

is entirely dependent on the alignment of atoms along the projection axis.

Silica Gel. An Approach to a Random Network Model

Figure 3 shows a HREM image of a silica gel¹² specimen. The corresponding optical transform (inset Figure 3) indicates that the Scherzer defocus condition is well-satisfied, with spacings in the range 2.4–6.3 Å appearing in the image. In this case there is no evidence for departures from randomness, either in the image or its optical transform, and it might be argued that this is consistent with a random network model for silica (see, for example, ref 13). However, our considerations in ref 4 imply that no structural information is available from such an image, since the film thickness is unknown. If it could be established that the film is <20-Å thick, then the most that could be deduced is that, since the image was recorded at the Scherzer defocus condition, and since dynamical scattering effects are small (cf. ref 4), the brighter areas

of intensity in Figure 3 may adequately locate void space in a particular projection of this specimen. One cannot rule out, a priori, the possibility that, for a thinner specimen, correlations of the kind indicated in Figure 1 may emerge. However, we are not aware¹⁴ of any reliable technique which would allow the thickness of such specimens to be determined, in situ, in the range 0–20 Å. This now emerges as one of the most important experimental problems in the application of HREM imaging to objects which, like silica gel, appear to approach very closely the random network model for amorphous materials.

Acknowledgment. This work was financially supported by the Science Research Council and the University of Melbourne. We thank Dr. S. Vasudevan for preparing the UO_2^{2+} -exchanged specimen, and Dr. G. R. Millward for help with the optical diffractometry.

(14) It is important to recognize that techniques applicable for thickness measurements when the samples are thicker than ca. 1000 Å are inapplicable under these circumstances. We cannot, for example, place much credence on measurement of bright-field image intensities (relative to the intensity in a hole) obtained by using minute objective apertures, or on measurement of intensity in energy loss spectra relative to zero loss intensity, or on measurement of rms contrast, though the second of these may, perhaps, prove to be of some value.

(12) The gel used was a specimen of a commercial RD-type silica gel manufactured by the Davison Chemical Division of W. R. Grace & Co.

(13) R. J. Bell and P. Dean, *Phil. Mag.*, 25, 1381 (1942).

Critical Micelle Concentration and the Transition Point for Micellar Size Distribution

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The equation assumed by Ben-Naim and Stillinger for the free energy of micellization is used to demonstrate that, contrary to their assertion, the critical concentration C_{crit} corresponding to a transition in the shape of the micellar size distribution has a value close to the conventional cmc. The ratio $\text{cmc}/C_{\text{crit}}$ is shown to decrease sharply from the large value of 20 obtained by Ben-Naim and Stillinger, to a value of 1.55, if one of the parameters (σ) is assigned a physically more plausible value. This value accounts better for the cooperative self-association of the surfactant molecules.

I. Introduction

In an earlier paper discussing the size distribution of micelles,¹ we defined a critical concentration C_{crit} as the total surfactant concentration at which the micellar size distribution displays a horizontal inflection point. Below the C_{crit} , this function decreases monotonically with size (Figure 1) indicating a small amount of aggregation. Above C_{crit} , it exhibits both a minimum and a maximum, and the concentration of the aggregates becomes significant. Far above C_{crit} , the size distribution goes through a minimum followed by a monotonic increase implying that a phase separation occurs. We anticipated that C_{crit} can be related to the conventional cmc because, at both of these concentrations, the number of micelles is small and only above them does it begin to increase appreciably. The connection between the two was tested by a number of illustrative calculations¹⁻³ which showed that the transition in the

shape of the size distribution is closely accompanied by abrupt changes in properties like osmotic pressure, light scattering, dye solubilization, etc. The results obtained for a homologous series of alkylhexoxyethylene glycol monoethers by using Tanford's expression for the free energy of micellization,^{4,5} and those obtained for homologous series of alkyl glucosides and sodium alkyl sulfates by using a statistical thermodynamic model,² have shown³ good agreement among the calculated C_{crit} , the calculated cmc, and the experimental cmc values.

However, in a recent paper, Ben-Naim and Stillinger,⁶ using an alternative equation for the free energy of micellization, arrived at the conclusion that the conventional cmc is about 20 times larger than C_{crit} over the range of parameter values they considered. Although they observe a parallelism between the conventional cmc and the C_{crit} ,

(3) E. Ruckenstein and R. Nagarajan, *J. Colloid Interface Sci.*, 57, 388 (1976).

(4) C. Tanford, "The Hydrophobic Effect", Wiley, New York, 1973.

(5) C. Tanford, *J. Phys. Chem.*, 78, 2469 (1971).

(6) A. Ben-Naim and F. H. Stillinger, *J. Phys. Chem.*, 84, 2872 (1980).

(1) E. Ruckenstein and R. Nagarajan, *J. Phys. Chem.*, 79, 2622 (1975).
(2) R. Nagarajan and E. Ruckenstein, *J. Colloid Interface Sci.*, 60, 221 (1977).

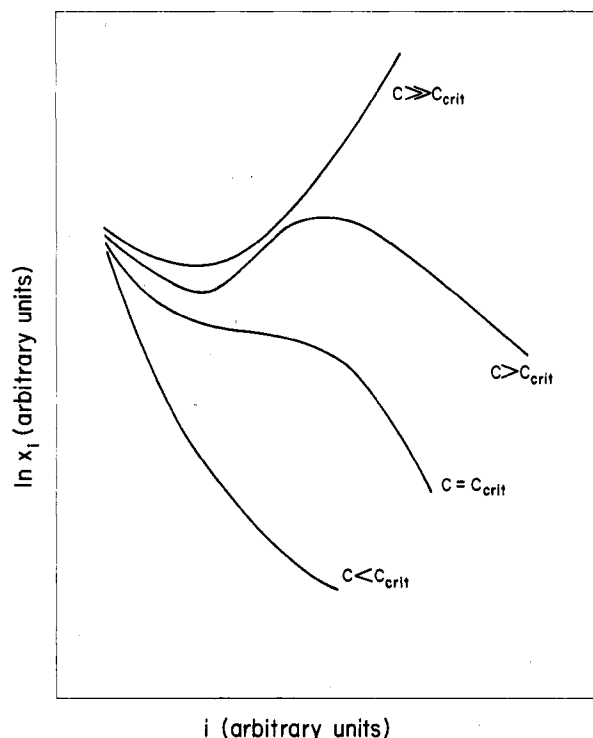


Figure 1. Qualitative micellar size distribution. The curves represent size distributions when the total surfactant concentration is less than C_{crit} , equal to C_{crit} , larger than C_{crit} , and far above C_{crit} .

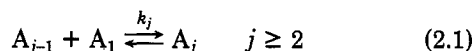
they nevertheless conclude that "if the conventional cmc is to be related to any specific attribute of the aggregate size distribution, then it must be more subtle than the mere occurrence of a horizontal inflection point".

It is the objective of this note to show that, contrary to the conclusions of ref 6, a small change in the value of one of the parameters, σ , which appears in their expression for the free energy, can significantly reduce the ratio between cmc and C_{crit} to values near unity. For example, a change in σ from 3 to 4.5 reduces the ratio cmc/ C_{crit} from about 20 to 2.5. A further increase of σ to 5.0 makes the above ratio as small as 1.55. We explain below that a value of 5 for σ is physically more plausible than the value of 3 used in ref 6, because it accounts better for the initial cooperative self-association of the surfactant molecules. Therefore, C_{crit} has values close to the conventional cmc, even for the free-energy expression assumed in ref 6, if a physically more plausible value is ascribed to σ .

In the following section, the micellization model and the free-energy expression used in ref 6 are described. In section III, the cmc and C_{crit} are calculated numerically for various values of σ . Because the numerical calculations for a complete parametric study would be too lengthy, approximate, analytical relations for the two concentrations are developed in section IV. Computations based on these relations show that, of all the parameters, σ is the only one which drastically affects the ratio between cmc and C_{crit} . The last section emphasizes again that C_{crit} has a value close to the conventional cmc as long as the expression used for the free energy is a physically acceptable one.

II. Micellization Model and Ben-Naim-Stillinger Free-Energy Expression

The micellization process can be described by the stepwise association equilibrium



where A refers to the amphiphilic aggregates, subscript j is the aggregation number, and k_j is the equilibrium constant for the stepwise association. The overall equilibrium constant K_i for i singly dispersed amphiphiles aggregating to form a micelle of size i is related to the stepwise association constants k_j by

$$K_i = \prod_{j=2}^i k_j = \prod_{j=2}^i (\rho_j / \rho_{j-1} \rho_1) \quad (2.2)$$

where ρ_j is the concentration of aggregates of size j .

A uniform stepwise association constant k_j cannot produce abrupt changes in the physical properties such as those accompanying micellization. This requires a cooperative self-association, i.e., k_j should increase with j in the initial stages.⁷

Ben-Naim and Stillinger⁶ have taken

$$K_i = k^{i-1} F(i) \quad (2.3)$$

where k is a constant

$$F(i) = 1 \quad i = 1$$

$$F(i) = 1 + \exp \left\{ \Delta - \left(\frac{i - n^*}{\sigma} \right)^2 \right\} \quad 1 < i \leq n_{\max} \quad (2.4)$$

$$F(i) = 0 \quad i > n_{\max}$$

and Δ , σ , n^* , and n_{\max} are parameters. The factor k^{i-1} corresponds to a uniform association with all the stepwise association constants equal. The factor $F(i)$ is a Gaussian function which introduces nonuniformity in the overall equilibrium constant K_i to account for the cooperative association of amphiphiles. The stepwise association constant k_j can be calculated from

$$k_j = K_j / K_{j-1} = k F(j) / F(j-1) \quad (2.5)$$

and the micellar size distribution is given by

$$\rho_i = K_i \rho_1^i \quad (2.6)$$

Introducing the quantities

$$x_i = k \rho_i \quad y = \sum_{i=1}^{n_{\max}} i k \rho_i \quad f = k \pi / RT \quad (2.7)$$

where π is the osmotic pressure, x_i is the reduced concentration of aggregates of size i , y is the reduced total concentration of surfactant, f is the reduced osmotic pressure, R is the universal gas constant, and T is the temperature in K, one can write

$$x_i = F(i) x_1^i \quad (2.8)$$

$$y = \sum_{i=1}^{n_{\max}} i F(i) x_1^i \quad (2.9)$$

$$f = \sum_{i=1}^{n_{\max}} F(i) x_1^i \quad (2.10)$$

In ref 6, $y(\text{cmc})$ is evaluated from a plot of f vs. y as the point at which an abrupt change in f occurs. $y(\text{crit})$ (denoted in ref 6 as $y(\text{RN})$) is computed as the value of y at which $\ln x_i$ vs. i shows a horizontal inflection point.

While the expression 2.3 appears to be reasonable from a qualitative point of view, our computations seem to show that it cannot satisfactorily reproduce the results of previous expressions, such as that of Tanford, which have been obtained on the basis of somewhat more detailed physical considerations.

(7) P. Mukerjee in "Micellization, Solubilization and Microemulsions", Vol. 1, K. L. Mittal, Ed., Plenum, New York, 1977, p 171.

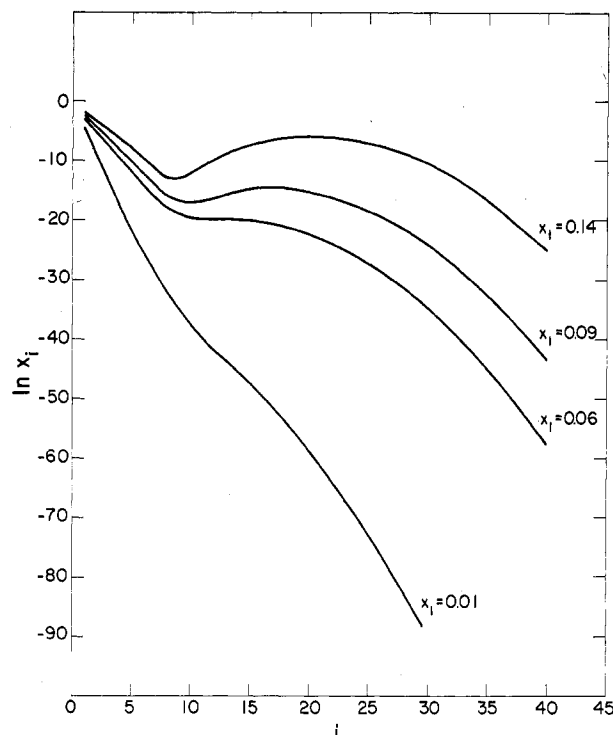


Figure 2. Aggregate size distributions for $\Delta = 50$, $\sigma = 4.5$, $n_{\max} = 50$, and $n^* = 40$. The curves are labeled for various values of the reduced single amphiphile concentration x_1 .

III. Estimation of $y(\text{cmc})/y(\text{crit})$ for Various Values of σ

Numerical computations of the reduced variables x_i , y , and f have been carried out by using the Ben-Naim-Stillinger expression for the free energy. In Figure 2 the size distribution is plotted for $\sigma = 4.5$, $\Delta = 50$, $n^* = 40$, and $n_{\max} = 50$. In this figure, all the parameters except σ have the values used in ref 6. The reduced osmotic pressure f is plotted in Figure 3 against the reduced total concentration y for the above values of the parameters and also for $\Delta = 60$ and $\Delta = 70$. Table I summarizes numerical results extracted from Figures 2 and 3. These results show that the difference between the cmc and C_{crit} is quite small when $\sigma = 4.5$ and is quite insensitive to changes in Δ . Additional computations have shown that if σ is increased further to a value of 5, the ratio $\text{cmc}/C_{\text{crit}}$ decreases to 1.55. We explain later that a value of 5 for σ is more plausible from a physical point of view than the value 3 taken in ref 6.

In the next section, using approximate analytical relations for the cmc and C_{crit} , we present a parametric study which shows that the ratio $\text{cmc}/C_{\text{crit}}$ is very sensitive to σ and less sensitive to all the other parameters.

IV. Relations between C_{crit} , cmc, and the Free-Energy Function

The transition in shape of the aggregate size distribution occurs when the size distribution displays a horizontal inflexion point, i.e., when

$$d \ln x_i / di = d^2(\ln x_i) / di^2 = 0 \quad \text{at } i = i_{\text{crit}} \quad (4.1)$$

Combining eq 2.8 with the above expressions, we obtain

$$d^2[\ln F(i)] / di^2 = 0 \quad \text{at } i = i_{\text{crit}} \quad (4.2)$$

$$\ln x_1(\text{crit}) = -d[\ln F(i)] / di \quad \text{at } i = i_{\text{crit}} \quad (4.3)$$

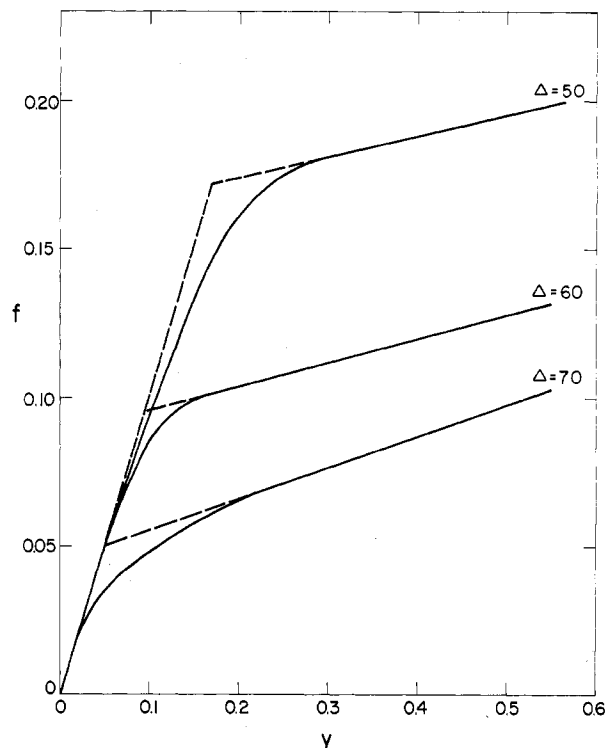


Figure 3. Reduced osmotic pressure f vs. reduced total amphiphile concentration y . The curves are labeled for various values of the parameter Δ . The values of the other parameters are $\sigma = 4.5$, $n^* = 40$, and $n_{\max} = 50$.

TABLE I: $y(\text{cmc})$ and $y(\text{crit})$ for Various Values of σ Obtained via Numerical Computations

	$\sigma = 3.0$	$\sigma = 4.5$	$\sigma = 5.0$
$\Delta = 50, n^* = 40, n_{\max} = 50$			
$y(\text{crit})$	0.013	0.064	0.078
$y(\text{cmc})$	0.285	0.166	0.121
$y(\text{cmc})/y(\text{crit})$	21.9	2.59	1.55
$\Delta = 60, n^* = 40, n_{\max} = 50$			
$y(\text{crit})$	0.008	0.042	
$y(\text{cmc})$	0.180	0.095	
$y(\text{cmc})/y(\text{crit})$	22.5	2.26	
$\Delta = 70, n^* = 40, n_{\max} = 50$			
$y(\text{crit})$	0.005	0.019	
$y(\text{cmc})$	0.115	0.050	
$y(\text{cmc})/y(\text{crit})$	23.0	2.63	

When the Ben-Naim-Stillinger expression for the free energy is used, the above equations lead to

$$\exp \left\{ \Delta - \left(\frac{i_{\text{crit}} - n^*}{\sigma} \right)^2 \right\} = \frac{2}{\sigma^2} (i_{\text{crit}} - n^*)^2 - 1 \quad (4.4)$$

$$\ln x_1(\text{crit}) = \left[\frac{2}{\sigma^2} (i_{\text{crit}} - n^*)^2 - 1 \right] / (i_{\text{crit}} - n^*) \quad (4.5)$$

It should be noted that the calculated $x_1(\text{crit})$ is almost equal to $y(\text{crit})$ (for the latter quantity, no simple analytical relation could be derived).

The conventional cmc can be approximately calculated by using the equation⁷⁻⁹

$$\ln y(\text{cmc}) = -\ln F(i) / i \quad \text{at } i = i_M \quad (4.6)$$

where i_M is the aggregation number corresponding to the

(8) P. Mukerjee, *J. Pharm. Sci.*, **63**, 972 (1974).

(9) P. Mukerjee, *J. Phys. Chem.*, **73**, 2054 (1969).

TABLE II: Comparison of $y(\text{cmc})/y(\text{crit})$ Estimated from Analytical Expressions with Those Obtained from Numerical Computations^a

Δ	50	60	70	80
From Analytical Equations				
i_{crit}	19.7	17.4	15.5	13.7
i_{M}	33.9	32.6	31.1	29.7
$y(\text{crit})$	0.0133	0.0084	0.0055	0.0037
$y(\text{cmc})$	0.259	0.194	0.139	0.102
$y(\text{cmc})/y(\text{crit})$	19.5	23.1	25.3	27.6
From Numerical Computations (Ref 6)				
i_{crit}	19	17	15	13
i_{M}	32	30	28	26
$y(\text{crit})$	0.013	0.008	0.005	0.003
$y(\text{cmc})$	0.285	0.180	0.115	0.075
$y(\text{cmc})/y(\text{crit})$	21.9	22.5	23.0	25.0

^a In both analytical and numerical computations, $\sigma = 3$, $n^* = 40$, and $n_{\text{max}} = 50$.

maximum in the size distribution curve. (Equations 4.6 and 4.7 involve setting $(i-1)/i \simeq 1$. Our numerical calculations have shown that this approximation is permissible.)

An upper bound on i_{M} is provided⁷ by the value of i corresponding to an extremum of the free energy per amphiphile:

$$\frac{d}{di} \left[\frac{1}{i} \ln F(i) \right] = 0 \quad \text{at } i = i_{\text{M}} \quad (4.7)$$

Near the cmc, the aggregation number corresponding to the maximum in the size distribution curve is lower than the value given by the above equation, but as the total surfactant concentration increases it approaches that value. Using the Ben-Naim-Stillinger expression for the free energy, we obtain

$$i_{\text{M}} = (n^* - \sigma^2 \Delta)^{1/2} \quad (4.8)$$

$$\ln y(\text{cmc}) = \frac{2}{\sigma^2} (i_{\text{M}} - n^*) \quad (4.9)$$

In deriving the above expressions, we assumed that

$$\exp \left\{ \Delta - \left(\frac{i_{\text{M}} - n^*}{\sigma} \right)^2 \right\} \gg 1 \quad (4.10)$$

an inequality which is valid for the entire range of parameters considered in ref 6 and in this paper.

The results obtained from these relations are compared in Table II with those obtained from the numerical computations carried out by Ben-Naim and Stillinger⁶ in order to verify the validity of the above approximate analytical expressions. The agreement between the analytical and the numerical results is very good. The somewhat higher values of the analytical $y(\text{cmc})$ compared to the numerical ones are due to the slight overestimation of the value of i_{M} . Therefore, the actual difference between $y(\text{cmc})$ and $y(\text{crit})$ is even smaller than that estimated by use of the above analytical relations.

The analytical expressions used to examine the effect of the model parameters n^* , n_{max} , Δ , and σ on $y(\text{crit})$ and $y(\text{cmc})$ are given in Table III. The results of the computations can be summarized as follows: $y(\text{crit})$ is insensitive to changes in n^* , whereas an increase in n^* from 40 to 50 (keeping $\Delta = 50$, $\sigma = 3$) results in a small increase in $y(\text{cmc})$ (by a factor of 1.36). A change in n_{max} has no influence on $y(\text{cmc})$ or $y(\text{crit})$ as long as n_{max} is chosen such that it accounts for all the aggregates which make a meaningful contribution to the total concentration. Even though an increase in the value of Δ causes a decrease in

TABLE III: Dependence of $y(\text{cmc})$ and $y(\text{crit})$ on the Parameters Appearing in the Free-Energy Expression (Eq 2.4)

parameter	$d[\ln y(\text{crit})]/d[\text{parameter}]$	$d[\ln y(\text{cmc})]/d[\text{parameter}]$
n^*	0	$\frac{2}{\sigma^2} \left[\frac{n^*}{i_{\text{M}}} - 1 \right]$
n_{max}	0	0
Δ	$\frac{2}{\sigma^2} [i_{\text{crit}} - n^*]^2 - 1$	$\frac{1}{i_{\text{M}}}$
σ	$\frac{2}{\sigma^2} (i_{\text{crit}} - n^*)^3$	$-\frac{4i_{\text{M}}(i_{\text{M}} - n^*) + 2\sigma^2 \Delta}{\sigma^3 i_{\text{M}}}$

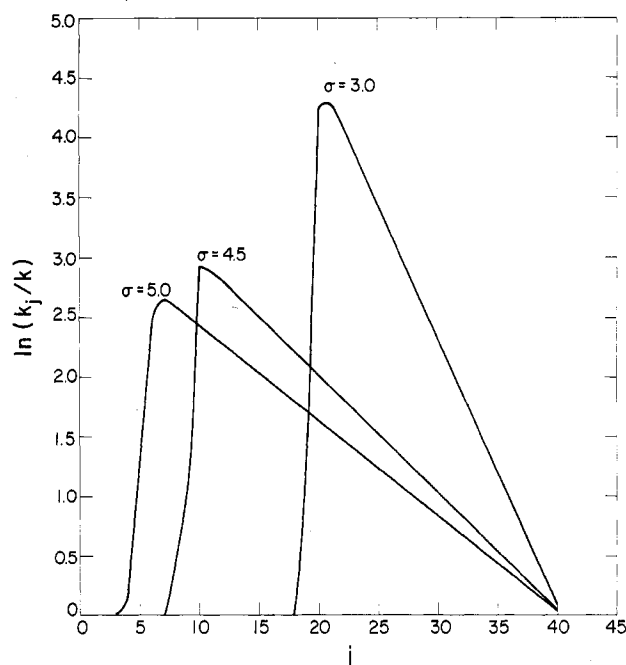


Figure 4. $\ln(k_j/k)$ vs. aggregation number j for various values of σ . k_j is the stepwise association constant and k is the uniform association constant appearing in eq 2.3. The values of the other parameters are $\Delta = 50$, $n^* = 40$, and $n_{\text{max}} = 50$.

both $y(\text{crit})$ and $y(\text{cmc})$ (see Table II), their ratio does not change too much. An increase in the value of σ produces a significant increase in $y(\text{crit})$ while $y(\text{cmc})$ slightly decreases; consequently, the ratio $y(\text{cmc})/y(\text{crit})$ decreases sharply. For example, keeping $\Delta = 50$, $n^* = 40$, a change in σ from 3 to 4.5 increases $y(\text{crit})$ from 0.0133 to 0.064 while decreasing $y(\text{cmc})$ from 0.259 to 0.166. Therefore, the ratio $y(\text{cmc})/y(\text{crit})$ is reduced from the value of 19.5 to a comparatively small value of 2.6. If σ is increased further to $\sigma = 5$, the ratio $y(\text{cmc})/y(\text{crit})$ decreases further to 1.55. The parametric study thus reveals that σ is the only parameter which has a significant influence on the value of the ratio $y(\text{cmc})/y(\text{crit})$.

V. Discussions and Conclusion

We have examined the sensitivity of the ratio $\text{cmc}/C_{\text{crit}}$ to the parameters of the Ben-Naim and Stillinger free-energy expression in order to show that this ratio is largely insensitive to variations in the parameters Δ , n^* , and n_{max} ,

while decreasing sharply when the parameter σ is increased. The main conclusion is that the concentration C_{crit} has values near those of the cmc if a sufficiently large value for σ , namely, $\sigma = 5$, is chosen.

Let us now emphasize that the value $\sigma = 5$ is more plausible from a physical point of view than the lower value $\sigma = 3$ taken in ref 6. Figure 4 shows the size dependence of the stepwise association constant. For the values of the parameters used in ref 6, namely, $\Delta = 50$, $n^* = 40$, $n_{\text{max}} = 50$, and $\sigma = 3$, the stepwise association constant remains constant up to $i = 17$. This implies that no cooperative association occurs until the aggregates contain 17 molecules. There is, however, good physical reason to expect this cooperation to set in from the beginning. Indeed, in the initial stages of micellar growth, the increment in the attractive interactions for each newly included amphiphile increases with the aggregation number and exceeds the increment in the repulsive head group interactions. This happens because in these initial stages an increase in the aggregation number gives rise to a larger number of interactions among the atoms of the hydrocarbon chains and, in particular, to an increasingly compact micellar core. The latter leads to greater and greater van der Waals attrac-

tions between the hydrocarbon tails as well as to a greater shielding from water. Consequently, the free energy per molecule associated with the hydrophobic bonding becomes more negative and the stepwise association equilibrium constant can be expected to increase with the aggregation number, i.e., an initial cooperativity of self-association^{7,8} is expected to occur. The choice of $\sigma = 3$, in ref 6, imposes an artificial constraint on the nature of the association process for $i < 17$. When the value of σ is increased to 4.5 or 5.0, the region of noncooperative uniform association is limited to $i < 7$ and $i \leq 3$, respectively.

As mentioned earlier, the expression taken by Ben-Naim and Stillinger even though meaningful qualitatively is not able to yield the results of expressions such as that of Tanford, which have a somewhat better physical foundation. For this reason detailed computations have been carried out by using all the expressions available in the literature for the free energy of micellization.¹⁰ These computations have shown that the ratio $\text{cmc}/C_{\text{crit}}$ seldom exceeds a value of 1.5.

(10) R. Nagarajan and E. Ruckenstein, submitted for publication.

Generation, Diffusivity, and Quenching of Singlet Oxygen in Polymer Matrixes Investigated via Chemiluminescence Methods

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Singlet oxygen ($^1\text{O}_2$) is generated in films of polystyrene (PS) and poly(methyl methacrylate) (PMMA) by decomposition of a naphthalene 1,4-endoperoxide. Inclusion of bis(2,2'-biphenylene)ethylene (A) in such polymer films results in chemiluminescence that is identical with fluorenone fluorescence. This chemiluminescence is decreased by addition of singlet oxygen quenchers (under conditions that photoexcited fluorenone fluorescence would not be quenched). An investigation of the chemiluminescence intensity as a function of the concentration of A allows determination of the diffusivity of $^1\text{O}_2$ in the polymer films, and the quenching of chemiluminescence intensity as a function of added quencher allows determination of the rate constants for quenching of $^1\text{O}_2$ in the polymer films.

Introduction

Singlet oxygen $^1\text{O}_2$ has been suggested as an important contributor to thermal and photochemical degradation of polymers.¹ In spite of a vast and ever-expanding literature, neither the method of generation of $^1\text{O}_2$ nor the details of the chemical pathways leading to polymer disintegration are known with certainty. We report a simple, nonphotochemical method for generation and quantitative investigation of the physical and chemical properties of $^1\text{O}_2$ in polymer films. Conceptually, our method (Scheme I) employs the following: (1) an endoperoxide (EO_2) which may be solubilized in polymer films and which is capable of generating $^1\text{O}_2$ thermally at convenient temperatures; (2) a singlet oxygen acceptor, A, which forms an adduct AO_2 upon reaction with $^1\text{O}_2$; (3) selection of adducts (AO_2) which are capable of decomposing in the polymer with the production of a chemiluminescent product A. Quantitative measurement of the chemiluminescence intensity I_{CL} as

a function of the concentration of A (C_A) at constant temperature provides information concerning physical properties (diffusivity) of $^1\text{O}_2$ in the polymer film. Measurement of I_{CL} as a function of the addition of singlet oxygen quenchers (Q) at fixed C_A and temperature provides information concerning the chemical properties (reactivity) of $^1\text{O}_2$ toward these quenchers in the polymer systems.^{2,3}

The compounds employed in this study are given in Scheme II. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) films were used as test matrixes to explore the feasibility of the method. Polymer films

(2) The high sensitivity toward measurement of chemiluminescence allowed the acquisition of statistically useful data over periods of time such that there was no experimental change in the measured intensity. For a discussion, see H. C. Steinmetzer, A. Yekta, and N. J. Turro, *J. Am. Chem. Soc.*, **96**, 282 (1974).

(3) For relevant work on the reactivity of singlet oxygen in polymers see: E. V. Bystritskaya and O. N. Karpukhin, *Dokl. Phys. Chem. (Engl. Transl.)*, **221**, 353 (1975); V. M. Anisimov, O. N. Karpukhin, and A. M. Mattuchi, *Dokl. Akad. Nauk SSSR*, **214**, 828 (1974); *Dokl. Phys. Chem. (Engl. Transl.)*, **214**, 93 (1974); E. V. Bystritskaya, E. V. Karpukhin, and O. N. Karpukhin, *Vysokomol. Soedin.*, **Ser. A**, **18**, 1969 (1976); *Polym. Sci. USSR (Engl. Transl.)*, **18**, 2242 (1976).

(1) (a) See "Singlet Oxygen Reactions with Organic Compounds and Polymers", B. Ranby and J. Rabec, Eds., Wiley, New York, 1978, for a comprehensive and recent review; (b) M. L. Kaplan and A. M. Trozzolo, "Singlet Oxygen", Academic Press, New York, 1979, p 575.