Kinetics Associated with the Change of the Number Density of Micelles in Solution

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Received: July 29, 1997[⊗]

The kinetics of fusion/fission of micelles, in the transition range between spherical and elongated micelles, has been investigated using an approach similar to those of Aniansson and Kahlweit. On the assumption that the relaxation process associated with the exchange of surfactant between micelles and solution is very fast and that the creation of large aggregates by stepwise association of monomeric surfactants is slow, the frequency of relaxation was found to depend on the average collision frequency, the micelle length distribution, and the number density of micelles. Well above the cmc, the relaxation frequency is equal to the ratio of the average fusion rate over the derivative of the aggregate number with respect to the number of surfactant molecules in micelles. The obtained expression applies to many length distributions from short micelles with a low or a large polydispersity to elongated micelles. Numerical simulations of the variation of the relaxation frequency with surfactant concentration are given for three different micellar energy distributions.

Introduction

Micellar kinetics has been widely investigated theoretically for both spherical micelles with a low size polydispersity and wormlike micelles with an exponential distribution of micellar lengths. For spherical micelles, the calculation of the relaxation time associated with the exchange of surfactant between micelles and solvent has been carried out by Aniansson et al.[1,2] For the same type of systems, Kahlweit et al.[3,4] have calculated the relaxation time corresponding to the change in the number density of micelles due to the fusion/fission mechanism. For wormlike micelles, Turner and Cates[5] have shown that this relaxation time is inversely proportional to the mean length of micelles.

Recent studies[6,7] have shown that *T*-jump setup coupled to a light scattering detection allows the observation of the return to equilibrium of the number density of micelles. This technique is best suited for solutions in the dilute regime or at the beginning of the semidilute regime, but it does not allow measurements of micellar relaxations when the micelles are strongly entangled.

The theoretical treatments reported up to now concern the asymptotic behaviors for spherical or elongated micelles but do not deal with the transition between these two limits and with the case of short micelles with a wide polydispersity. However these latter cases are rather easy to study with a *T*-jump setup equipped with scattered light detection. This paper concerns the micellar kinetics in the transition range between spherical and elongated micelles.

The approach used is similar to those of Aniansson and Kahlweit. The relaxation process is divided according to two time scales: a short time scale corresponding to surfactant exchanges between micelles and solvent and a long time scale corresponding to the formation/breakup of the micelles. The obtained results allow the determination of the parameters that control the relaxation time of the number density of aggregates in solution. It is valid for surfactant solutions where the surfactant exchange between solvent and aggregates is fast and where the creation of large aggregates by stepwise association of monomeric surfactants is slow.

The derived equations are used in conjunction with some simple energy distributions, to obtain the variation of the relaxation frequency with surfactant concentration in various cases.

Kinetics in Micellar Solutions

Two reaction process control the variation of the number X_n of micelles made up of n surfactant molecules. One is the exchange of one surfactant molecule between a micelle and the solvent:

$$X_n + X_1 \underset{k'}{\overset{k}{\rightleftharpoons}} X_{n+1} \tag{1}$$

The other is the fusion of two aggregates into a larger one:

$$X_k + X_{i-k} \underset{b_k^i}{\overset{a_k^i}{\rightleftharpoons}} X_i \tag{2}$$

Reactions 1 modify the micellar distribution in two ways. One way is the aggregate formation from one surfactant by stepwise addition of i surfactant molecules in solution. As shown by Aniansson, the probability that such reactions occur is very low for low concentration of oligomers or for very small number density of the smallest aggregates. In this study, this event is neglected.

The other way, addition of one surfactant to one existing aggregate, does not modify the number Z of aggregates in the solution, and it can be assumed that this process is faster than reaction 2, which changes Z.

With these assumptions, the calculation of the relaxation process can be split in two parts corresponding to the two time scales. First, one considers a time scale longer than the kinetics of the exchange between micelles and solvent but shorter than the relaxation time of Z. At this time scale, Z is not an equilibrium value, but the fast process is at equilibrium for this instantaneous value of Z. The micelle−solvent exchange imposes relations between $X_1(t)$, $X_n(t)$, and $Z(t)$ which have to be satisfied at any time during the relaxation process of Z. These relations allow one to calculate the relaxation frequency associated with the number Z of micelles according to the probabilities of fission and fusion.

Surfactant Exchange Process. To make easier the calculation, the variables X_1 (number of free surfactant), X_n, and Z are split into static and dynamic parts:

$$X_1 = \overline{X_1} + \Delta X_1(t); \quad X_n = \overline{X_n} + \Delta X_n(t); \quad Z(t) = \bar{Z} + \Delta Z(t) \tag{3}$$

For these variables, the dynamic part vanishes at very long times.

In the short time range, the fast process imposes a relation between X_n and X_{n+1}:

$$\frac{X_n X_1}{X_{n+1}} = K_n \tag{4}$$

where K_n is the equilibrium constant of the reaction.

If the value of X_n is close to the equilibrium value, eq 4 gives

$$\frac{\Delta X_n(t)}{\overline{X_n}} + \frac{\Delta X_1(t)}{\overline{X_1}} = \frac{\Delta X_{n+1}(t)}{\overline{X_{n+1}}} \tag{5}$$

This recurrence has as a solution

$$\frac{\Delta X_n(t)}{\overline{X_n}} = n\frac{\Delta X_1(t)}{\overline{X_1}} + C(t) \tag{6}$$

During the micellar kinetics the number of surfactant molecules present in solution is constant:

$$\sum_{n>n_0} n\Delta X_n(t) = \sum_{n>n_0}\left(n^2 \overline{X_n}\frac{\Delta X_1(t)}{\overline{X_1}} + n\overline{X_n}C(t)\right) = -\Delta X_1 \tag{7}$$

where n_0 is the minimum value of the aggregation number. The number of aggregates that are smaller than n_0 is very low, and their contribution can be neglected in the sums. This condition provides the value of $C(t)$:

$$C(t) = -m_w\frac{\Delta X_1(t)}{\overline{X_1}} - \xi_1\frac{\Delta X_1(t)}{\overline{X_1}} \tag{8}$$

where m_w is the weight average number of micelles:

$$m_w = \frac{\displaystyle\sum_{n>n_0} n^2 X_n}{\displaystyle\sum_{n>n_0} nX_n} \tag{9}$$

and ξ_1 is the ratio between the number of free and micellized surfactants:

$$\xi_1 = \frac{\overline{X_1}}{\displaystyle\sum_{n>n_0} nX_n} \tag{10}$$

Combining eqs 6 and 8 yields the relation between ΔX_n and ΔX_1:

$$\frac{\Delta X_n(t)}{\overline{Xn}} = (n - (m_w + \xi_1))\frac{\Delta X_1(t)}{\overline{X_1}} \tag{11}$$

$\Delta Z(t)$ is equal to the sum of ΔX_n, and during the relaxation process of Z, $\Delta X_1(t)$ depend on the value of $\Delta Z(t)$:

$$\frac{\Delta X_1(t)}{\overline{X_1}} = -\frac{1}{((m_w + \xi_1) - m)}\frac{\Delta Z(t)}{Z} \tag{12}$$

where m is the average aggregation number.

The fast exchange of surfactant molecules between the micelles and the solvent links the modification of the micelle length distribution to the instantaneous value of the number of aggregates present in the solution.

Time Variation of the Number of Micelles. The variation of Z during the relaxation process is due to the fission/fusion of micelles:

$$\frac{dZ}{dt} = -P_f + P_c \tag{13}$$

where P_f is the number of micelles per unit time that disappear by fusion of two micelles and P_c is the number of micelles created by fission per unit time.

The kinetic reaction of fusion−fission is given by eq 2. The number of micelles with $i - k$ surfactant molecules that merge with micelles with k surfactant molecules is

$$P_f(i,k) = a_k^i X_{i-k} X_k \tag{14}$$

The number of micelles with an aggregation number i that break in two micelles with aggregation numbers k and $i - k$ is

$$P_c(i,k) = b_k^i X_i \tag{15}$$

The number of micelles formed is obtained by summing all possible fissions and the number of disappearing micelles by summing all possible fusions:

$$P_f = \sum_{i,k} a_k^i X_{i-k} X_k; \quad P_c = \sum_{i,k} b_k^i X_i \tag{16}$$

At equilibrium, the kinetic equation (2) gives

$$a_k^i = b_k^i\frac{\overline{X_i}}{\overline{X_k X_{i-k}}} \tag{17}$$

Using eqs 3, 13, 16, and 17 and taking only the first-order development for Δ variables, the time variation of Z is given by

$$\frac{d\Delta Z(t)}{dt} = \sum_{i,k}\overline{X_i}b_k^i\left(\frac{\Delta X_k(t)}{\overline{X_k}} + \frac{\Delta X_{i-k}(t)}{\overline{X_{i-k}}} - \frac{\Delta X_i(t)}{\overline{X_i}}\right) \tag{18}$$

Inserting relations 11 and 12 between ΔX_1, ΔX_n, and ΔZ due to the fast exchange process into eq 18 leads to

$$\frac{d\Delta Z(t)}{dt} = -\frac{m_w + \xi_1}{(m_w + \xi_1) - m}\sum_{i,k}\overline{X_i}b_k^i\frac{\Delta Z}{\bar{Z}} \tag{19}$$

Introducing β, the average probability for micellar fission, and θ, a parameter that depends on the micellar distribution, defined as

$$\beta = \frac{\displaystyle\sum_{i,k}\overline{X_i}b_k^i}{\bar{Z}} = \bar{Z}\sum_{i,k}\frac{\overline{X_i}\,\overline{X_k}}{\bar{Z}\,\bar{Z}}a_k^i; \quad \theta = \frac{m_w + \xi_1}{m} \tag{20}$$

eq 19 becomes

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$$\frac{d\Delta Z(t)}{dt} = -\frac{\theta}{\theta-1}\beta\Delta Z(t) \tag{21}$$

After a perturbation the value of Z goes exponentially to its equilibrium value with the time constant τ given by

$$\frac{1}{\tau} = \frac{\theta}{\theta-1}\beta \tag{22}$$

The relaxation frequency $F_r = (1/2)\pi\tau$ can also be written as a function of the collision frequency:

$$F_r = \frac{\theta}{2\pi(\theta-1)}\bar{Z}\alpha \tag{23}$$

with

$$\alpha = \sum_{i,k}\frac{\overline{X_i}}{\bar{Z}}\frac{\overline{X_k}}{\bar{Z}}a_k^i \tag{24}$$

If the surfactant concentration is larger than the cmc ($\xi_1 \ll m_w - m$), the relaxation time is given by (see the Appendix)

$$\tau = \frac{dm}{d(X-X_1)}\frac{1}{\alpha} = \frac{d\log(m)}{d\log(X-X_1)}\frac{1}{\beta} \tag{25}$$

In this calculation, the only assumptions are that the exchange of surfactant molecules is fast and that the aggregate formation by stepwise association of surfactants is very slow. The equations hold for many widths of the distribution function. Well above the cmc, the relaxation time is proportional to dm/dX, and the variation of the relaxation time with concentration allows the determination of the micellar growth. In this model, the relaxation of Z controls the slow relaxation process; m_w, which is the parameter observed in T-jump experiments with scattered light detection, varies for a long time as Z. At short time, the fast surfactant exchange controls the variation of m_w. These kinetics are supposed to be fast compared to the time of diffusion of micelles at the wavelength considered and, in the case studied, cannot usually be measured. Indeed the limiting time in T-jump experiments is the diffusion time measured by dynamic light scattering.

Asymptotic Behaviors

Short Micelles with a Narrow Length Distribution. When the micelles are short and the width of length distribution is narrow, m_w is close to m. The difference between these two numbers is

$$m_w - m = \sigma^2/m \tag{26}$$

where σ^2 is the variance of the length distribution. With these notations one obtains the Kahlweit expression of $1/\tau$:

$$\frac{1}{\tau} = \frac{m_w}{\xi_1 + \sigma^2/m}\beta \approx \frac{m}{\xi_1 + \sigma^2/m} \tag{27}$$

Short Micelles with Submicellar Aggregates. Aniansson et al. have proposed a model for the calculation of the relaxation time of exchange between micelles and small aggregates. In their model, only the exchange of surfactant molecules between aggregates and solution is taken into account. The collision between submicellar aggregates and micelles is not considered.

If for any size, the fission/fusion process is slower than the exchange between aggregates and solution, the relaxation

process described in first part can be extended to the small aggregates by taking into account the collision between micelles and small aggregates.

Wormlike Micelles. When the micelles are very elongated, the distribution of micelle lengths obeys an exponential law and θ is equal to 2. The probability of fission b_k^i is independent of the position where the break occurs, and the splitting probability for one micelle is proportional to its length. The average probability β is

$$\beta = \frac{\sum\overline{X_i}ik_b}{\bar{Z}} = mk_b \tag{28}$$

where k_b is the breakup probability by length unit. The relaxation time is the same as that reported by Cates:

$$\tau = 1/2mk_b \tag{29}$$

In this model, the surfactant exchange kinetics has been supposed very fast, but this assumption fails for giant micelles. Indeed, as shown by Marquez et al.,[8] the relaxation time associated with the exchange process is proportional to m when the relaxation time associated to the fission−fusion process is inversely proportional to m. However, for the experimentalist, the crossover between these two relaxation times may be very difficult to observe because the expression of the relaxation time for the fusion/fission kinetics of wormlike micelles is the same for the two models.

Numerical Simulations

The relaxation time obtained is very sensitive to the variation of micelle length with the concentration. Contrary to the case of elongated micelles for which the growth law is known, the description of the onset of micellar growth is very limited. For this reason, the micellar length and the relaxation frequency are calculated for three simple energy distributions. The number of micelles is assumed to vary with n as

$$X_n \propto F(n)\exp(-\mu n) \tag{30}$$

where $F(n)$ dependents on the Gibbs energy in the micelles of n surfactant molecules, and μ is a chemical potential that is chosen so that the cmc is very low.

Three form of $F(n)$ are presented:

(i)

$$F(n) = 0 \qquad \text{for} \quad 1 < n < n_0$$

$$F(n) = 1 - \exp^{-p(n-n_0)} \quad \text{for} \quad n > n_0 \tag{31}$$

In this case, the end-cap energy is constant; the lower the parameter p, the softer the cutoff of the micellar length distribution.

(ii)

$$F(n) = 0 \quad \text{for} \quad n < n_0$$

$$F(n) = 1 + p \quad \text{for} \quad n_0 < n < n_1 \tag{32}$$

$$F(n) = 1 \quad \text{for} \quad n > n_1$$

The number of short micelles can be favored by increasing the parameter p. For example, the model proposed by MacKintoch et al.[9] to describe the electrostatic effect on micellar growth
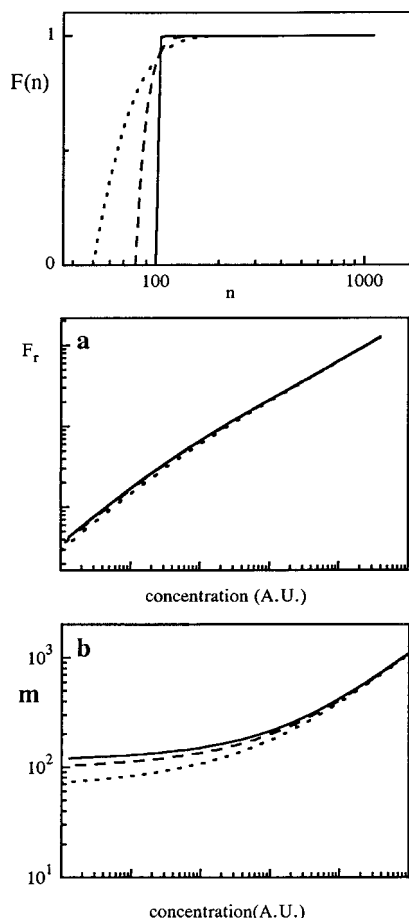
Figure 1. Variation of the relaxation frequency F_r and the average aggregation number m versus concentration for different forms of $F(n)$ given by eq 31 and represented at the top of the figure. (a) Variation of the relaxation frequency F_r with concentration. (b) Variation of average aggregate number m with concentration. The same concentration range is used for F_r and m.

Figure 2. Variation of the relaxation frequency F_r and the average aggregation number m versus concentration for different forms of $F(n)$ given by eq 32 and represented at the top of the figure. (a) Variation of the relaxation frequency F_r with concentration. (b) Variation of average aggregate number m with concentration. The same concentration range is used for F_r and m.

can be roughly approximated by this distribution.

(iii)

$$F(n) = 0 \quad \text{for} \quad n > n_0$$

$$F(n) = 1 \quad \text{for} \quad n_0 < n < n_1 \quad \text{and} \quad n > n_2 \qquad (33)$$
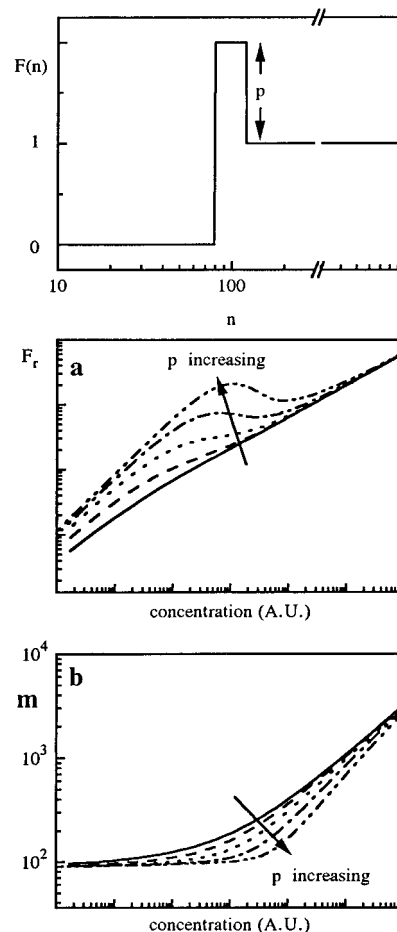
$$F(n) = 1 - p \quad \text{for} \quad n_1 < n < n_2$$

In this case, a given micelle length range can be favored or not by changing p.

The relaxation frequency F_r obtained by using eq 23 with a fusion probability α independent of the micelle length is plotted as function of concentration in Figures 1a, 2a, and 3a. The average micelle lengths are also reported for the same parameters and the same concentration range in Figures 1b, 2b, and 3b.

For all cases reported, the relaxation frequency and the average micelle length vary as the square root of concentration in the high concentration range. In the low concentration range m varies only slightly with concentration, whereas the exponent of the scaling law for relaxation frequency is larger than 1/2.

In the transition range between these two asymptotic behaviors, no variation or a maximum/minimum variation can be observed for F_r in Figures 2a and 3a, while the variation of m exhibits a continuous behavior.

In the case presented in Figure 1, the shape of the curves depends only slightly on the parameter p. It will be difficult

for an experimentalist from the measurements of m or of F_r to ascertain one of the three $F(n)$ functions.

In the two other cases, the flat variation or the maximum of the relaxation frequency is easily observed, and the T-jump experiments should show clearly that the spherical micelles are favored.

These examples show that the variation of the relaxation frequency is more sensitive to the energy distribution than the variation of m. Thus, as the experiments are performed generally over a limited concentration range, even if a crude model describes satisfactorily the variation of m at the beginning of the micellar growth, more sophisticated models might be necessary to explain the relaxation frequency measurements.

In this study, the average collision frequency is assumed independent of micellar length and of the concentration, whereas Kahlweit et al. assume a constant average fission probability. Our assumption is crude because the collision probability between two spherical micelles may differ from that between two rodlike micelles or that between two flexible wormlike micelles. But in the range of limited growth where the polydispersity is low, this assumption is valid. The assumption of Kalhweit et al. stating a constant average fission probability seems unrealistic. Indeed, at equilibrium, the average probability that one micelle collides with another micelle is equal to the average scission probability, and the average collision probability for one micelle is proportional to the number of micelles per unit volume.

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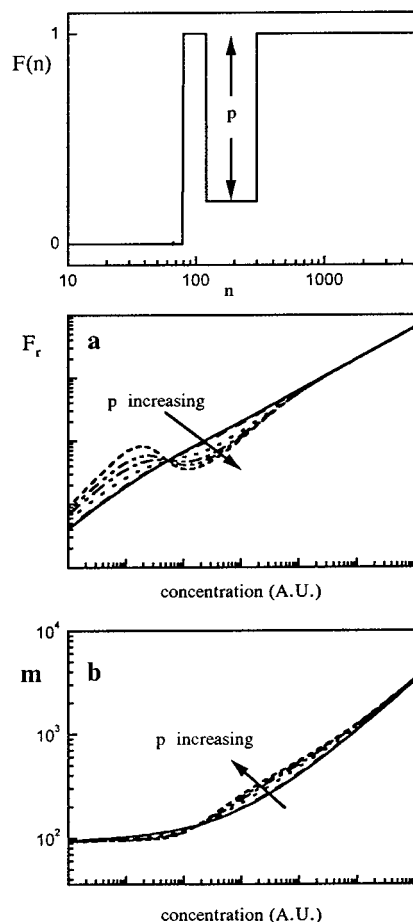
Figure 3. Variation of the relaxation frequency F_r and the average aggregation number m versus concentration for different forms of $F(n)$ given by eq 33 and represented at the top of the figure. (a) Variation of the relaxation frequency F_r with concentration. (b) Variation of average aggregate number m with concentration. The same concentration range is used for F_r and m.

For narrow length distribution, the main contribution to the average fission probability is provided by the largest aggregates, and their number increases always with the surfactant concentration.

Conclusion

The kinetics of fusion/fission of micelles has been investigated using an approach similar to those of Aniansson and Kahlweit. On the assumptions that the relaxation process associated with the exchange of surfactant between micelles and solution is very fast and that the formation of large aggregates by stepwise association of surfactants is slow, the frequency of relaxation was found to depend on the average collision frequency, on the micelle length distribution, and on the number density of micelles. Well above the cmc, the relaxation frequency is equal to the average collision rate divided by the derivative of the aggregate number with respect to the number of surfactant molecules in the micelles. The relaxation frequency obtained for wormlike micelles is identical with that given by the Cates formula.

Very simple models are presented which show that, for the micellar growth, the local scaling law exponent for m increases continuously with concentration, until 1/2. The exponent for the scaling law of F_r is always larger than 1/2 in the low concentration range and equal to 1/2 in the high concentration range. At the onset of growth, F_r may present no variation or successively a maximum and a minimum. Measurements that

were carried out on solution of hexadecyltrimethylammonium bromide in the presence of potassium bromide[6] exhibit a slight variation of the relaxation time at low surfactant concentration and a exponent of the scaling law larger than 1/2 when the micelles grow. This behavior is relatively close to those observed in Figure 2a,b. This example shows that the study of relaxation times at the onset of micellar growth should allow one to refine the Gibbs energy distribution of micelles.

Appendix

The X_n are a function of X_1:[10]

$$X_n = C_n X_1^{\ n} \qquad (A1)$$

The derivative of the aggregate number with respect to the number of surfactant molecules in micelles X_m is

$$\frac{dm}{dX_m} = \frac{d}{dX_m}\left(\frac{X_m}{\sum C_{nX_1^n}}\right) = \frac{m}{X_m} - \frac{m^2}{X_m}\frac{1}{X_1}\frac{dX_1}{dX_m}\sum n C_n X_1^{\ n} \qquad (A2)$$

with

$$X_m = X - X_1 \qquad (A3)$$

the conservation of matter is

$$\sum n C_n X_1^{\ n} = X_m \qquad (A4)$$

and the derivative of the number of free surfactant molecules is

$$\frac{1}{X_1}\frac{dX_1}{dX_m} = \frac{1}{\sum n^2 c_n X_1^{\ n}} \qquad (A5)$$

Equations A2 and A5 give

$$\frac{dm}{dX_m} = \frac{m}{X_m} - \frac{m^2}{X_m m_w} = \frac{m_w - m}{Z m_w} \qquad (A6)$$

and

$$\frac{m_w - m}{m_w} = \frac{d\log(m)}{d\log(X_m)} = Z\frac{dm}{dX_m} \qquad (A7)$$

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