the curvature, if experimentally detectable, is ignored. In many systems the curvature is so great that it is beyond experimental access and the results show two linear regions.

In a more precise mathematical sense the c.m.c. may therefore be defined as the point of greatest curvature in a plot of some property,  $P$ , of the system against amphiphile concentration,  $X$ , i.e. the point at which the rate of change of the gradient of  $P$  is at a maximum, of<sup>7</sup>

$$\frac{\partial^3 P}{\partial X^3} = 0. \quad (9)$$

If  $X_1$  is chosen as the property  $P$ , then

$$\frac{\partial^3 X_1}{\partial X^3} = 0 \quad (10)$$

can be taken as the c.m.c. One could just as well define the c.m.c. to be the zero of the third derivative of any other colligative property, such as the total number of species (aggregates) in solution with respect to total concentration of amphiphile. This criterion is more physically recognizable than the RN criterion, wherein the proximity of c.m.c.<sub>RN</sub> and the experimental c.m.c. depends on how suddenly  $\Delta G_i^\circ$  causes the onset of large  $i$  aggregates. Instead, eqn (10) measures the point where this change is occurring most quickly.

## THEORY

The variation of monomer concentration with total amphiphile concentration is described analytically by eqn (1) and (4) together, *viz.*

$$X = \sum_{i=1}^{\infty} iX_1^i \exp(-\Delta G_i^{\circ}). \quad (11)$$

It is straightforward to proceed from here to the formulation of  $\partial^3 X_1 / \partial X^3$  for an arbitrary  $\Delta G_i^{\circ}$ . We obtain

$$\frac{\partial^3 X_1}{\partial X^3} = M / X_1^2 \left( \sum_{i=1} i^2 X_1^{i-1} \exp(-\Delta G_i^{\circ}) \right)^5 \quad (12)$$

where

$$M = 3 \left( \sum_{i=1} i^2(i-1) X_1^{i-1} \exp(-\Delta G_i^{\circ}) \right)^2 - \left( \sum_{i=1} i^2(i-1)(i-2) X_1^{i-1} \exp(-\Delta G_i^{\circ}) \right) \left( \sum_{i=1} i^2 X_1^{i-1} \exp(-\Delta G_i^{\circ}) \right) \quad (13)$$

and clearly possesses a zero for finite, positive  $X$ , so that  $X_{\text{cmc}}$  is the value of  $X$  at which  $M = 0$ .

With our selected energy parametrization, [eqn (6)], eqn (13) may be simplified by scaling the monomer concentration. We introduce the scaled concentration variable  $y$  defined by

$$y = (\ln X_1 + a) / (bc)^{1/2} \quad (14)$$

and two dimensionless parameters ( $\Gamma$ ,  $I$ ) given by

$$\Gamma = b^2 / c \quad (15)$$

$$I = (b/c)^{3/2} \quad (16)$$

which provide appropriate scaling parameters for the energy,  $\Delta G_i^{\circ}$ , and aggregation number,  $i$ . Note that  $i_{\text{RN}}$  [eqn (8b)] is equal to  $I/2^{3/2}$ , which we shall show to be less than the value of the aggregation number far above the c.m.c.

Thus eqn (13) becomes

$$M(y) = 3 \left( \sum_{i=1} i^2(i-1) \exp[-G(y, i)] \right)^2 - \left( \sum_{i=1} i^2(i-1)(i-2) \exp[-G(y, i)] \right) \left( \sum_{i=1} i^2 \exp[-G(y, i)] \right) = 0 \quad (17)$$

where

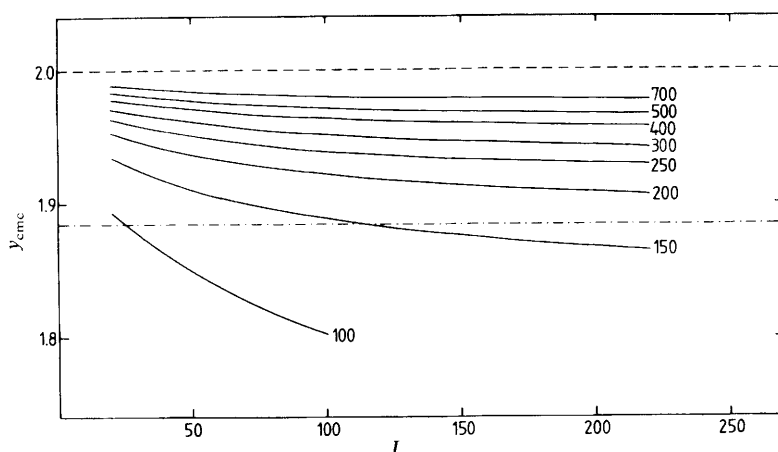
$$\begin{aligned} G(y, i) &= \Delta G_i^{\circ} - (i-1) \ln X_1 \\ &= \Gamma \left[ -y \left( \frac{i-1}{I} \right) + \left( \frac{i-1}{I} \right)^{2/3} + \left( \frac{i-1}{I} \right)^{4/3} \right]. \end{aligned} \quad (18)$$

The c.m.c. may thus be determined by first finding the zero,  $y_{\text{cmc}}$ , of  $M(y)$  (for given values of  $\Gamma$  and  $I$ ) and then determining  $X_{\text{cmc}}$  from

$$X_1 = \exp[y(bc)^{1/2} - a] \quad (19)$$

$$X = X_1 \sum_{i=1} i \exp[-G(y, i)] \quad (20)$$

with  $y = y_{\text{cmc}}$ .



**Fig. 1.** Plot of the solution to eqn (17),  $y_{\text{cmc}}$ , against the aggregation number scaling parameter,  $I$ , for different values of  $\Gamma$  (marked on curves). Also shown are the upper bound for  $y$  (---) (see text) and the RN criterion for the c.m.c. (- · - · -).

## RESULTS

The zero of  $M(y)$  is found by an interval halving technique in the range  $y_{\text{low}} < y < y_{\text{high}}$ , where  $y_{\text{low}}$  and  $y_{\text{high}}$  are suitable bounds. It was found that a suitable upper bound is

$$y_{\text{high}} = 2. \quad (21)$$

This corresponds to the value of  $y$  for which the conditions

$$G(y, i) = 0 \quad (22)$$

$$\frac{\partial G(y, i)}{\partial i} = 0 \quad (23)$$

are simultaneously satisfied. From eqn (18) this occurs at  $y = 2$  and  $i = I$ . This corresponds to the experimental situation (expected to occur far above the c.m.c.) where the maximum in the  $X_i$  against  $i$  curve (for  $i > 1$ ) is equal to  $X_1$ . Clearly this is on the high side of the Ruckenstein–Nagarajan criterion,<sup>3</sup> which seeks the onset of any maximum in the  $X_i$  curve.

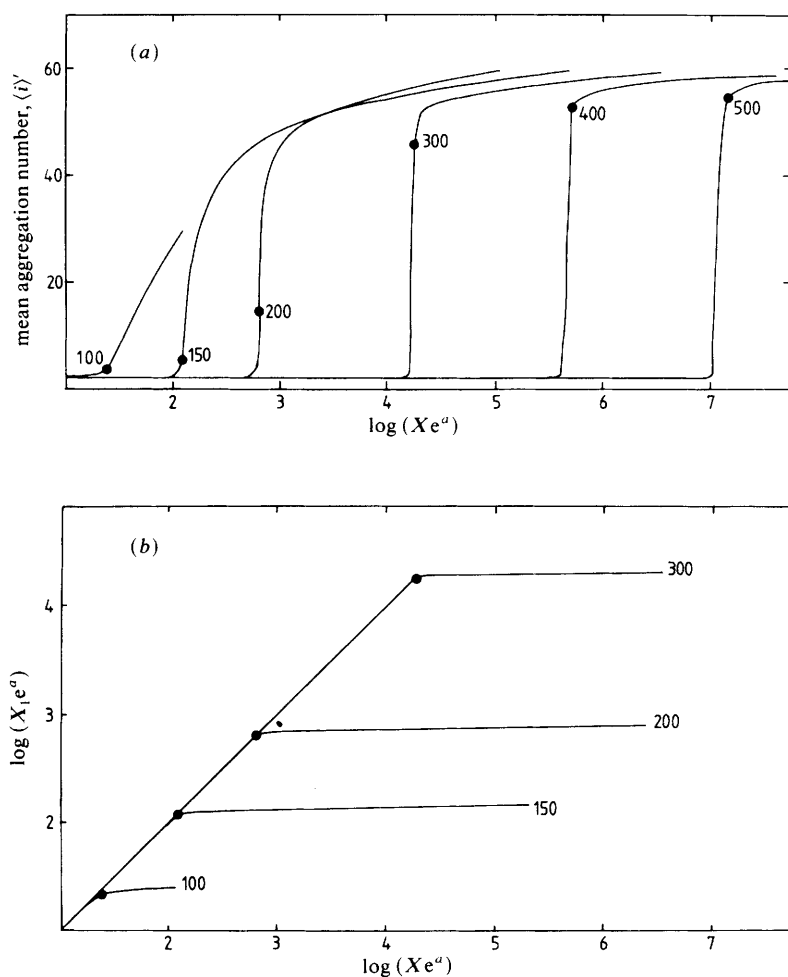
Often a suitable lower bound can be taken as

$$y_{\text{low}} = 2^{5/2}/3 \quad (24)$$

which corresponds to the RN c.m.c. criterion as given by eqn (8a). For low values of  $\Gamma$  this lower bound is sometimes inappropriate; however, by testing the value of  $M(y)$  at  $y_{\text{low}}$  and systematically decreasing  $y_{\text{low}}$  from  $2^{5/2}/3$  until  $M(y) < 0$ , suitably tight upper and lower bounds can be obtained.

Results obtained for scaled monomer concentration at the c.m.c. as a function of both  $I$  and  $\Gamma$  are shown in fig. 1. Also shown are the upper and lower (RN criterion) limits to  $y$ . Note that for most conditions  $y_{\text{RN}}$  is below the zero of  $M(y)$ ; this is only violated for small values of  $\Gamma$  as discussed above.

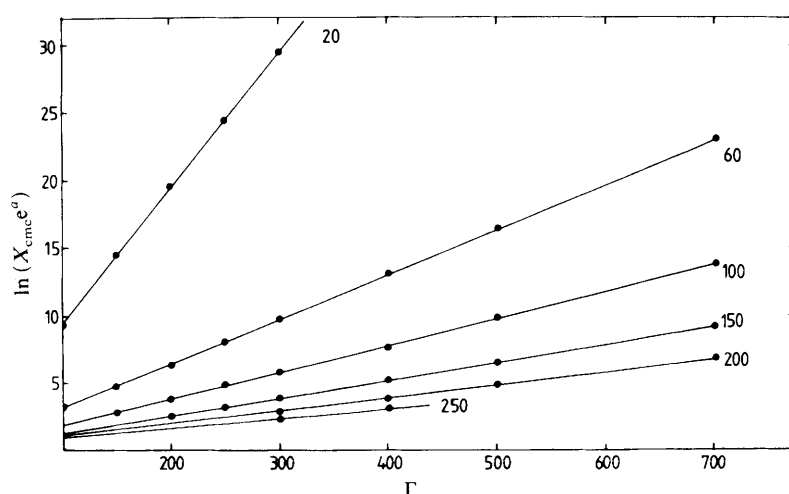
In fig. 2(a) the number-average aggregation number,  $\langle i \rangle'$ , is shown as a function of total concentration,  $X$ , for various  $\Gamma$  with  $I = 60$ . The concentration has been



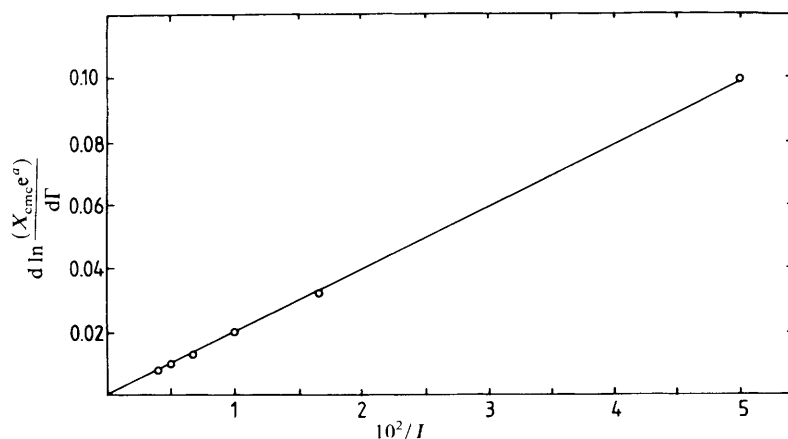
**Fig. 2.** (a) Plot of the number-average aggregation number  $\langle i' \rangle$  against the scaled total amphiphile concentration for  $I = 60$  and different values of  $\Gamma$  (marked on curves). The value of  $\langle i' \rangle$  at the c.m.c. is also shown for each  $\Gamma$  (●). (b) Plot of scaled monomer amphiphile concentration against total concentration for  $I = 60$  and different values of  $\Gamma$  (marked on curves). The c.m.c. and monomer concentration at the c.m.c. is shown in each case (●).

scaled by a factor  $e^a$  in order that the effect of headgroup parameters can be clearly seen. Also marked on fig. 2(a) is the value of  $\langle i' \rangle$  at the c.m.c. The value of  $\langle i' \rangle'_{\text{cmc}}$  varies markedly with  $\Gamma$  in direct contrast to  $i_{\text{RN}}$ , which is always  $I/2^{3/2}$ . Fig. 2(b) shows a plot of monomer concentration against scaled total concentration for the same values of  $\Gamma$  and  $I$  as in fig. 2(a). The monomer concentration becomes approximately constant quite suddenly for large  $\Gamma$ , and even for quite small values of  $\Gamma$  the transition is relatively sharp when plotted in this way. This is not the case for plots of  $\langle i' \rangle$  against  $X$ , as in fig. 2(a) where the transition region is more diffuse as  $\Gamma$  decreases.

Numerical solutions for the c.m.c. for a wide range of values of  $\Gamma$  and  $I$  are shown in fig. 3. We see from these plots that for fixed  $I$  the c.m.c. varies linearly



**Fig. 3.** Plot of calculated c.m.c. scaled by  $e^a$  against energy-scaling parameter  $\Gamma$  for different values of  $I$  (marked on curves). Solid lines correspond to the best linear regression fit to the numerical results.



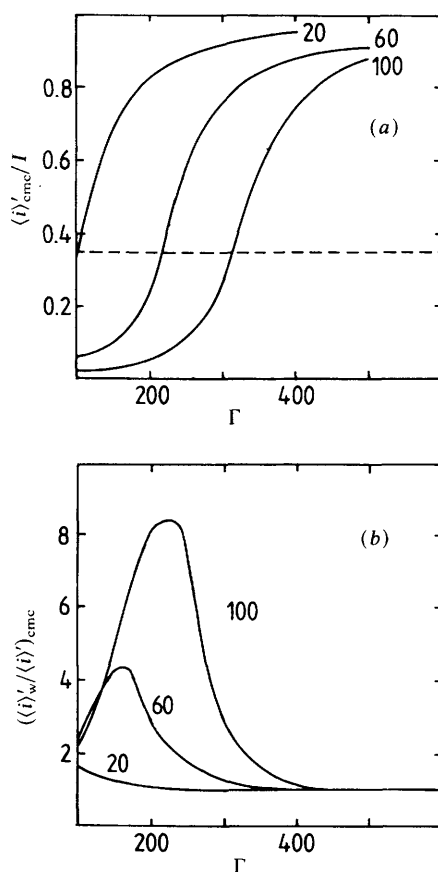
**Fig. 4.** Plot of the best linear regression fit to the gradients of the lines shown in fig. 3 against  $I^{-1}$ .

with  $\Gamma$ . This is shown by the single line in fig. 4; we have

$$\begin{aligned} \ln X_{\text{cmc}} &= -a + 2\Gamma/I \\ &= -a + 2(bc)^{1/2} \end{aligned} \quad (25)$$

where all the lines in fig. 3 pass through the origin.

The mean aggregation number at the c.m.c. is unfortunately not so simple to describe. Fig. 5(a) shows  $\langle i' \rangle / I$  at the c.m.c. as a function of  $\Gamma$  for three values of  $I$ . The 'polydispersity index',  $\langle i'_w \rangle / \langle i' \rangle$ , which is a measure of the breadth of the size distribution function, is shown in fig. 5(b) for the same systems at their c.m.c. For all these systems  $\langle i'_w \rangle / \langle i' \rangle$  tends to 1 far above the c.m.c. (i.e. monodispersity) and both  $\langle i'_w \rangle$  and  $\langle i' \rangle$  are approximately equal to  $I$  in this limit.



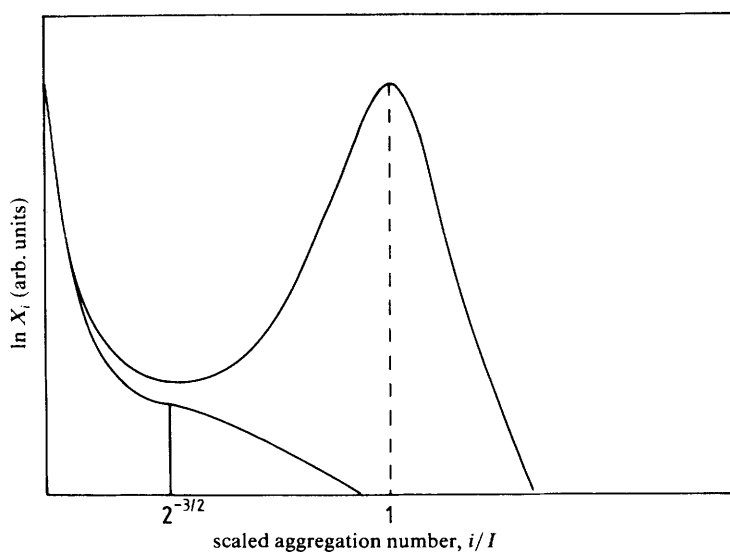
**Fig. 5.** (a) Number-average aggregation number at the c.m.c. scaled by  $I$  against  $\Gamma$  for different values of  $I$  (marked on curves). Also shown is the aggregation number at c.m.c.<sub>RN</sub>,  $i_{\text{RN}}$  (see text) (---). (b) Plot of polydispersity index  $\langle i \rangle'_w / \langle i \rangle'$  at the c.m.c. against  $\Gamma$  for different values of  $I$  (marked on curves).

## DISCUSSION

The most striking feature of this analysis is the simple relationship obtained for the c.m.c. as a function of the parameters  $a$ ,  $b$  and  $c$  [eqn (25)]. Its similarity to the RN result [eqn (8a)] lends some support to the rationale behind their criterion, but also implies astounding sensitivity of the solution properties to the total concentration of amphiphile near the c.m.c. Eqn (25) in fact corresponds to the situation used for the upper limit of  $y$ , where  $X_i = X_1$  for some  $i$ . As may be seen from fig. 1, this is a better approximation for  $y$  at the c.m.c. than c.m.c.<sub>RN</sub> for most values of  $\Gamma$  and  $I$ .

Physically one would expect  $y = 2$  to be far above the c.m.c., but as the monomer concentration becomes almost constant at the c.m.c., the error introduced is negligible. An approximation such as eqn (25) which overestimates  $y$  thus introduces far smaller errors than an underestimate because  $X_1$  (and hence  $y$ ) varies so little with  $X$  above the c.m.c. The size distribution corresponding to this situation ( $y = 2$ ) is depicted schematically in fig. 6, together with the situation describing the RN





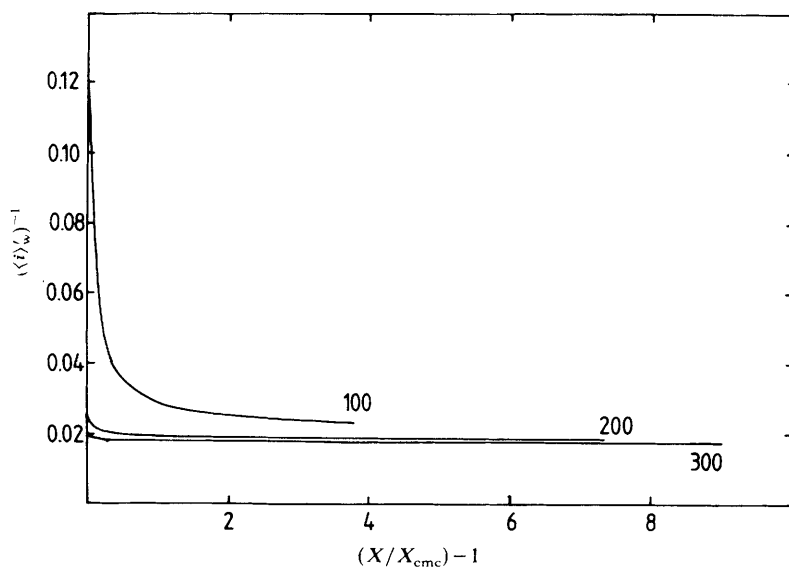
**Fig. 6.** Schematic diagram of micelle size distributions  $X_i$ , scaled by  $I$ , corresponding to both the RN condition and the  $y = 2$  criterion. Also shown are the  $i/I$  values corresponding to the solutions of the RN criterion ( $2^{-3/2}$ ) and the  $y = 2$  criterion ( $i/I = 1$ ).

criterion. Our criterion for the c.m.c. lies between these limits for most values of  $\Gamma$  and  $I$ . This implies that there are significant numbers of micelles in solution at the c.m.c., i.e. the size distribution function at the c.m.c. has a distinct maximum for some  $i$ , the value of which is quite sensitive to the values of  $\Gamma$  and  $I$ .

For most values of  $\Gamma$  and  $I$ , the RN criterion (i.e. the appearance of an inflection point in the  $X_i$  curve) is a precursor to the micellization point and can occur at significantly smaller  $X$  values than  $X_{\text{cmc}}$ .

The values of  $\Gamma$  and  $I$  for which the c.m.c. is less than  $\text{c.m.c.}_{\text{RN}}$  exhibit a more diffuse transition regime in their solution properties than for large values of  $\Gamma$  (where  $\text{c.m.c.} > \text{c.m.c.}_{\text{RN}}$ ). This is especially so for  $\langle i \rangle'$ , as can be seen in fig. 2. In all cases, however, the upper limit  $y = 2$  describes a solution with a size distribution sharply peaked about  $i = I$ . It is therefore a useful description of a solution far above the c.m.c. The size distribution being so peaked, the average aggregation numbers will collapse together to give  $\langle i \rangle' \approx \langle i \rangle'_w \approx I$ . This makes  $I$  a far more useful parameter than  $i_{\text{RN}}$ .

It is now possible to proceed from these results to generate experimental data of various kinds. Indeed,  $\langle i \rangle'$  may immediately be expressed as reduced osmotic pressure for comparison with experiment. We have generated scaled Debye plots of light-scattering data for various values of  $\Gamma$  with  $I$  fixed at 60. These are shown in fig. 7. The light-scattering experiment is simulated by calculating  $1/\langle i \rangle'_w$ . This is the experimental parameter obtained from light-scattering data when plotted in the conventional way to correct for scattering from both the solvent and from monomeric amphiphile, once the molecular weight of the amphiphile has been taken into account. The virial corrections for a solution of non-interacting spheres were examined<sup>8</sup> but the data were changed only marginally and are therefore not included here. Note the large curved region in the low  $\Gamma$  scattering curve, which tends to become sharper and the plot more linear as  $\Gamma$  increases. This corresponds to growth



**Fig. 7.** Simulated Debye plots, scaled by molecular weight of the amphiphile, against the concentration scaled by the c.m.c. for  $I = 60$  and different values of  $\Gamma$  (marked on curves). The inverse of the weight-average aggregation number,  $\langle i \rangle_w^{-1}$ , is conventionally taken as the intercept of the linear portion of such a plot extrapolated to  $(X/X_{cmc}) - 1 = 0$ .

to a near monodispersion of micelles over a small concentration range, whereas small  $\Gamma$  produces a more gradual change [see fig. 2(a)].

The c.m.c. determined by light scattering is not related in any simple way to our c.m.c. criterion [eqn (10)]. However, an alternative definition of the c.m.c. in terms of the total number of aggregate species,  $Y$ , is clearly related to  $\langle i \rangle_w'$ :

$$Y = \sum_{i=2}^{\infty} X_i \quad (26)$$

Eqn (11) and (26) together give the simple relationship

$$\begin{aligned} \frac{\partial Y}{\partial X} &= \left( \frac{\sum_{i=2}^{\infty} i^2 X_i \exp(-\Delta G_i^\circ)}{\sum_{i=2}^{\infty} i X_i \exp(-\Delta G_i^\circ)} \right)^{-1} \\ &= \langle i \rangle_w'^{-1}. \end{aligned} \quad (27)$$

The steepest point of the plot of  $\langle i \rangle_w'^{-1}$  against  $X$  therefore corresponds to  $\partial^3 Y / \partial X^3 = 0$ . This, however, will not necessarily be the same value as our criterion. Any experimental parameter may, of course, be selected for use in the third-derivative c.m.c. criterion<sup>7</sup> and we see that these can all lead to slightly different numerical results unless the change in the experimental quantity is exceptionally abrupt.

## CONCLUSIONS

By a numerical solution of the third derivative of the monomer concentration with total concentration we have obtained a straightforward empirical relationship between the c.m.c. and the free energy of micellization for a three-parameter description of the free energy. Although similar to an expression derived by Ruckenstein and Nagarajan<sup>3</sup> for the c.m.c., several important differences suggest that the c.m.c. is a more subtle parameter than simply an inflection point in the size distribution.

Simulated light-scattering data behave as expected for micellar solutions with widely varying head-group interaction energies, reflecting the different rates of growth of micelles with total amphiphile concentration.

The value of parametrizations such as eqn (5) and (6) is now revealed. We see that head-group interactions ( $c \neq 0$ ) and surface-energy contributions ( $b \neq 0$ ) cause shifts in the value of the c.m.c. and so control the average micelle aggregation number. Indeed if  $c$  is put equal to zero the model predicts infinite aggregation numbers. As discussed extensively by Tanford,<sup>1</sup> such 'opposing forces' are essential in providing even a qualitative description of the process of micelle formation.

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