

Kinetics Associated with the Length Change of Micelles in SDS Solutions

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In this communication, we have measured, using a T-jump with light scattering detection, the relaxation time associated with the fusion–fission process in a surfactant concentration range where the shape of micelles varies from a sphere to rodlike or wormlike. The Sodium dodecyl sulfate (SDS) was chosen because SDS micelles grow at high ionic strength. Measurements have been carried out in brine with 0.6–1 mol/L NaCl at 35 °C. The measurements of the relaxation frequency as a function of the SDS concentration have been fitted by a theoretical expression. The fits dismiss the fact that the end cap of micelles is a simple hemisphere. Assuming that the end cap diameter is larger than that of the cylindrical part, a size distribution is proposed which favors the spherical micelles. This hypothesis disadvantages the micelles with sizing close to twice the length of a spherical micelle, because they have negative bending without the cylindrical part. We obtained values of the fusion probability of micelles.

Introduction

It is well-known that the surfactant molecules self-assemble into micelles if their concentration is higher than the critical micelle concentration (cmc). The size of these aggregates depends on the nature of the surfactant molecule and varies with the surfactant concentration and with the temperature. It depends also on the nature and concentration of added salt. In some brine, some surfactants make up spherical micelles above the cmc. With increasing surfactant concentration, these micelles grow into rodlike objects, and when the micellar length becomes larger than the persistence length, the micelles have a wormlike shape. The bonds between surfactant aggregates are weak, and the micelles continuously exchange molecules with the solvent, break, and merge.

These kinetic processes have been widely investigated theoretically. Aniansson et al.^{1,2} give the theoretical treatment of the exchange of surfactant molecules between micelles and solvent. They determined the relaxation time associated with the aggregate formation from one surfactant by stepwise addition of surfactant molecules. The fusion–fission has been studied by Kahlweit^{3,4} for spherical micelles and by Cates⁵ for elongated micelles. In a recent paper,⁶ the relaxation time associated with the fusion–fission kinetics is determined for some micellar shapes.

Experimentally these kinetics are widely investigated by ultrasonic relaxation absorption method for the molecular exchange between micelles and the bulk phase and in the case of the fusion–fission process of quasispherical micelles using T-jump technique with light absorption detection. Use of some absorbency probe is often necessary in this last technique.

With the T-jump technique with light scattering detection, the fusion–fission kinetic can be studied without probes if the weight aggregation number of micelles varies enough with temperature. This last technique is the best suited for solutions in the dilute regime or at the beginning of the semidilute regime,

but it does not allow measurements of micellar relaxation when the micelles are strongly entangled.

In this paper, we have attempted, using a T-jump with light scattering detection, to measure the relaxation time associated with the fusion–fission process in a surfactant concentration range where the shape of micelles varies from the sphere to the rodlike or wormlike. The sodium dodecyl sulfate (SDS) was chosen because the micelles of SDS grow at high ionic strength. Measurements have been carried out in brine with 0.6–1 mol/L NaCl and at 35 °C. In these solutions, the variation of the ionic strength with the change of the SDS concentration is low and the Debye length is unaffected by the dissociation of the surfactant molecules. Also, the observed variations of measured relaxation time depend only on surfactant concentration.

Theoretical background

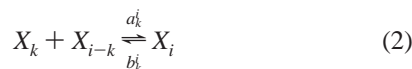
Shape of Micelles. The surfactant molecules in solution aggregate and make up micelles with a distribution size depending on physicochemical conditions and on surfactant concentration. Israelachvili⁷ showed that the distribution can be written as $F(n) e^{-\mu n}$, where μ is chemical potential. $F(n)$ depends on Gibbs energy of the micelle formed with n surfactant molecules. For large micelles, $F(n)$ depends only on the scission energy of an elongated micelle which is independent of the micelle size. When the average length of micelles m is high, the size distribution is an exponential and m varies with the surfactant concentration C as $C^{1/2}$.

Micellar Kinetics. Two reaction processes 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,



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

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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 a solution. As shown by Aniansson, the probability that such reactions occur is very low and this event can be 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. At short time, the micelles and solvent exchange molecule surfactant but the micelles have no time to merge. At long time, the fusion can occur and Z varies. In this time scale, Z is not at equilibrium value but the fast process is at equilibrium for the instantaneous value of Z .

With these assumptions, the relaxation time⁶ is

$$\tau = \frac{dm}{d(X-X_1)} \frac{1}{a} = \frac{d \log m}{d \log(X-X_1)} \frac{1}{\beta} \quad (3)$$

Where m is the average aggregation number of micelles, a is the average fusion probability, and β is the average fission probability.

For elongated micelles, the average probability of the fission is proportional to the average micellar length and the relaxation time obtained with eq 3 is the same than this given by Cates,

$$\tau = \frac{1}{2k_b m}$$

where k_b is the breakup probability per unit length.

Variation of Scattering Intensity under T-Jump. In the dilute range, a variation of micellar size brings on a change of scattering light intensity. In the strongly entangled regime, the intensity change is due to the variation of the correlation length with the temperature. In the vicinity of the crossover between the dilute and semidilute regime, both effects can coexist, and if the associated relaxation times are different enough, time-resolved experiments allow analysis of both of them. The amplitudes of these two relaxations are given by two semi-empirical formulas:⁸

$$\left(\frac{\Delta I}{I}\right)_{\text{break}} \cong \frac{1}{1 + 0.95(C/C^*)^{1.64}} \quad (4)$$

$$\left(\frac{\Delta I}{I}\right)_s \cong \frac{(C/C^*)^{1.64}}{1 + 1.05(C/C^*)^{1.64}} \quad (5)$$

where C^* is the crossover concentration.

Materials and Methods

The micellar solutions were prepared, at high temperature, by dissolution of SDS (Fluka Biochemika grade) used without purification.

The T-jump, scattering light, and viscometer devices have been described in ref 8.

Numerical calculus simulates the variation of the relaxation frequency with the surfactant concentration. For an assigned energy distribution $F(n)$, the value of m is computed

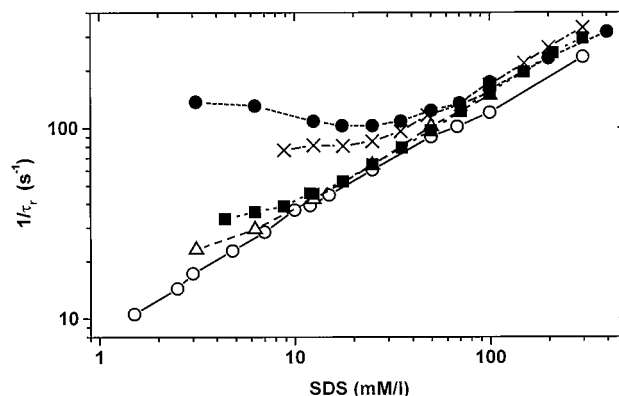


Figure 1. Inverse of relaxation time vs SDS concentration for different NaCl concentrations: (○) 1 mol/L; (△) 0.8 mol/L; (■) 0.76 mol/L; (×) 0.65 mol/L; (●) 0.60 mol/L.

for different values of the surfactant concentration with the equation set

$$m = \frac{\sum_{n_0}^{\infty} nF(n)}{\sum_{n_0}^{\infty} F(n)} \quad c = \sum_{n_0}^{\infty} nF(n)$$

where c is the surfactant concentration and n_0 is the aggregation number of spherical micelles.

The obtained curve is numerically derived and the result is multiplied by the fusion rate.

The light scattering intensity I_s is proportional to

$$I_s \propto cm_w = \sum_{n_0}^{\infty} n^2 F(n)$$

Experimental Section Results

T-Jump Experiments. The relaxation curves after T-jump are strongly depending on the surfactant concentration range investigated. At low concentration, a single relaxation process is observed with an associated time independent of scattering wave vectors. These measurements are carried out in a dilute regime. At high concentration, two relaxation processes are observed. In this case, the time of the fast process depends on scattering wave vectors, whereas the time of slow process is independent of the wavelength of light and diffusion angles. The solutions are studied in the vicinity of the overlap concentration. In CTAB solutions, the same behavior has been observed.⁸

Figure 1 shows the surfactant concentration dependence of the reciprocal of the slow relaxation time τ_r , which is independent of the scattering wave vector for SDS solutions in five salt concentrations (NaCl = 0.6, 0.65, 0.76, 0.8, and 1 mol/L). In 0.6 mol/L NaCl solutions, the relaxation time is nearly constant at low SDS concentration and decreases only on the high concentration range. When the salt concentration increases, the relaxation frequency is nearly independent of NaCl concentration for high SDS concentrations. On the low SDS concentration range, the weak variation of τ_r , that is observed for 0.6 mol/L NaCl solutions cannot be measured at upper NaCl concentration because the scattered light intensity is too low. Only the beginning of this behavior is observed. In the 1 mol/L NaCl solutions, the relaxation frequency obeys a scaling law with an

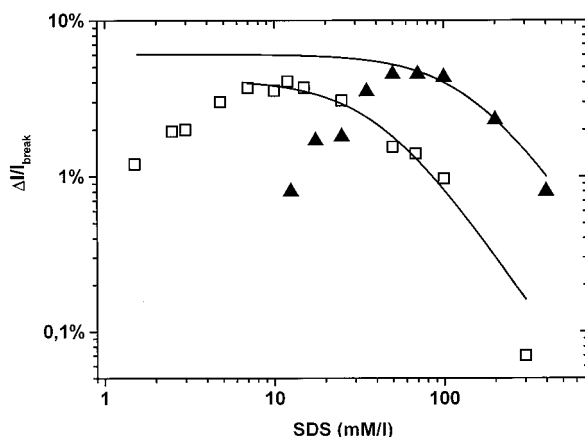


Figure 2. $\Delta I/I_{\text{break}}$ vs SDS concentration for two NaCl concentrations: 1 mol/L (open symbols); 0.6 mol/L (close symbols).

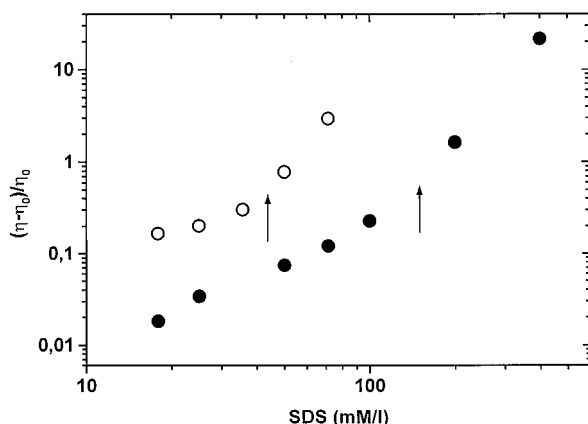


Figure 3. Relative viscosity vs SDS concentration for two NaCl concentrations: (○) 1 mol/L; (●) 0.6 mol/L. The arrows indicate the concentration corresponding to C^* .

exponent equal to 0.58 which is very close of the value expected for elongated micelles.

We have reported in Figure 2 the SDS concentration dependence of the relaxation amplitudes $\Delta I/I_{\text{break}}$ ratio associated with the q -independent time for a diffusion angle of 90° . The curves are the best fit of eq 4 to $\Delta I/I_{\text{break}}$ measurements and allow C^* to be determined. The shape of the curve at 0.6 mol/L NaCl brine is very similar to those at 1 mol/L, but its maximum is shifted. This shift shows that the crossover concentration C^* is different for the two salt concentrations. The C^* values are 43 and 150 mmol/L for, respectively, 1 and 0.6 mol/L NaCl solutions.

The concentration variation of $\Delta I/I_s$ is similar to the observed variation for CTAB solutions.⁸

Viscosity and Light Scattering Measurements. Capillary viscosity measurements of SDS solutions were performed on the two extreme brine concentrations (0.6 and 1 mol/L NaCl). Relative viscosity is reported in Figure 3. The crossover between dilute and semidilute regimes is characterized by a large increase in the viscosity. The arrows indicate the C^* value determined from $\Delta I/I_{\text{break}}$ fit with eq 4 and show that the onset of the viscosity increase is close to the C^* .

Figure 4 shows the variation with surfactant concentration of the scattered light intensity I_s and of the hydrodynamic radius R_h obtained respectively by static and dynamic light scattering techniques. The ionic strengths of samples are the same as in the viscosity measurements. This figure shows clearly that for a given SDS concentration the micellar length is longer at 1 mol/L NaCl than at 0.6 mol/L NaCl.

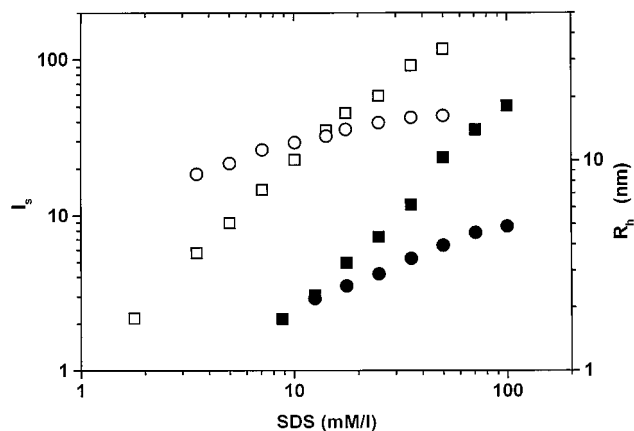


Figure 4. Scattered intensity (■) (left axis) and hydrodynamic radius (○) (right axis) vs SDS concentration for two NaCl concentrations: 1 mol/L (open symbols); 0.6 mol/L (close symbols).

Discussion

From Figure 1 let us discuss the information obtained on the highest and the lowest ionic strength. The measurements in middle brine solutions illustrate continuous adjustment of the relaxation curve between these two extremes.

At 1 mol/L NaCl, the relaxation time obeys a scaling law with an exponent of 0.58, close to 0.5 which is the theoretical value for the wormlike micelles. The measured value is unaffected by the transition between the dilute and semidilute regime. The constant value of the exponent on the overall surfactant concentration range studied is an indication that the fusion process is not controlled by diffusion. Indeed, the ordinary assumption that the break up probability by unit length is independent of the micellar length implies that the fusion probability is also independent of the micellar length. Also, it is very unrealistic that the volume explored by the end of a micelle by unit time is the same in the dilute regime as in the semidilute regime.

At 0.6 mol/L NaCl, the relaxation frequency is nearly constant in the low concentration range, and above 70 mmol/L SDS it increases with the concentration. In this concentration range, the exponent of the scaling law is very close to the one found with 1 mol/L NaCl solutions.

Numerical simulations of the variation of the frequency relaxation with surfactant concentration were given in a recent paper.⁶ They show the possibility of a weak variation of the relaxation frequency with the concentration at the beginning of the growth process. This behavior can be observed when the spherical micelles are energetically favored or when a gap appears in the energy distribution. The above results on SDS solutions can be fitted by similar simulations.

In the first case, where the short micelles are favored (Figure 5a), fit simulations give the relaxation frequency and the scattering light intensity versus concentration illustrated respectively in parts b and c of Figure 5. The value of I_s is proportional to the product of the weight-average aggregation number by the surfactant concentration. The parameters for the short micelles are selected to give a good fit, but the accuracy of the parameters is poor. Indeed, a decrease of the peak width of $F(n)$ can be corrected by taking an energy value which favors more the short micelles.

In parts a–c of Figure 6 are reported the results of fits for a gap in the size distribution. The accuracy of the parameters is also poor. In the first case, the exponent of the scaling law of the relaxation frequency tends toward 0.5 when the surfactant concentration increases but with a value lower than 0.5 whatever

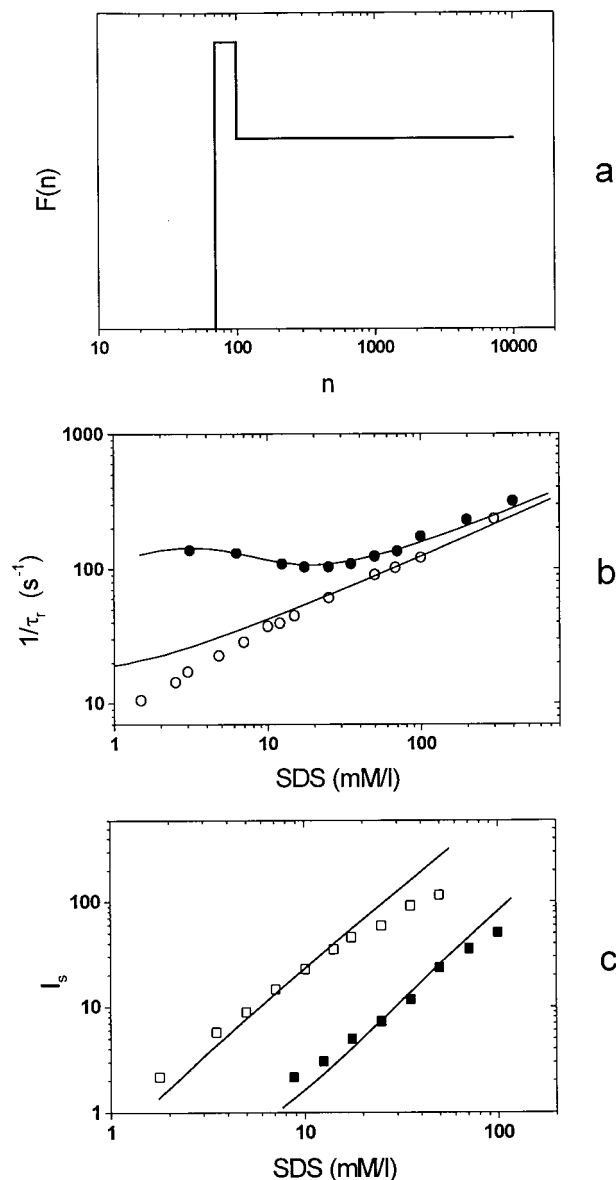


Figure 5. Measurements and simulation results: (a) shape of model; (b) inverse of relaxation time; (c) scattered intensity; for 1 mol/L NaCl (open symbols) and 0.6 mol/L NaCl (close symbols).

the choice of parameters. In the second case, it tends toward 0.5 with a larger value (see ref 6, Figures 2 and 3).

A third case where an energy distribution favors the spherical micelles and which reduces the number of micelles sizing close to $2n_0$, has been reported in Figure 7a. A good fit can be obtained for the relaxation time (Figure 7b) and for the scattered intensity (Figure 7c). The accuracy of the parameters is poor because the relaxation frequency cannot be accurately measured under the concentration of the relaxation frequency minimum. Indeed, the micelle size varies slowly with the temperature, and the variation of the scattered intensity is too small to do accurate measurements.

The parameter $F(n)$ is an evaluation of the energy value of the micelle fission. Its values for the three models are reported in Table 1 and the fusion probability in Table 2. The $F(n)$ values are close to each other, and these simulations show a large sensitivity of relaxation frequency to the energy distribution. Indeed, for the last simulation, the fission of an elongated micelle into two elongated micelles requires $1.4kT$ more than the fission into a spherical micelle and an elongated micelle and $0.7kT$ less

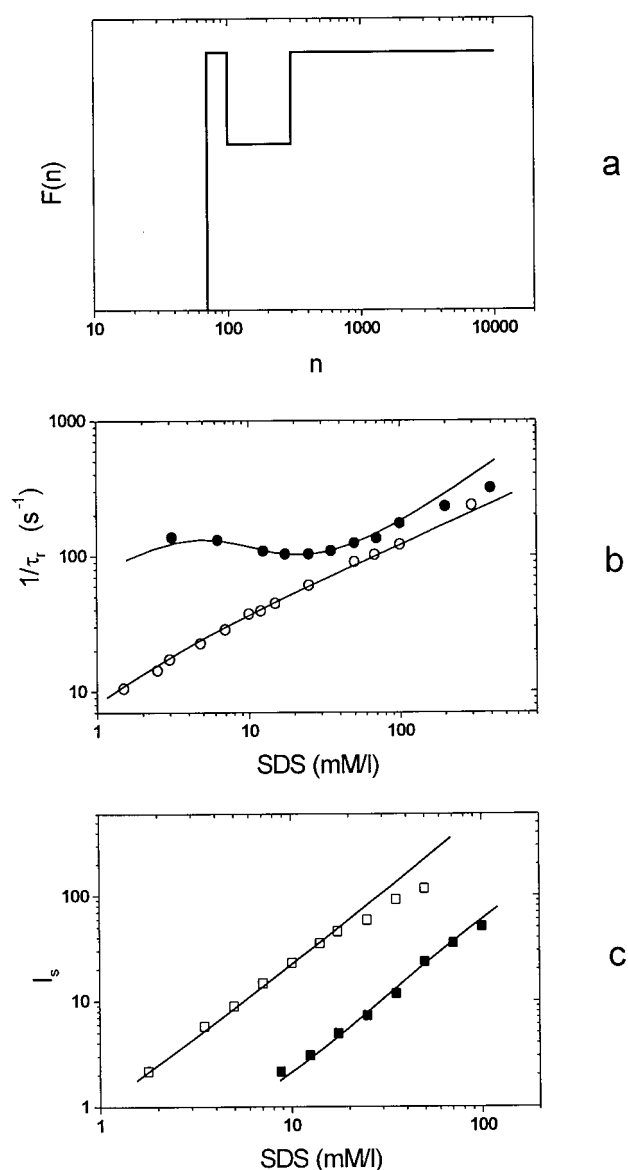


Figure 6. Same legend as for Figure 5.

than the fission into a micelle of sizing close to $2n_0$ and an elongated micelle.

In Table 1 is also reported the value which has been obtained by Missel⁹ et al. from dynamic light scattering. This value is very close to our value for elongated micelles.

For the 1 mol/L NaCl brine, reported values of $F(n)$ are the product of the $F(n)$ values at 0.6 mol/L NaCl brine by a constant which gives a good fit for the scattered intensity. We have not tried to determine the $F(n)$ values from the relaxation frequency in the absence of a relaxation frequency minimum.

The spherical or elliptical shape has been assumed¹⁰ for short micelles. For the elongated micelles, the radius of the end cap is assumed to be the same as the radius of the cylindrical part of micelles. This assumption simplifies the calculus and is negligible when the micellar length is larger than the minimum length of micelles. In a theoretical paper, Nagarajan et al.¹¹ work out the radius of the spherical part and that of the cylindrical part of elongated micelles. They found for SDS micelles that the radius of the cylindrical part is smaller than that of the spherical part. They assume an end cap with a spherical shape but larger than a hemisphere. Under this assumption, the weld between the end cap and the cylindrical part of micelles has a

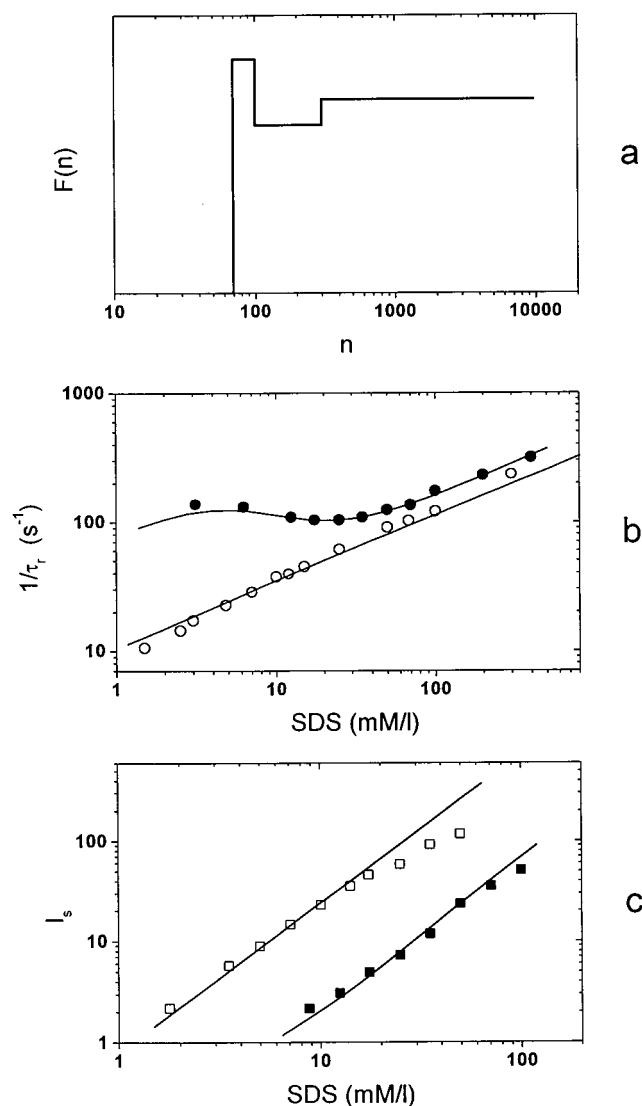


Figure 7. Same legend as for Figure 5.

TABLE 1: $-\log(F(n))^a$

C_{NaCl} (mol/L)	$n = 70-100$		$n = 100-300$		$n = 300$ to infinity	
	0.6	1	0.6	1	0.6	1
Figure 5	11.9	15.3	11.9	15.3	14.2	17.6
Figure 6	10.7	16.9	12.6	18.8	10.7	16.9
Figure 7	11.2	16.3	13.3	18.1	12.6	17.4
Missel	12.2 ⁹ , 13.5 ¹²	18	12.2, 13.5	18	12.2, 13.5	18

^a In the last row, $F(n)$ values are the reciprocal of Missel's K values. Missel using a molecular concentration ratio in surfactant mole by water mole, we have recalculated his values in mol/L.

TABLE 2: Fusion Probability (mol/L s)⁻¹

	C_{NaCl} (mol/L)	
	0.6	1
Figure 5	0.25×10^6	1.3×10^6
Figure 6	0.13×10^6	0.9×10^6
Figure 7	0.15×10^6	1.1×10^6

negative bending. The energy cost of a negative bending is larger than that of a positive bending for micelles, and it is easier to bind two hemispheres than to bind a spherical end cap to the cylindrical part of micelles.

Under these assumptions, micelles with a size close to $2n_0$ are disadvantaged because they have the negative curving part without the cylindrical part.

The values of the fusion rate reported in Table 2 are lower than the value of the collision rate frequency which is for spherical micelles with the same radius:

$$\frac{4kT}{3\eta}$$

The estimated value of the potential barrier is $11kT$ for 0.6 mol/L NaCl samples and $8kT$ for 1 mol/L samples. These large values for solutions with high salt concentration cannot be explained by electrostatic repulsion only if the attractive potential is unusually low. The fusion of micelles is not controlled by the diffusion. This assumption is consistent with the fact that, in the case of SDS in 1 mol/L NaCl brine, the exponent of the scaling law is the same in the dilute regime as in the semidilute regime. The limiting step for fusion or fission of micelles is perhaps to make up a constriction on the cylindrical part. This constriction has a negative bending, and the probability that the cylindrical part of an elongated micelle has a segment with a negative bending is very low. This probability increases with the salt concentration, and the potential barrier decreases. We have taken a constant value for the fusion probability. This assumption supports that the energy value of one constriction is independent of the micelle length.

Conclusion

For SDS micelles in NaCl brine, the relaxation times associated with the fusion–fission process vary little in the low SDS concentration range. This concentration range corresponds to the range where the growth of micelles begins. The measurements of the relaxation frequency as a function of the SDS concentration have been fitted by the theoretical expression. Analysis of these fits dismisses the fact that the end cap is a simple hemisphere. Assuming that the end cap diameter is larger than the one of the cylindrical part, a size distribution is proposed which favors the spherical micelles. This hypothesis disadvantages also the micelles of sizing close to $2n_0$, because they have negative bending without the cylindrical part. The values of the fusion probability of micelles are obtained. The kinetics of the fusion–fission is not controlled by the diffusion but by a step following collision of two micelles.

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