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THE EFFECT OF THE PROPAGATION COEFFICIENT ON SIZE DISTRIBUTION IN MICELLAR SYSTEMS

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In this study the effect of the propagation coefficient on the molar distribution function in a modified shell model for micellar systems was examined. The sharpness of the micelle size distribution boundary was found to depend less on the degree of polymerization, n, than on the propagation coefficient, P. Although Kegeles (J. Phys. Chem. 83 (1979) 1728) has reported a marked sharpening of the distribution boundary when $P = 2.0$, we found the boundary to be fairly broad at this point. However, as values of the propagation coefficient were increased from 3 to 10, the micelle distribution boundary became increasingly sharp. The possibility of such a change in the reaction boundary arising from a structural transition, accompanied by a change in the rate of dissociation of monomer from the shell, is also discussed.

1. Introduction

Several models have been proposed to describe the micellar equilibria [1–9], and the kinetics of surfactant micellization have been widely examined [3,10–19]. In considering a shell model for the size distribution of micelles, Kegeles [9] has shown that for true micellar solutions, the intrinsic equilibrium constant K for all oligomers above dimer is different from the K value for a monomer-dimer equilibrium. That is, the monomer-dimer reaction can be assumed to be a nucleation step for the formation of micelles and can be appropriately weighted with respect to all subsequent reactions by a nucleation factor, f, in the molar distribution function in a micellar system.

$$[A_i]/[A_o] = f\left[\frac{n!}{(n-i)!}\right]\left[\frac{1}{i+1}\right]\left[\frac{K[A_o]}{n}\right]^i$$
$$i = 1,2,\ldots,n$$

where $[A_i]$ and $[A_o]$ are the concentration of ith oligomer and free monomer, respectively.

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The basic premises of the shell model [9] for size distribution and critical micelle behavior have been well established: that if the preexisting oligomer in a hypothetical shell is proportional to the number of empty holes, $n - i$, as well as the number of monomers in the system $(i + 1)$, and the probability of monomer being added to the shell is $(i + 1)$, then the probability of monomer being dissociated from this preexisting shell is proportional to the number of monomers, $(i + 2)$, i.e.

$$[A_{i+1}]/[A_i] = \left[\frac{n-i}{n}\right]\left[\frac{i+1}{i+2}\right]K[A_o]$$
$$i = 0,1,\ldots,(n-1)$$

The product of the intrinsic formation constant for the addition of a monomer to any oligomer and the concentration of free monomer, $[A_o]$, forms a propagation coefficient, $K[A_o]$, greater than unity to produce concerted or cooperative growth. $(n - i)/n$, where $0 \leqslant \frac{n-i}{n} < 1$, is taken as a steric factor, the maximum space available and the maximum growth limit of the ith oligomer in a given shell which can be added to one preexisting mono-

mer, provided that ith additional monomers are already present in the shell. It has been traditionally accepted that $K[A_o]$ is slightly less than or equal to unity at all concentrations above the critical micelle concentration [3,4,10,13,20].

Kegeles' extensive consideration of the nature and possible ramifications of a shell model for size distribution in micelles has stimulated this further study of the effect of the propagation coefficient on the molar distribution function in micellar systems. In particular, we have examined the extent to which the propagation coefficient continues to affect the micellar distribution boundary at values greater than 2.0.

2. Formulation of the distribution function

In this study, we assume that a hypothetical shell has n holes to be filled, forming a micelle, where n represents the degree of polymerization, which can be experimentally determined by sedimentation equilibrium measurements or scanning molecular sieve chromatography [21]. Letting the present shell have i monomers, then we can assume, in general, that the probability of a monomer being associated into one of the empty spaces is $\alpha_i[A_1]$, while the probability of monomer being dissociated from the shell is denoted as β_i, where the concentration of monomer in solution is $[A_1]$. Hence, α_i is simply the formation rate constant describing a single hole in the shell to be filled and

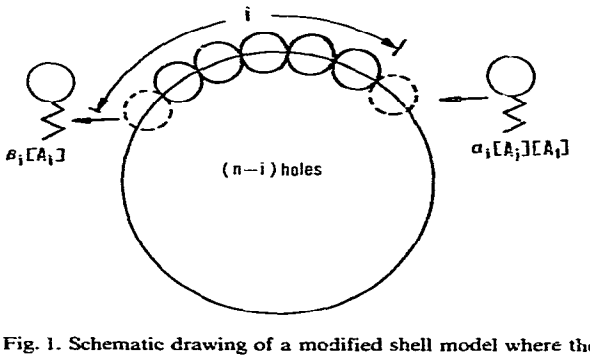

Fig. 1. Schematic drawing of a modified shell model where the rate of association of monomer into the preexisting ith oligomer having n holes is $\alpha_i[A_i][A_1]$, and the rate of dissociation of monomer from the shell is $\beta_i[A_i]$.

β_i is the dissociation rate constant describing a single monomer to be released from the shell. The kinetics of micellization of such a shell model can be described schematically as shown in fig. 1, based on the law of mass action [22] and ignoring thermodynamic nonideality. Thus, the follow expression may be derived:

$$-\frac{d[A_1]}{dt} = \left(\sum_{i=1}^{n} \alpha_i[A_i]\right)[A_1] - \sum_{i=2}^{n} \beta_i[A_i]$$

$$-\frac{d[A_2]}{dt} = (\alpha_2[A_1] + \beta_2)[A_2] - \alpha_1[A_1]^2 - \beta_3[A_3]$$

$$\vdots$$

$$-\frac{d[A_i]}{dt} = (\alpha_i[A_1] + \beta_i)[A_i] - \alpha_{i-1}[A_1][A_{i-1}]$$
$$\vdots \qquad -\beta_{i+1}[A_{i+1}]$$

$$-\frac{d[A_n]}{dt} = \beta_n[A_n] - \alpha_{n-1}[A_1][A_{n-1}] \qquad (1)$$

For a system at chemical equilibrium, i.e., $\frac{d[A_i]}{dt} = 0$, or $[A_1] + [A_i] \underset{\beta_i}{\overset{\alpha_i}{\rightleftharpoons}} [A_{i+1}]$,

$$\beta_2[A_2] = \alpha_1[A_1]^2$$
$$\beta_3[A_3] = \alpha_2[A_2][A_1]$$
$$\vdots$$
$$\beta_{i+1}[A_{i+1}] = \alpha_i[A_i][A_1]$$
$$\vdots$$
$$\beta_n[A_n] = \alpha_{n-1}[A_{n-1}][A_1] \qquad (2)$$

Rearrangement of this expression gives the molar distribution ratio with respect to $[A_1]$, which is

$$\frac{[A_2]}{[A_1]} = \frac{\alpha_1}{\beta_2}[A_1]$$
$$\frac{[A_3]}{[A_1]} = \frac{\alpha_1\alpha_2}{\beta_2\beta_3}[A_1]^2$$
$$\frac{[A_4]}{[A_1]} = \frac{\alpha_1\alpha_2\alpha_3}{\beta_2\beta_3\beta_4}[A_1]^3$$
$$\vdots$$
$$\frac{[A_i]}{[A_1]} = \frac{\alpha_1\alpha_2\alpha_3\ldots\alpha_{i-1}}{\beta_2\beta_3\cdots\beta_i}[A_1]^{n-1}$$
$$\vdots$$
$$\frac{[A_n]}{[A_1]} = \frac{\alpha_1\alpha_2\alpha_3\cdots\alpha_{n-1}}{\beta_2\beta_3\cdots\beta_n}[A_1]^{n-1} \qquad (3)$$

This is a formulation of the general distribution function for a shell model. The molar distribution of $[A_i]$ depends on the values of α_i, β_i and $[A_1]$. In general, α_i is also dependent on the number of monomers in the shell and the number of empty sites that can be filled, while β_i depends on the number of monomers already present in the shell.

In the Kegeles shell model [9], α_i is directly proportional to the number of empty holes, as well as the number of monomers in the system, i being the number of monomers in the shell. β_i is proportional to the number of monomers in the system. In other words, Kegeles assumed two proportionality constants, α and β, such that

$$\beta_i = i\beta$$

$$\alpha_i = \left(\frac{n-i+1}{n}\right) i\alpha = (n-i+1)i\left(\frac{\alpha}{n}\right) \tag{4}$$

The general shell model described by eq. 5 becomes

$$\frac{[A_{i+1}]}{[A_1]} = \frac{n!}{(n-i)!}\left(\frac{1}{i+1}\right)\left\{\frac{\alpha}{\beta}[A_1]/n\right\}^i \tag{5}$$

which is identical to the expression developed by Kegeles [9]. We may argue that while a shell with ith monomers has $(n-i)$ empty holes or spaces, each of the monomers can only share $(n-i)/i$ spaces. For this reason we propose that $\alpha_i = \{(n-i)/i\}i\alpha = (n-i)\alpha$, as shown in fig. 1, where i represents the monomeric binding sites, $(n-i)/i$ the number of holes to be filled by each of the monomers and α is the proportionality constant. With a proper substitution of $\alpha_i = (n-i)\alpha$ into eq. 3, the molar distribution function may be expressed as:

$$\frac{[A_i]}{[A_1]} = \frac{(n-1)(n-2)\cdots(n-i+1)}{2\cdot 3\cdots\cdots i}\frac{\alpha^{i-1}}{\beta^{i-1}}[A_1]^{i-1}$$

$$= \frac{1}{n}\binom{n}{i}\left\{\left(\frac{\alpha}{\beta}\right)[A_1]\right\}^{i-1}. \tag{6}$$

where $i = 1,2,\ldots\ldots n$. If we define $K = \alpha/\beta$, the intrinsic equilibrium constant, and define the initial concentration, $[A_0]/[A_1] = \frac{1}{n}\{K[A_1]\}^{-1}$, then the total concentration, $C_T = \sum_{i=0}^{n}[A_i] = (1 + K[A_1])^n/(nK)$. Then the relative concentration of $[A_i]$ becomes

$$\frac{[A_i]}{C_T} = \binom{n}{i}(K[A_1])^i/(1+K[A_1])^n,$$

$$i = 0,1,2,\ldots\ldots n \tag{7}$$

which is a binomical distribution function. Here $[A_0]$ * can be considered as the concentration of a shell without monomers in it, and since the term does not alter eq. 7, the relationship $\sum_{i=0}^{n} i[A_i] = \sum_{i=1}^{n} i[A_i]$ still holds true. The molar distribution function $[A_i]$ may be expressed as a binomial distribution function [23,24] of the form $(a+b)^n$.

$$[A_i]/C_T = \binom{n}{i}\{K[A_1]\}^i/\{1+K[A_1]\}^n$$

$$= \binom{n}{i}\left\{\frac{K[A_1]}{1+K[A_1]}\right\}^i\left\{\frac{1}{1+K[A_1]}\right\}^{n-i}$$

or

$$= \binom{n}{i}\left\{\frac{P}{1+P}\right\}^i\left\{\frac{1}{1+P}\right\}^{n-i} \tag{8}$$

Thus, $[A_i]/C_T = (a+b)^n = \binom{n}{i}a^i b^{n-i}$ [23] where $a = P/(1+P)$, $b = 1/(1+P)$ and the propagation coefficient, P, is equal to $K[A_1]$. **

* The notation $[A_0]$ used here differs from $[A_o]$, defined in section 1 as the concentration of free monomers. It is also possible to obtain the distribution functions C_T, $[A_i]/C_T$ and μ without considering the concentration of shells, using the expressions:

$$C_T = \sum_{i=1}^{n}[A_i] = \frac{1}{nK}\{(1+K[A_1])^n - 1\},$$

$$\frac{[A_i]}{C_T} = \binom{n}{i}(K[A_1])^i/\{(1+K[A_1])^n - 1\},$$

and

$$\mu = \frac{nP(1+P)^{n-1}}{(1+P)^n - 1},$$

which is identical to eq. 11 and to eqs. 29–13 of Tanford [25].

** The propagation coefficient $K[A_1]$, describing the kinetics of micellization of this model, is equivalent to $K[A_o]$ of the shell model described in section 1.

3. The centroid position of the micelle distribution and the emergence of critical micelle concentration

If the mean value of distribution is denoted as μ, then

$$\mu = \left(\sum_{i=0}^{n} i[A_i]/C_T \right) \tag{9}$$

The centroid position of such a distribution can readily be evaluated as follows:

$$\mu = \sum_{i=0}^{n} i\binom{n}{i}\{K[A_1]\}^i/\{1+K[A_1]\}^n$$

$$= \frac{n\{K[A_1]\}\{1+K[A_1]\}^{n-1}}{(1+K[A_1]^n)} \tag{10}$$

With a proper substitution of propagation coefficients, eq. 10 yields

$$\mu = \frac{nP}{(1+P)} \tag{11}$$

It is clear from eq. 11 that the centroid position, μ, reflects the existence and position of the micelle peak in the molar distribution of $[A_i]$.

The distribution function $[A_i]/C_T$ from eq. 8 of this shell model will decrease monotonically as a function of i, provided that the propagation coefficient, P, is very small. In this instance, it is not possible to separate an emerging micelle peak from the overall distribution of monomer, $[A_1]$. It has been pointed out by Kegeles [9] that the concentration of oligomer in the shell, $[A_i]$, reaches a maximum when $d\ln[A_i]/di = 0$, i.e.

$$\frac{d\ln[A_i]/C_T}{di} = \frac{d}{di}\ln\left[\frac{n!}{i!(n-i)!}P^i(1+P)^{-n}\right]$$

$$= \ln\left[\frac{n-i}{i}\right] + \ln P = 0 \tag{12}$$

Eq. 12 is solved for the maximum micelle number, i_m, where $i_m = nP/(1+P)$. The propagation coefficient, P, can also be evaluated from the following expression,

$$P = [i_m/(n-i_m)] \tag{13}$$

It becomes clear that no micelle peak will emerge from the molar distribution boundary under conditions such that $P \leq 2/(n-1)$ where $[A_1] \geq [A_2] \geq [A_3] \cdots$. The critical micelle peak emerges when $P > 2/(n-1)$, since

$$\binom{n}{1}\left(\frac{P}{1+P}\right)\left(\frac{1}{1+P}\right)^{n-1} < \binom{n}{2}\left(\frac{P}{1+P}\right)^2\left(\frac{1}{1+P}\right)^{n-2} \tag{14}$$

4. The sharpness of the boundary distribution

The sharpness of any boundary distribution is defined by the variance, σ^2, representing the dispersion of the molar distribution function $[A_i]/C_T$. Let $\sigma = \sqrt{\sigma^2}$ be the standard deviation. By definition, σ is a measure of the spread of $[A_i]/C_T$ about the mean value of μ. It has previously been shown that the distribution function is sharper if a large value for n is assumed and the value of the propagation coefficient lies close to unity, as predicted by the Kegeles shell model [9].

Upon closer examination, it appears that the sharpness of the distribution depends less on the degree of polymerization, n, than on the propagation coefficient. By definition the variance is expressed as:

$$\sigma^2 = \left(\sum_{i=0}^{n} i^2[A_i] \right)/C_T - \left(\sum_{i=0}^{n} i[A_i] \right)^2/C_T^2 \tag{15}$$

Eq. 15 may also be written as

$$\sigma^2 = \frac{n(n-1)\{K[A_1]^2\}\{1+K[A_1]\}^{n-2}}{\{1+K[A_1]\}^n}$$

$$+ n\left\{\frac{K[A_1]}{1+K[A_1]}\right\}\left\{1-\frac{nK[A_1]}{1+K[A_1]}\right\} \tag{16}$$

Thus, eq. 16 becomes

$$\sigma^2 = nP/(1+P)^2 \tag{17}$$

Given two values of a propagation coefficient such that $P_1 > P_2$, then $\mu_1 > \mu_2$ from eq. 11, suggesting that as the propagation coefficient increases, the centroid position tends to increase. However, the sharpness of distribution, expressed in terms of σ^2, will either increase or decrease depending on the product of P_1P_2. If $P_1P_2 < 1$, then $\sigma_1^2 > \sigma_2^2$, and the distribution becomes broader. If $P_1P_2 > 1$, then $\sigma_1^2 < \sigma_2^2$, resulting in a sharper distribution. It should be noted that a sharpening of the boundary which results from a

shift in the centroid position does not necessarily reflect a change in the variance, σ^2.

5. Numerical simulation of eq. 10

It is possible to generate the concentration of oligomer with respect to the total concentration, C_T, using eq. 8. A program for Fortran 370 has been developed, in which values for n and P are specified and the combinatorial coefficients are computed using the sum of the logarithms of the natural numbers, i.e., $n! = \exp(\sum_{i=1}^{n} \ln i)$. This computation has been determined to be accurate to five decimal places.

The binomial distribution function, $[A_i]/C_T$, is then plotted as a function of i, using a 'dotplt' routine. In this computer simulation, P varies from 0.01 to 10.0. Representative results are shown in fig. 2.

6. Results and discussion

As shown in fig. 2, the micelle distribution boundary becomes increasingly broad as the propagation coefficient increases from 0.01 to unity, when $n = 100$. At $P = 0.01$, the micelle distribution monotonically decreases from $[A_i]/C_T = 0.03$ to zero at $i = 5$, at which point the boundary disap-

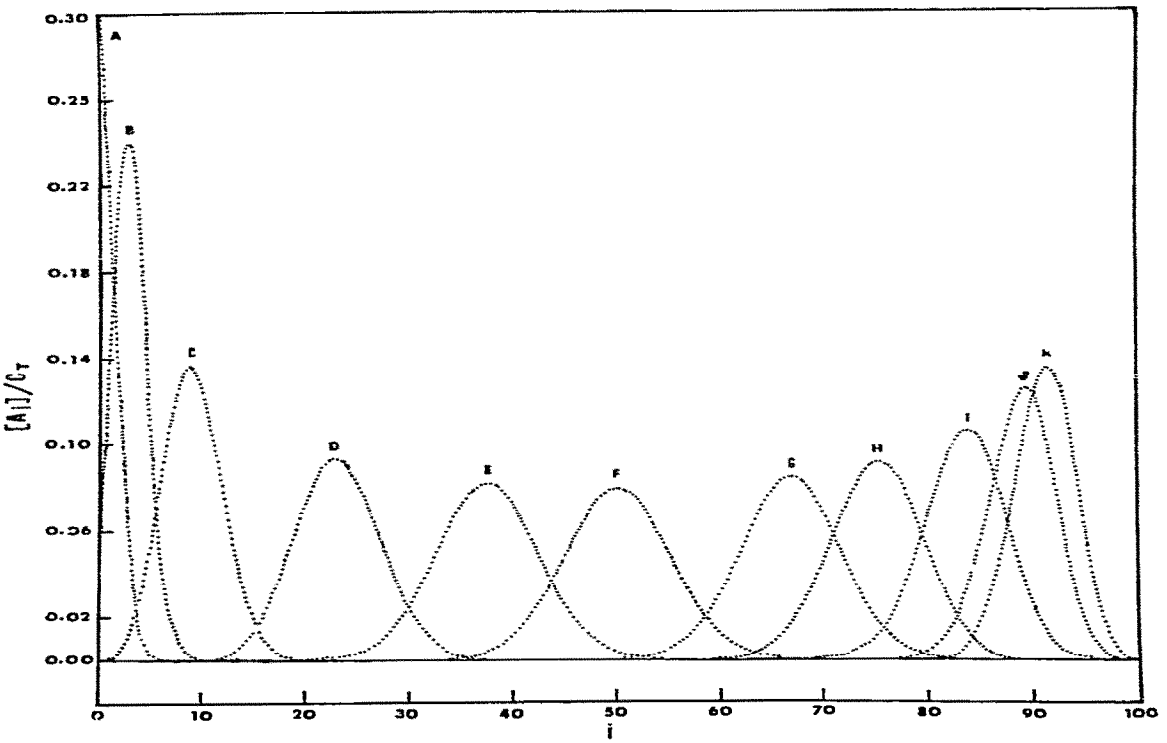

Fig. 2. Micelle molar distribution function $[A_i]/C_T$ as a function of i showing the effect of the propagation coefficient, P, on the shape of the reaction boundary, when $n = 100$. (A) $P = 0.01$, (B) $P = 0.03$, (C) $P = 0.10$, (D) $P = 0.30$, (E) $P = 0.60$, (F) $P = 1.00$, (G) $P = 2.00$, (H) $P = 3.00$, (I) $P = 5.00$, (J) $P = 8.00$, (K) $P = 10.0$

pears. At $P = 0.05$, we observe a sharp initial boundary with a centroid position at $i = 5$ and a maximum at $[A_i]/C_T = 0.223$. At $P = 0.1$, the centroid position of the boundary peak is at $i = 9$ and the maximum at $[A_i]/C_T = 0.138$. When $P = 0.6$, a broadening of the boundary is observed with a centroid position at $i = 37$ and a maximum at $[A_i]/C_T = 0.08$. At $P = 1.0$, $i = 50$ and $[A_i]/C_T = 0.06$. These theoretical boundary distribution functions are consistent with experimental results from scanning molecular sieve chromatography [21] or other transport techniques.

It also is evident that the micelle distribution boundary becomes increasingly sharp as values of the propagation coefficient are increased from 1 to 10, an observation which is consistent with earlier findings by Kegeles [9] as shown in fig. 2. It should be noted that we did not observe a marked sharpening of the distribution boundary where $P = 2.0$, as Kegeles has reported. At $P = 3.0$, $i = 75$ and $[A_i]/C_T = 0.08$. At $P = 5.0$, $i = 84$ and $[A_i]/C_T = 0.12$. When $P = 8.0$, $i = 89$ and $[A_i]/C_T = 0.13$; while at $P = 10.0$, $i = 92$ and $[A_i]/C_T = 0.139$. Our results indicate that as values for the propagation coefficient exceed 10, the micelle distribution boundary becomes increasingly hypersharp.

7. Skewing and bimodality in micellar reaction boundary

Skewing and bimodality in the micellar system can arise from the heterogeneity of the surfactant micelle as well as structural intermediates present in the system. In order to account for these observed boundary shapes, we assume the following boundary conditions: (i) If the shell size increases from j to $j+1$, there is a structural transition, where the rate of dissociation of monomers β_i changes from β_i to $i\beta^*$. (ii) At this point, the intrinsic equilibrium constant will change, from K to K^*. Hence, if $\beta^* < \beta$, then in the region from j to n, the tendency to grow cooperatively into tightly bound micelles increases. Thus, the K region may represent a nucleation process, while the tendency in the K^* region is to form tightly bound micelles. Thus, β and β^* will influence the structural transition which occurs. (iii) If $\beta = \beta^*$, the system simply obeys a binomial distribution function as described by eq. 7, which is always unimodal. (iv) Based on the assumption given in (i), and the general expression for a shell model given in eq. 3, the following distribution functions may be generated:

$$\frac{[A_i]}{[A_1]} = \frac{1}{n}\binom{n}{i}\{K[A_1]\}^{i-1},\ i = 1,2,\ldots,j \text{ and}$$

$$\frac{[A_i]}{[A_1]} = \frac{1}{n}\binom{n}{i}\left\{\frac{K}{K^*}\right\}^{j-1}\{K^*[A_1]\}^{i-1},$$

$$i = j+1, j+2, \ldots, n \qquad (18)$$

It is apparent that eq. 5 describes a symmetrical, unimodal boundary, in contrast to eq. 18, in which two distribution functions are combined to describe a reaction boundary which exhibits skewing or bimodality. The following cases can be derived from eq. 18:

(a) Unimodal reaction boundary, skewed in the trailing edge. In this case $nK \geq j(1 + K)$ and $nK^* > j(1 + K^*)$.

(b) Unimodal reaction boundary, skewed in the leading edge. Here, $nK < j(1 + K)$ and $nK^* > j(1 + K^*)$.

(c) Bimodal boundary, where $nK < j(1 + K)$ and $nK^* > j(1 + K^*)$. The centroid positions of such a distribution occur at $\mu_1 = nK/(1 + K)$ and $\mu_2 = nK^*/(1 + K^*)$, with a minimum at j, if $(j + 1) \leq (n - j)K^*[A_1]$ and at $j + 1$ if $(j + 1) \geq (n - j)K^*[A_1]$.

(d) No skewing of the bimodal boundary will be observed when the centroid positions μ_1 and μ_2 defined in (c) are far apart.

The variation in boundary shape for micellar distribution as a function of j, β and β^* is shown in fig. 3. Skewing of the boundary, s, and the kurtosis, λ, which measures the closeness to a normal boundary distribution, may be determined using the following expression:

$$s = \left\{\sum_{i=1}^{n}(i-\mu)^3\frac{[A_i]}{C_T}\right\}/\sigma^3 \qquad (19)$$

$$\lambda = \left\{\left[\sum_{i=1}^{n}(i-\mu)^4\frac{[A_i]}{C_T}\right]/\sigma^4\right\} - 3$$

where $C_T = \sum_{i=1}^{n}[A_i]$, $\mu = \sum_{i=1}^{n} i[A_i]/C_T$ and $\sigma^2 = \sum_{i=1}^{n}(i - \mu^2)[A_i]/C_T$. The boundary parameters s

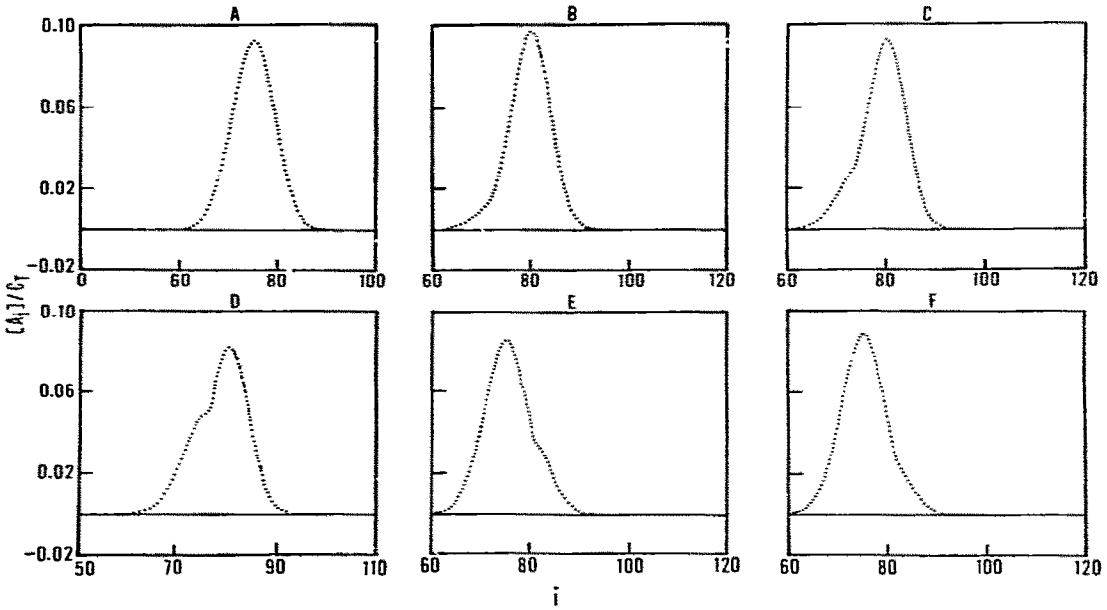

Fig. 3. The boundary shapes for micellar distribution $[A_i]/C_T$ as a function of i showing the effect of j, β and β^*, given $\alpha = 1.0$ and $[A_1] = 1.0$. The variations in boundary shape for micellar distribution as a function of j, β and β^* are shown in this figure. Skewing of the boundary and the kurtosis, λ, which measures the closeness to a normal boundary distribution, may be determined using the following expression:

$$C_T = \sum_{i=1}^{n} [A_i],\ \mu = \sum_{i=1}^{n} i[A_i]/C_T \text{ and } \sigma^2 = \sum_{i=1}^{n} (i-\mu^2)[A_i]/C_T$$

The boundary parameters s and λ are used to define the relationship between the experimentally determined distribution and an ideal Gaussian distribution. The boundary shapes for micellar distribution $[A_i]/C_T$ as a function of i showing the effect of j, β and β^*, given $\alpha = 1.0$ and $[A_1] = 1.0$, are as follows: (A) $\beta = \beta^* = 0.333$, $s = 0.115$, $\lambda = -0.0066$, $i = 75$ at μ. (B) $j = 72$, $\beta = 0.333$, $\beta^* = 0.250$, $s = -0.437$, $\lambda = 0.563$, $i = 80$ at μ. (C) $j = 74$, $\beta = 0.333$, $\beta^* = 0.250$, $s = -0.510$, $\lambda = 0.337$, $i = 80$ at μ. (D) $j = 76$, $\beta = 0.333$, $\beta^* = 0.250$, $s = -0.373$, $\lambda = 0.218$, $i = 75$, 80 at μ. (E) $j = 81$, $\beta = 0.333$, $\beta^* = 0.250$, $s = 0.146$, $\lambda = 0.0147$, $i = 75$ at μ. (F) $j = 82$, $\beta = 0.333$, $\beta^* = 0.250$, $s = 0.122$, $\lambda = 0.123$, $i = 75$ at μ.

and λ are used to define the relationship between the experimentally determined distribution and an ideal Gaussian distribution. Thus, as shown in fig. 3, if any structural transition occurs during the micellization process, it will be reflected by a skewing or bimodality of the reaction boundary (fig. 3). Thus, the K region showing in fig. 3 represents a nucleation process where the intrinsic micellization constant is inversely proportional to the critical micelle concentration (CMC). The propagation coefficient for a micellization via structural transition, the K^* region, is $K^*[A_1]$. It must be assumed, for this transition to occur, that $\beta \neq \beta^*$ and $K^* \neq 1/\text{CMC}$.

The apparent effect of the propagation coefficient on the micelle distribution boundary appears to be two-fold. First, the sharpening of the boundary as the value of the propagation coefficient increases above 3.0 suggests the formation of micelles of a uniform size and distribution. Second, the propagation coefficient is an indicator of the rate at which monomer is associated into the

ith oligomer in the shell and also the rate at which monomer is dissociated from the shell. When the value of the propagation coefficient is high, the n holes of each shell are cooperatively filled by the existing monomeric species, resulting in a uniform distribution of micelles.

It is possible to derive a series of kinetic rate expressions for a shell model such as is shown in fig. 1, based on the modal distribution function for the system at equilibrium and consistent with this distribution function. In terms of the rate of disappearance of the monomeric species in solution, $[A_1]$, this expression would be

$$-\frac{d[A_1]}{dt} = \sum_{i=0}^{n-1} \alpha(n-i)[A_i][A_1] - \beta \sum_{i=1}^{n} i[A_i] \qquad (20)$$

where the equilibrium constant $K = (\alpha/\beta)$ and letting the apparent equilibrium constant, $K' = i[A_i]/[n-(i-1)][A_{i-1}][A_1]$. Thus, eq. 20 becomes

$$-\frac{d[A_1]}{dt} = \sum_{i=1}^{n} \left\{ \alpha \frac{1}{K'} i[A_i] - \beta i[A_1] \right\}$$

$$= \alpha \left\{ \frac{1}{K'} - \frac{1}{K} \right\} \sum_{i=1}^{n} i[A_i] \qquad (21)$$

Although the kinetics of this reaction remain to be examined, it is apparent that the rate at which the monomeric species is associated into the shell and the corresponding rate at which monomer is dissociated from the shell back into solution at equilibrium conditions are crucial to any consideration of formation and size distribution of micelles in interacting systems.

Preliminary data in our laboratory from scanning molecular sieve chromatographic studies of sodium deoxycholate in 0.1 mM pinacyanol chloride, 0.2 M $NaHCO_3$ buffer, pH 8.5, indicate that the micellization process involves an initial formation of a small, metastable complex from surfactant monomer rather than the shell formation which might be theoretically predicted, prior to the formation of micelles. We are currently investigating the kinetics of micellization and the nature of any structural intermediate formations in the system [21].

It is of interest to note that the maxima of the micellar boundary peaks, i_m, as a function of the propagation coefficient, shown in fig. 2, decrease monotonically to a minimum plateau, then increase monotonically over the range where $P = 0-10$ or more. This suggests that it might be useful in future studies to evaluate intrinsic equilibrium constants of micellization, once the concentration of monomer or weight fraction monomer have been evaluated by scanning molecular sieve chromatography or sedimentation equilibrium measurements. A plot of the propagation coefficient and n in eq. 11 vs. the ith oligomer as a function of temperature, pH, and ionic strength, should also provide additional information on the thermodynamics of micellization.

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References

1 P. Mukerjee, J. Phys. Chem. 76 (1972) 565.
2 T. Nakagawa, Colloid Polym. Sci. 252 (1974) 56.
3 J. Lang, C. Tondre, R. Zana, R. Bauer, H. Hoffmann and W. Ulbright, J. Phys. Chem. 79 (1975) 276.
4 C. Tanford, J. Phys. Chem. 78 (1974) 2469.
5 F.J.C. Rossotti and H. Rossotti, J. Phys. Chem. 65 (1961) 1376.
6 C.A. Hoeve and G.C. Benson, J. Phys. Chem. 61 (1957) 1149.
7 E.A.G. Aniansson and S.N. Wall, J. Phys. Chem. 78 (1974) 1024.
8 I. Reich, J. Phys. Chem. 60 (1956) 257.
9 G. Kegeles, J. Phys. Chem. 83 (1979) 1728.
10 P.J. Mijnlieff and R. Ditmarsch, Nature 208 (1965) 899.
11 G.C. Kresheck, E. Hamori, G. Davenport and H.A. Scheraga, J. Am. Chem. Soc. 88, (1966) 246.
12 N. Muller, J. Phys. Chem. 76 (1972) 3017.
13 P.J. Sams, E. Wyn-Jones and J. Rassing, Chem. Phys. Lett. 13 (1972) 233.
14 G. Schwarz, J. Mol. Biol. 11 (1965) 64.
15 E.A.G. Aniansson and S.N. Wall, J. Phys. Chem. 79 (1975) 857.

16 E.A.G. Aniansson, S.N. Wall, M. Almgren, H. Hoffmann, I. Kielmann, W. Ulbright, R. Zana, J. Lang and C. Tondre, J. Phys. Chem. 80 (1976) 905.
17 G. Kegeles, Arch Biochem. Biophys. 200 (1980) 279.
18 G. Kegeles, J. Colloid Interface Sci. 73, (1980) 274.
19 G. Kegeles, ACS North Reg. Meeting, June 30. ACS Abstr. (1980) 106.
20 K.H. Meyer and A. van der Wyk, Helv. Chim. Acta 20 (1937) 1321.
21 J.Q. Oeswein and P.W. Chun, unpublished results (1981).
22 G. Kegeles, Arch. Biochem. Biophys. 144 (1971) 763.
23 W. Mendenhall, Introduction to probability and statistics, 4th edn. (Duxbury Press, North Scituate, MA, 1975).
24 H. Margenau and G.S. Murphy, The mathematics of physics and chemistry (D. Van Nostrand Co. Inc., 1943).
25 C. Tanford, Physical chemistry of macromolecules (John Wiley and Sons, New York, 1961).