Critical Micelle Concentration and the Size Distribution of Surfactant Aggregates

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A simple aggregation model for aqueous surfactant solutions is introduced to examine the relation between critical micelle concentrations and the size distribution of molecular aggregates. This model assumes ideal solution behavior for the aggregates and lends itself readily to numerical study. For ranges of parameter values that yield identifiable critical micelle behavior we find that the critical micelle concentration lies far above the concentration at which the size distribution changes from monotonically decreasing to nonmonotonic. This provides a vivid counterexample to the Ruckenstein–Nagarajan suggestion that these properties universally should occur together.

1. Introduction

The critical micelle concentration (cmc) exhibited by many surfactants in water represents an abrupt change in the solution from a state with mostly unassociated molecules to a state with large molecular aggregates or micelles. This transition can be monitored by corresponding abrupt changes in any of a wide variety of properties, including osmotic pressure, electrical conductance, light scattering, viscosity, and dye solubilization. Micelles typically have sizes ranging from twenty to several hundred surfactant molecules.[1]

Recently Ruckenstein and Nagarajan[2-4] proposed an intriguing connection between the occurrence of the cmc on the one hand, and a qualitative change in the size distribution of aggregates on the other hand. At very low total surfactant concentration the aggregate size distribution decreases monotonically with increasing size, i.e., monomers are the most frequently encountered species, dimers are less frequent, trimers even rarer, etc. However, as the total surfactant concentration increases a point is reached at which this monotonicity disappears. Subsequently, the aggregate size distribution continues to decline with size only for small sizes, passes through a subsequent minimum and maximum, and then reverts to monotonicity. Ruckenstein and Nagarajan identify the transition between these two regimes (the concentration at which the size distribution displays a horizontal point of inflection) with the cmc. It is our aim in this paper to test the Ruckenstein–Nagarajan proposal for an elementary aggregation model.

For present purposes it is sufficient to suppose that the surfactant solution is ideal with respect to all aggregation species (this assumption is implicit in ref 2-4). Then the concentration ρ_i of i-molecule aggregates can be written

$$\rho_i = K_i \rho_1^{\,i} \tag{1.1}$$

where ρ_1 is the monomer concentration and K_i is an association constant related to the standard Gibbs free energy of forming the aggregate from monomers:

$$\Delta G_i^\circ = -RT \ln K_i \tag{1.2}$$

The total surfactant concentration is obviously given by the expression

$$\rho_t = \sum_{i=1}^{\infty} i\rho_i = \sum_{i=1}^{\infty} iK_i\rho_1^{\,i} \tag{1.3}$$

while the ideal-solution osmotic pressure Π is

$$\Pi/RT = \sum_{i=1}^{\infty} \rho_i = \sum_{i=1}^{\infty} K_i\rho_1^{\,i} \tag{1.4}$$

The specific model employed by Ruckenstein and Nagarajan has its source in Tanford's ideas[5,6] about the various contributions to ΔG_i°. Details are unimportant here. The generic form assigned to ΔG_i° is the following (at least for nonionic surfactants):

$$\Delta G_i^\circ = \alpha i^{4/3} - \beta i + \gamma i^{2/3} \tag{1.5}$$

where α, β, and γ are positive parameters that depend on temperature and the molecular structure of the surfactant. It is the difference in sign between terms in ΔG_i° which permits occurrence of nonmonatonic behavior for the ρ_i vs. i at sufficiently large ρ_t.

The specific calculations carried out by Ruckenstein and Nagarajan assign definite values to α, β, and γ for a series of surfactants, and then compare experimental cmc's for those substances with total concentrations ρ_t at which the aggregate size distribution ρ_i exhibits a horizontal point of inflection. The agreement is quite remarkable. Unfortunately there was no simultaneous demonstration that any property such as the osmotic pressure undergoes the required abrupt change at these "cmc's". Nevertheless, the results seemed favorable enough to offer hope that a precise mathematical criterion for the cmc in terms of the size distribution could aid in resolving modest discrepancies that arise in determining this quantity from distinct experimental techniques.

2. Elementary Association Model

One can view the formation of an i-molecule aggregate (A_i) as the result of a stepwise association, whereby monomers (M) are sequentially added. For the reversible step

$$A_{j-1} + M \rightleftarrows A_j \qquad (j \geq 2) \tag{2.1}$$

the equilibrium constant may be denoted by

$$k_j = \rho_j/(\rho_{j-1}\rho_1) \tag{2.2}$$

then the previously introduced K_i are given by

$$K_i = \prod_{j=2}^{i} k_j \tag{2.3}$$

If the standard free energy were the same for each aggregation step (2.1) then all k_j would have a common value, e.g., k, and so

$$K_i = k^{i-1} \tag{2.4}$$

With such a uniform stepwise association it is not possible

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to produce a nonmonotonic size distribution for aggregates. Furthermore, calculations of the type described below show that this uniform stepwise association produces no abrupt changes in physical properties which could reasonably be identified with a critical micelle phenomenon.

In order to model the behavior of surfactants realistically, the k_j must evidently display a strong nonuniformity with respect to j, so that the resulting K_i will deviate markedly (and in the proper manner) from the form shown in eq 2.4. In particular, the K_i should exhibit a preferential range of micelle sizes over which these constants are substantially larger than might be indicated by the trend established by stepwise association of small numbers of surfactant molecules. The physical reason is well-known qualitatively, namely, that after achieving a certain critical size the aggregates are structurally capable of "hiding" their hydrophobic units completely from the water in the micellar interior. This advantage is simply not available to small aggregates of, e.g., two to ten monomers. The Ruckenstein–Nagarajan K_i's, based on free energy expression 1.5, implicitly incorporate this sort of nonuniform association behavior, as the resulting size distributions demonstrate at sufficiently high overall concentration. We might note in passing that other calculations of aggregate size distributions, such as those by Hoeve and Benson[7] and by Poland and Scheraga,[8] also incorporate nonuniform stepwise association which, like that of the Ruckenstein–Nagarajan study, produces nonmonotonic size distributions with a single maximum at a most probable micelle size.

It has not been our aim in the present study to develop a complete molecular theory of surfactant solutions. Instead, we have been content to examine the implications of a phenomenological, but physically reasonable, family of *nonuniform* association constants. In particular we have investigated the case where

$$K_i = k^{i-1}F(i) \tag{2.5}$$

with the following modulation function F:

$$\begin{aligned} F(i) &= 1 \quad (i = 1) \\ &= \exp[\Delta - (i - n^*)^2/\sigma^2] + 1 \quad (1 < i \leq n_{max}) \\ &= 0 \quad (i > n_{max}) \end{aligned} \tag{2.6}$$

Here Δ, n^*, σ, and n_{max} are parameters which determine the character of the modulation. The previous case of uniform association is recovered in the limit $\Delta \to -\infty$, $n_{max} \to +\infty$. For finite values of these parameters, however, there will be an enhancement of the tendency to form aggregates of sizes near to n^*. The quantity σ controls the range of sizes over which enhanced aggregation occurs, while Δ controls the strength of the enhancement. No aggregation is permitted to occur beyond size n_{max}; while this absolute cutoff may seem arbitrary it is computationally convenient below, and only is permitted to occur beyond the size range of physical relevance.

While no fundamental significance from the standpoint of surfactant science can be attached to the Gaussian function invoked in eq 2.6, its general qualitative properties are easily understood. Furthermore, we claim that the resulting K_i can (with proper choice of parameters Δ, n^*, σ, and n_{max}) closely mimic the association constants that would follow from a more detailed molecular theory such as that which yields ΔG_i° in eq 1.5. For our modest purposes eq 2.5 and 2.6 are quite sufficient. If the Ruckenstein–Nagarajan hypothesis has the universality claimed, then in particular it must be valid for the model association process represented by eq 2.5 and 2.6. It is this presumption that we set out to test quantitatively.

3. Numerical Procedure

In order to simplify numerical analysis of our association model we found it advisable to use the following reduced variables in place of ρ_1, ρ_t, and osmotic pressure Π:

$$x = k\rho_1 \qquad y = k\rho_t \qquad f = k\Pi/RT \tag{3.1}$$

As a result the basic equations become

$$y = \sum_{i=1}^{n_{max}} i\,F(i)x^i \tag{3.2}$$

$$f = \sum_{i=1}^{n_{max}} F(i)x^i \tag{3.3}$$

For a given set of parameters Δ, n^*, σ, and n_{max} our procedure involved first selecting a value for y and then solving the resulting polynomial equation (3.2) for that real positive root x_1 which has the property

$$\lim_{x_1 \to 0} (y/x_1) = 1 \tag{3.4}$$

The substitution of this root x_1 into eq 3.3 then yields the osmotic pressure (reduced). The separate terms in the f expression are in fact the concentrations of aggregates of different sizes, so we obtain the size distribution from the set of quantities

$$x_i = k\rho_i = F(i)x_1^i \tag{3.5}$$

Our decision to treat y rather than x as the independent variable stems from the experimental fact that the total surfactant concentration ρ_t is under control, not the monomer concentration. The reverse procedure (x the independent variable, y dependent) can inadvertently lead one to consider states with absurdly large total surfactant concentrations.

In all of the calculations to be reported here we have set

$$n^* = 40 \qquad \sigma = 3 \qquad n_{max} = 50 \tag{3.6}$$

The parameter Δ was given five distinct values:

$$\Delta = -\infty,\ 50,\ 60,\ 70,\ 80 \tag{3.7}$$

For each Δ the reduced total density y was assigned 100 equally spaced values in the range $0 < y \leq 0.5$.

A series of exploratory calculations with alternative n^*, σ, and n_{max} choices has also been carried out. No behavior essentially distinct from that to be reported below for the set in (3.6) was uncovered.

4. Results

Figures 1–5 show logarithmic plots of the aggregate size distributions for each of the Δ choices in eq 3.7. The first of these choices produces straight lines since this case has $F \equiv 1$ for all sizes below the cutoff. But as we switch on the Gaussian function by increasing Δ the influence of the preferred aggregation size becomes obvious. And indeed we then observe the typical behavior that has been reported by previous authors,[2,3,7,8] namely, that monotonic distributions at low total concentration convert to nonmonotonic distributions at higher total concentration. We note that when a maximum in the size distribution first occurs it does so at a size substantially less than n^*. But this maximum position shifts closer to n^* as the total concentration increases.

Figure 6 shows how the reduced monomer concentration x_1 varies with y. When $\Delta = -\infty$ there is only a smooth featureless increase. But as Δ increases toward the maximum value 80 a region of large curvature develops, separating regimes with distinctly different slopes. We

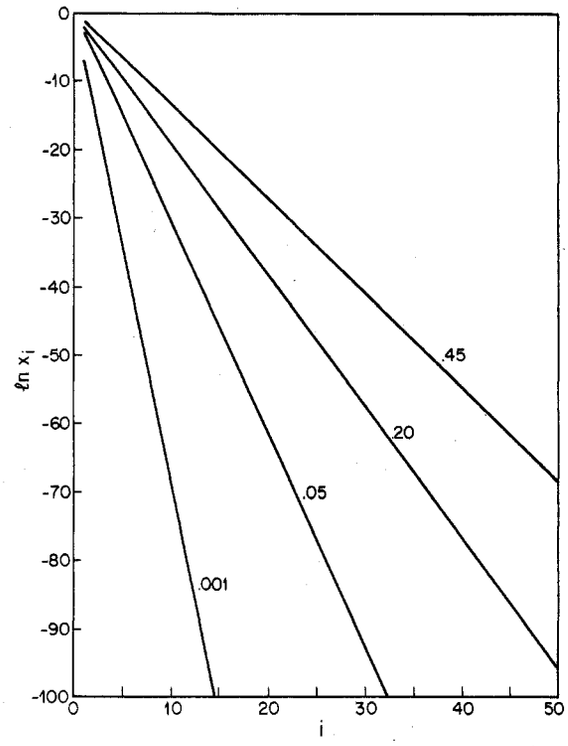

Figure 1. Aggregate size distributions for $\Delta = -\infty$. The curves are labeled by the values of reduced total concentration y. For this case the curves are strictly linear for $n \leq n_{max} = 50$.

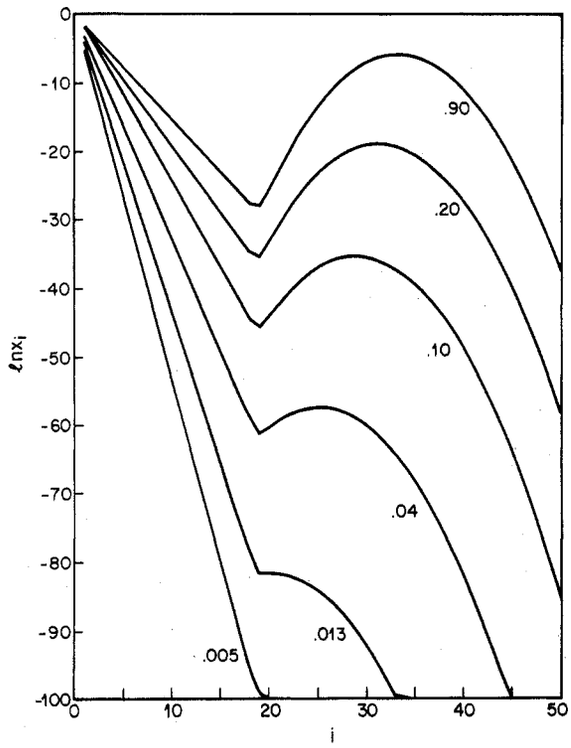

Figure 2. Aggregate size distributions for $\Delta = 50$. The labels are the corresponding y values.

identify this abrupt change in slope with micelle formation, and following Phillips[9] it will be convenient to define the cmc as that y value for which

$$|d^2x_1/dy^2| = \text{maximum} \qquad (4.1)$$

Notice that as Δ increases the sharper the transition becomes, and the lower the y value at which it appears. The cmc values obtained by numerical differentiation of $x_1(y)$

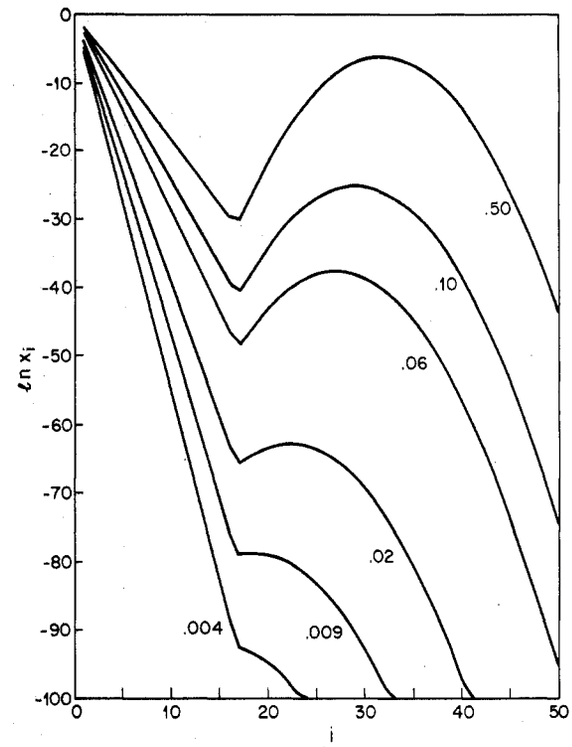

Figure 3. Aggregate size distributions for $\Delta = 60$, labeled with the corresponding y values.

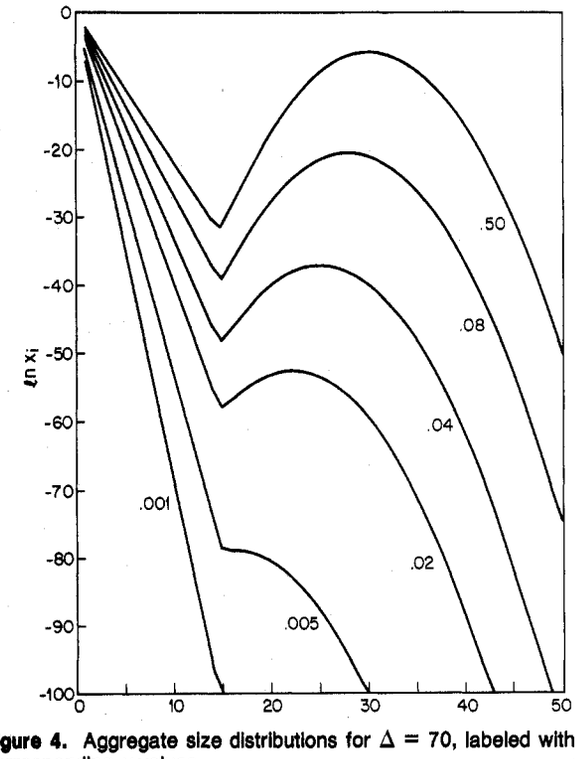

Figure 4. Aggregate size distributions for $\Delta = 70$, labeled with the corresponding y values.

TABLE I: Parameters Computed for Micelle Aggregation Model

Δ	50	60	70	80
y(cmc)	0.285	0.180	0.115	0.075
x_1(cmc)	0.186	0.136	0.096	0.068
$d^2x_1/dy^2\|_{cmc}$	−0.0234	−0.0540	−0.100	−0.164
y(RN)	0.013	0.008	0.005	0.003

are listed in Table I, first row, where they are denoted y(cmc).

Figure 7 presents curves for the reduced osmotic pressure quantity f plotted vs. y. Once again we see the

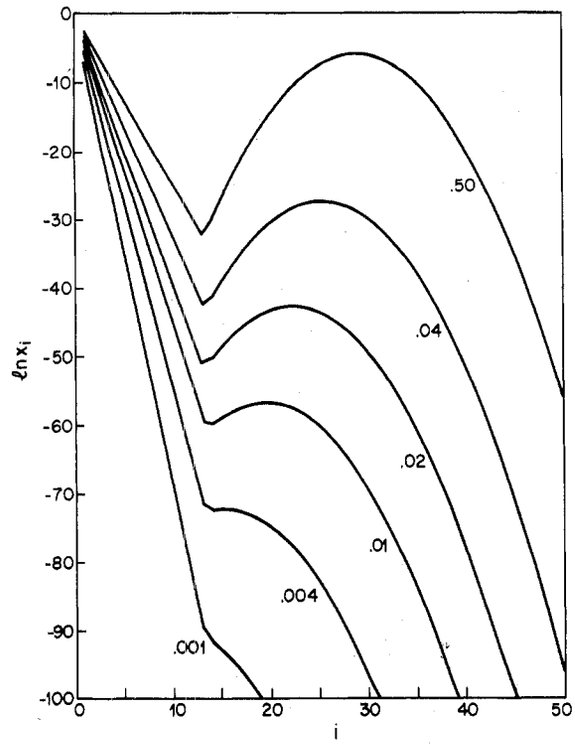

Figure 5. Aggregate size distributions for $\Delta = 80$, labeled with the corresponding y values.

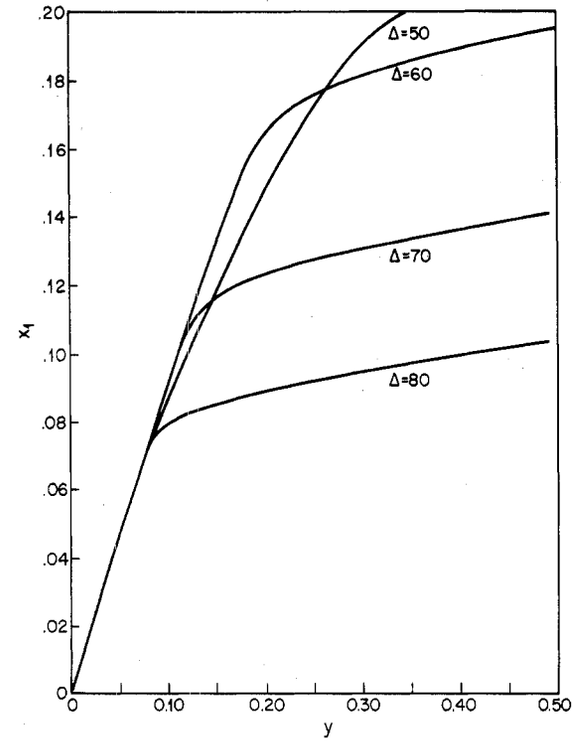

Figure 6. Monomer concentration x_1 vs. total concentration y, each in reduced units.

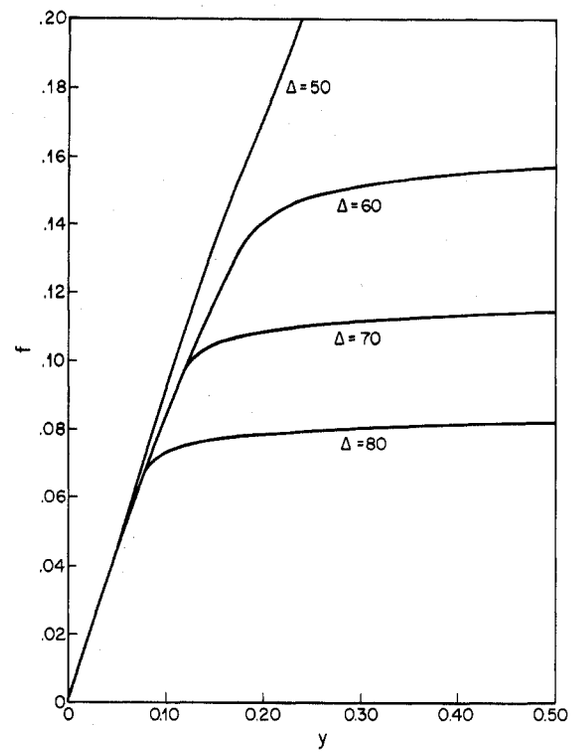

Figure 7. Reduced osmotic pressure f vs. reduced total concentration y.

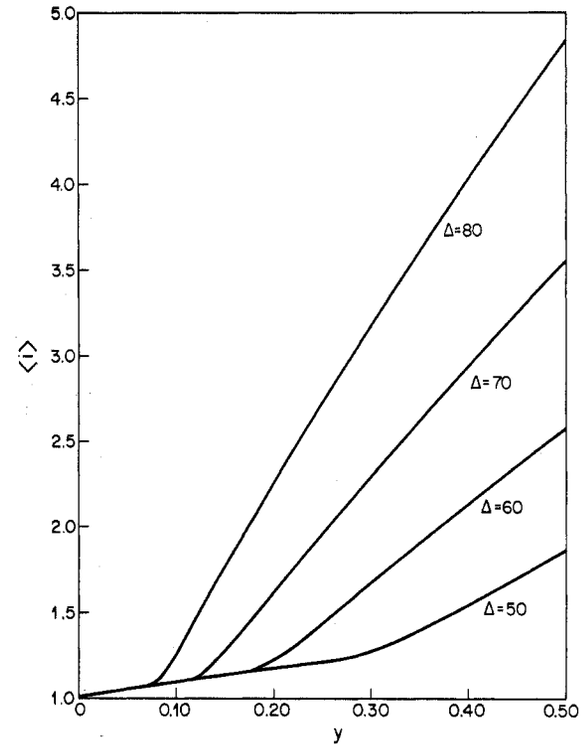

Figure 8. Average aggregation number $\langle i \rangle$ vs. reduced total concentration y.

emergence of an increasingly abrupt transition as Δ increases. The positions of maximum curvature in these curves stand in substantial agreement with the cmc's listed in Table I from criterion 4.1.

From eq 3.2 and 3.3 it is easy to see that the mean aggregation number is given by

$$\langle i \rangle = y/f \tag{4.2}$$

This quantity is displayed as a function of y in Figure 8. As before, increasing Δ tends to sharpen the transition between regions of distinctly different slopes, and the position of maximum curvature once again corresponds very closely to the cmc values listed in Table I.

In addition to the cmc values of y, Table I also lists the values of y [denoted by y(RN)] at which the size distribution satisfies the Ruckenstein–Nagarajan criterion of a horizontal inflection point. These were obtained by simple interpolation from our numerical results at preassigned y values. The table also gives values of x_1 and of d^2x_1/dy^2 at y (cmc).

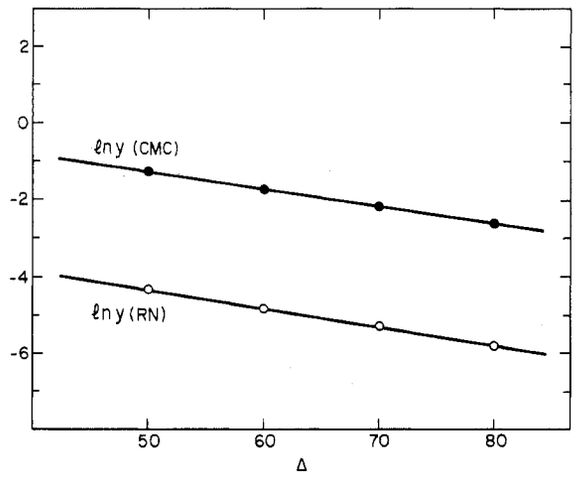

Figure 9. Logarithmic plots of cmc and the Ruckenstein–Nagarajan concentration vs. the aggregation strength parameter Δ.

5. Discussion and Conclusion

It is obvious from the first two rows in Table I that the Ruckenstein–Nagarajan criterion fails to locate the cmc's for the present aggregation model. Furthermore, the failure is quite dramatic since y(cmc)/y(RN) tends to be about 20. Evidently, the desired logical connection between the cmc and the occurrence of a horizontal inflection point in the aggregation size distribution cannot universally be realized.

Ruckenstein and Nagarajan have found agreement from their *theoretical* calculations (predicated upon their inflection point criterion) and *experimental* cmc's for homologous series of surfactants (hexoxyethylene glycol monoethers,[2] and alkyl glucosides and sodium alkyl sulfates[3]). In view of the present work it appears that the agreement may have been fortuitous. It is not at all clear that their model would exhibit conventional cmc behavior (abrupt breaks in properties vs. total concentration) anywhere close to the occurrence of horizontal inflection points.

The fact that apparent agreement in the Ruckenstein–Nagarajan studies extends over homologous series of compounds is not in itself persuasive. Our calculations show that while y(cmc) and y(RN) may substantially disagree they nevertheless tend to behave in similar fashion with respect to strength of aggregation. In homologous series of surfactants this strength is primarily determined by the chain length n_c of nonpolar hydrocarbon moieties. The corresponding quantity in our simple model is Δ, which should roughly be proportional to n_c. Figure 9 shows plots of ln y(cmc) and ln y(RN) vs. Δ, prepared from entries in Table I. The curves are linear (as are plots of experimental values for ln ρ_t(cmc) vs. n_c[10]) and close to parallel. If this parallelism is generally the case for all aggregation models, then fortuitious agreement for one member of a homologous series would imply agreement for the remaining members.

We are forced to conclude that if the cmc is to be universally related to some specific attribute of the aggregate size distribution then that attribute must be more subtle than mere occurrence of a horizontal inflection point.

References and Notes

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Direct Observation of the Kinetic Behavior of a Charge-Transfer Reaction on the Cation-Scavenging Reaction for Cation Radicals of *N*-Vinylcarbazole and *N*-Ethylcarbazole by Using a Pulse Radiolysis Technique

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The cation-scavenging reaction has been directly observed by using the pulse radiolysis method for cation radicals of both *N*-vinylcarbazole ($VCZ^{+}\cdot$; the initiating species of radiation-induced cationic polymerization of VCZ) and *N*-ethylcarbazole ($EtCZ^{+}\cdot$, nonpolymerizing model compound) in order to elucidate the role of inhibitors in radiation-induced cationic polymerization. The rate constants for the reactions of $VCZ^{+}\cdot$ with triethylamine, diphenylamine, and dimethylaniline in nitrobenzene solution have been determined to be 1.3×10^9, 2.0×10^9, and 3.9×10^9 M^{-1} s^{-1}, respectively, which are almost the same as those for $EtCZ^{+}\cdot$ with these three scavengers.

Introduction

It is well-known that pulse radiolysis is a very powerful method to observe directly the initial species formed by irradiation. Its first application to a polymerizing system was made in the polymerization of α-methylstyrene by Katayama et al.[1]

Cationic polymerization of *N*-vinylcabazole (VCZ) was studied by means of the puise radiolysis technique, and

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