Simulation Study to Model Extremely Slow Reaggregation Processes in Micelle Solutions

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Photon correlation measurements on the dodecylpyridinium iodide/water system as nuclei had shown that large micelles are formed after a temperature jump from 80 to 25 °C. The micellar radius exhibits relaxation characteristics with extremely long relaxation times, reaching values up to several hours. Proceeding from a thermodynamic approach of the size distribution of aggregates, model calculations have been performed in which the nonlinearized rate equations of the underlying isodesmic reaction scheme have been used to describe the micelle kinetics. The results of these calculations give valuable indications of the mechanism behind the extremely slow relaxation. In the solutions under consideration, the nucleation of a sufficient number of micellar aggregates obviously is hindered by the extremely unfavorable equilibrium concentration of intermediates of submicellar size. This leads to a strongly deviating nonequilibrium distribution with an excess of extra large micelles during thermal equilibrium. Establishing the final equilibrium is then a very slow process, due to the low monomer concentration, which is maintained by the presence of the extra large micelles. Our model is also capable to verify the slow and fast relaxation process as predicted by the linearized Aniansson−Wall model. It also shows up the ultrafast process of oligomer formation as studied recently by broadband ultrasonic spectrometry.

1. Introduction

Much attention has been directed toward the self-assembly of surfactant molecules in water, forming microstructures named micelles. Micelles are capable of forming a variety of shapes, and they can display a rich dynamic behavior. Micelles are thus considered useful systems for the study of molecular aggregation processes.[1−3] Surfactant systems with small critical micelle concentration cmc, in which predominantly 'proper' micelles are formed, normally exhibit kinetics of aggregation that can be described in terms of an isodesmic reaction scheme. On the basis of this scheme, the widely accepted Aniansson−Wall model[4−8] predicts the mechanism of micelle formation/disintegration to be characterized by two relaxation times, τ_s, and τ_f. Relaxation time τ_s, which is in the order of milliseconds or seconds, reflects the formation and disintegration of micelles at almost constant mean aggregation number $\bar{m}$ of the equilibrium micellar size distribution $\bar{N}_i$. The relaxation time τ_f is related to the change of $\bar{m}$ at nearly constant number of micellar species. Within the framework of the Aniansson-Wall model the equilibrium concentration $\bar{N}_i$ of micelles, made of i monomers, at $i > 10$, is assumed to follow a Gaussian distribution function. The latter ('f') process in the size distribution reformation proceeds considerably faster than the former ('s'). Hence, τ_f adopts values in the range of nanoseconds or microseconds.

Recently, both ultrafast (uf) and extremely slow (es) relaxation processes in micelle solutions have been reported.[9,10] The ultrafast process ($\tau_{uf} < 1$ ns) seems to be characteristic for micelle solutions with surfactant concentration near the cmc. It has been shown[11] to be due to the reactions of monomers with submicellar structures ($i < 10$). The extremely slow process, with a relaxation time τ_{es} of minutes or hours, is the nonlinear response of the micellar system to strong disturbances. In Figure 1 the time dependence of the mean micellar radius $\bar{r}$, as recorded by dynamic light scattering,[10] is displayed after a rapid change in temperature of a 5.5 mM aqueous solution of *n*-dodecylpyridinium iodide (DoPI). The variation of the mean radius shown in this diagram reflects the extremely slow reformation of the micellar size distribution after the temperature had been changed from 80 °C (cmc ≈ 8.6 mmol/L > c) to 25 °C (cmc ≈ 5.1 mmol/L < c.[10]).

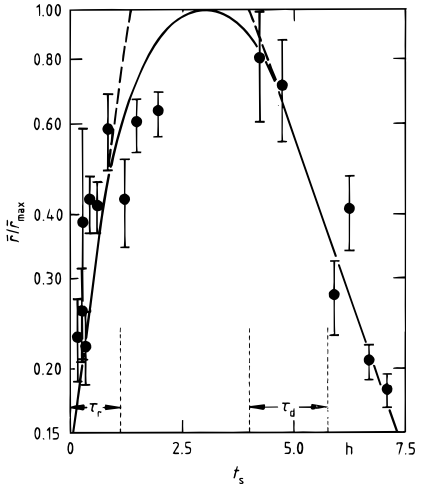

Figure 1. Mean radius $\bar{r}$ of micelles in a 5.5 millimolar aqueous solution of *n*-dodecylpyridinium iodide, normalized to the maximum value $\bar{r}_{max}$, logarithmically displayed as a function of the interval t_s after application of a temperature jump from 80 to 25°.[10] Parameters τ_r and τ_d denote the rise time and decay time, respectively, for the changes in $\bar{r}$.

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In this article, results of a model simulation study are reported to show that the unusual slow relaxation process can be explained theoretically if the rate equations resulting from the simple isodesmic reaction scheme of micelle formation are not linearized with respect to the relative deviations of actual concentrations from their equilibrium values. As a byproduct, our model, applied to surfactant concentrations slightly above the cmc, also evidences the existence of the ultrafast relaxation process.

2. NonLinearized Isodesmic Reaction Scheme

It is one aim of this study to find out whether the isodesmic reaction scheme of micelle kinetics[4−8] is capable of explaining the afore described extremely slow reaggregation process. This scheme of coupled reactions may be expressed by the N-1 individual steps

$$N_1 + N_{i-1} \underset{k_i^b}{\overset{k_i^f}{\rightleftharpoons}} N_i, \quad i = 2, ...N \tag{1}$$

with N_i denoting the concentration of aggregates made of i surfactant molecules and with k_i^f and k_i^b being the forward and backward rate constants, respectively. Applying the above reaction scheme, it is assumed that the monomer concentration N_1 substantially exceeds the concentrations N_i of the multimers ($i = 2, ..., N$) so that direct association of higher order structures is of low significance.

Within the framework of this model the response of the surfactant system to an external disturbance is treated in terms of the relative deviations

$$\xi_i(t) = (N_i(t) - \bar{N}_i)/\bar{N}_i \tag{2}$$

of the actual concentrations N_i(t) from the equilibrium values $\bar{N}_i$. For all multimers, except the largest micelles, the time dependence of concentration is governed by the rate equations ($2 \le i \le N - 1$)

$$\bar{N}_i \frac{d\xi_i(t)}{dt} = k_{i+1}^b \bar{N}_{i+1}[\xi_{i+1} - \xi_i(1 + \xi_1) - \xi_1] - k_i^b \bar{N}_i[\xi_i - \xi_{i-1}(1 + \xi_1) - \xi_1] \tag{3}$$

In order to restrict the reaction scheme to a finite number of equilibria, the micelles containing N monomers are assumed to be prevented from further growth. Hence

$$\bar{N}_N \frac{d\xi_N(t)}{dt} = -k_N^b \bar{N}_N [\xi_N - \xi_{N-1}(1 + \xi_1) - \xi_1] \tag{4}$$

According to the underlying set of coupled equilibria (eq 1), monomers do not just react with other monomers but also with all surfactant multimers so that

$$\bar{N}_1 \frac{d\xi_1(t)}{dt} = 2k_2^b \bar{N}_2[\xi_2 - 2\xi_1 - \xi_1^2] + \sum_{i=2}^{N} [k_i^b \bar{N}_i(\xi_i - \xi_{i-1}(1 + \xi_1) - \xi_1)] \tag{5}$$

In the Aniansson−Wall model,[4−8] the rate eqs 3−5 have been considered for small disturbances only. Consequently, quadratic terms $\xi_i\xi_1$ have been neglected throughout. In addition, the micellar sizes have been supposed to follow a Gaussian distribution function with mean aggregation number $\bar{m}$ and variance σ^2, and it has been also assumed that the concentration of oligomers is small as compared to the monomer concentration $\bar{N}_1 \approx$ cmc. The time dependence of the system is then characterized by the aforementioned slow (τ_s) and fast (τ_f) relaxation times, given by the relations

$$\tau_s^{-1} = \frac{\bar{m}^2}{N_1} F \left(1 + \frac{\sigma^2}{\bar{m}} X\right)^{-1} \tag{6}$$

and

$$\tau_f^{-1} = k^b \sigma^{-2} \left(1 + \frac{\sigma^2}{\bar{m}} X\right) \tag{7}$$

where

$$X = (N_{tot} - \bar{N}_1)/\bar{N}_1, \quad N_{tot} = \sum_{i=1}^{N} iN_i \tag{8}$$

is the ratio of concentration of amphiphiles in aggregates to that of monomers. In eq 6

$$F = [\sum_{i=2}^{N_0} (k_i^b \bar{N}_i)^{-1}]^{-1} \tag{9}$$

denotes the small flux in the transition range between monomers and micelles. Here N_0 is the maximum aggregation number of oligomers that are considered to belong to this range. In eq 7 k^b denotes the mean backward rate constant for micelles with sizes at around the mean ($k^b \approx k_{\bar{m}}^b$). The relaxation time τ_f represents a fast exchange of monomers between micelles by which the number of micelles remains unaltered. This exchange process has been studied recently by ultrasonic spectrometry and it was found that, in the case of short-chain amphiphiles, eq 7 does not apply for the experimental findings at concentrations slightly above the cmc.[9] The relaxation time τ_s is characteristic of the formation/decay of micelles. It is thus accompanied by a change in the total concentration $\sum_{i=2}^{N} \bar{N}_i$ of micelles. As already mentioned in the Introduction the slow relaxation time τ_s typically adopts values in the order of milliseconds or seconds. Hence the redistribution reflected by the process with relaxation time τ_s also cannot be the reason for the extremely slow approach of a new equilibrium as observed in the light scattering study (Figure 1). Because of the strong change in temperature applied here to the sample under test, it appears to be useful to consider the nonlinearized version of the system of kinetic equations. Unfortunately, however, the set of coupled nonlinear differential equations 3−5 cannot be solved analytically. In order to study the kinetics of micelle formation, the rate equations have thus been treated numerically.

3. Numerical Evaluation. Size Distribution and Rate Constants

Integrating the system of differential equations 3−5 the Runge−Kutta method[12−15] appeared to be superior to the Bulirsch−Stoer and the predictor−corrector routines.[16] In the numerical calculations we always used constancy of the total concentration N_{tot} (eq 8) of amphiphile molecules as an indication for the stability of the solutions ($\Delta N_{tot}/N_{tot} < 10^{-12}$).

In the recent treatment of the micelle kinetics in solutions of short-chain surfactants[9] the size distribution of aggregates has been derived from empirical relations for the forward and backward rate constants, based on reasonable assumptions. Here we proceed from a size distribution function which we have

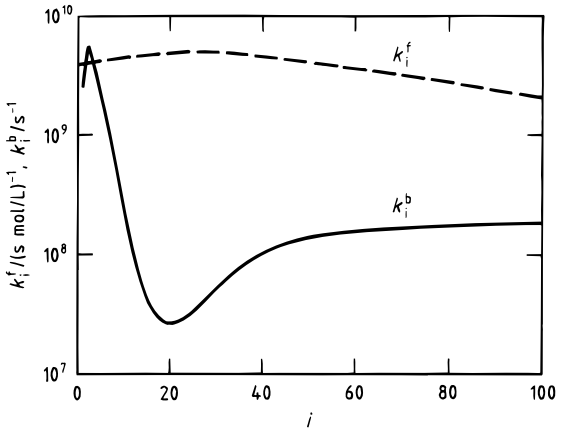

Figure 2. The forward and backward velocity constant k_i^f and k_i^b, respectively, as used in the model calculations, displayed versus the aggregation number i of surfactant.

recently deduced from thermodynamic principles.[17] Analyzing possible relevant enthalpic and entropic contributions driving aggregation, it was found that an hydrophobic entropy, resulting from a reduction in allowed orientations of solvent hydrogen bonds in the neighborhood of hydrophobic parts of solute molecules (or aggregates), is the dominating factor influencing the size distribution. The distribution function is given by known molecular quantities and only a few free parameters.

In addition to the size distribution, one set of velocity constants has to be known in order to allow for the development in time of the surfactant system. We prefered to select an empirical function for the forward rate constants and to derive the backward constants applying the law of mass action

$$k_i^b = k_i^f \bar{N}_1 \bar{N}_{i-1}/\bar{N}_i, \quad i = 2, ..., N \tag{10}$$

with equilibrium concentrations obtained from a thermodynamic model.[10]

The forward rate constants reflect the probability for a monomer to enter, within a given period, an aggregate of $i - 1$ monomers and thereby to form an i-mer. Hence the k_i^f are first given by the effective cross section which an $(i - 1)$-mer offers to the surfactant monomers. Assuming spherically shaped particles[18] of radius r_i

$$k_i^f \propto (D_{i-1} + D_1)(r_{i-1} + r_1) \tag{11}$$

follows. Here the D_i denote the diffusion coefficients of the particles. If, according to the Einstein−Stokes relation,[19] $D_i \propto r_i^{-1}$ is used and $r_i = r_1(i)^{1/3}$ is inserted, the k_i^f may be written as

$$k_i^f = \hat{k}^f(i)[1 + (i - 1)^{1/3}]^2 (i - 1)^{-1/3} \tag{12}$$

Herein $\hat{k}_f(i)$ is a function describing the probability for a monomer that reached the surface of an aggregate to become incorporated into the micelle.With increasing i the molecules within micelles get more and more tightly packed. Hence at high i there will be less free volume available for an additional molecule to get in. At least in the micelle regime $\hat{k}_f(i)$ is thus expected to decrease with i. In conformity with the assumptions of ref 9, we used a k_i^f-versus-i relation as displayed in Figure 2. Numerical calculations have been also performed with other forward rate constant profiles, for instance assuming $\hat{k}_f(i)$ (= 10^9 s^{-1} $(mol/L)^{-1}$) to be independent of i. It was found that the results discussed below are only insignificantly affected by the particular details of the k_i^f-versus-i relation.

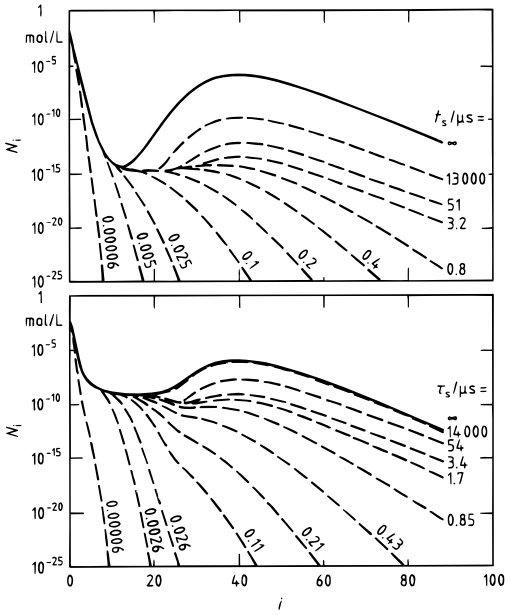

Figure 3. The size distribution $N_i(i)$ of surfactant aggregates at various intervals t_s after application of a temperature jump from 80 to 25 °C. The upper diagram shows the results from model calculations that have been started with the original distribution. The lower plot gives results from calculations which have proceeded from a modified distribution containing higher oligomer concentrations. The full curves represent the equilibrium distributions at 25 °C toward which the surfactant systems tend.

Time dependent size distributions, after disturbance by a temperature change of a solution with concentration $c = 1.01$ cmc, have first been calculated in order to verify the predictions from the linearized Aniansson−Wall model. When simulating a temperature jump from 80 to 25 °C, as applied in the light scattering experiments, it turned out that very long computing times were required to completely follow the approach of the new equilibrium distribution. It was nevertheless possible to verify the fast relaxation mechanism in the Aniansson−Wall model ($\tau_f = 5 \times 10^{-7}$ s). In order to effectively reduce the computing time and to be, therefore, able to also study the second process with relaxation time τ_s, the equilibrium size distribution of aggregates has been modified in the oligomer region by increasing the concentration at the relative minimum from about 10^{-15} mol/L to almost 10^{-9} mol/L. The time development of the resulting distribution function is discussed in the following chapter.

4. Results and Discussion

The time development of the size distribution of aggregates, when a temperature jump from 80 to 25 °C has been applied, is shown in Figure 3. Results from numerical simulations for the original system as well as for that with modified oligomer content are presented for comparisons. In these calculations all surfactant has been assumed to be molecularly dispersed at 80 °C. After the short period of 400 ns, when a noticeable amount of small aggregates has been formed from the monomers, a comparatively broad size distribution results for both systems. This distribution somewhat sharpens at increasing concentration of large micelles. The equilibrium concentration of the original model is not reached after a period of 13 ms (corresponding with a computing time of 2 days). The modified model, however, adopts its new equilibrium during that period.

In order to look for the relevance of the modified model we also studied the system of coupled differential equations at small

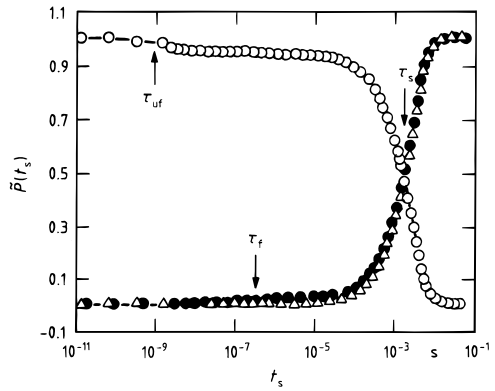

Figure 4. Relative variation $\tilde{P}$ (eq 13) of some parameters with the time interval t_s after application of a small distortion to the sample under consideration. The following quantities as derived from the model calculations are shown: (○) N_1 ($P(0) = 17.99 \times 10^{-3}$ mol/L, $\hat{p} = -1.51 \times 10^{-4}$), (●) $\sum_{i=2}^{N} iN_i$ ($P(0) = 5.98 \times 10^{-4}$ mol/L, $\hat{p} = 5.1 \times 10^{-3}$), and (△) $\sum_{i=2}^{N} N_i$ ($P(0) = 1.42 \times 10^{-5}$ mol/L; $\hat{p} = 3.35 \times 10^{-3}$; $\hat{p} = (P(\infty) - P(0))/P(0)$).

disturbances from equilibrium. In those runs the equilibrium distribution has been altered by less than 0.5%. The response of the modified model is displayed in Figure 4, where the relative variation

$$\tilde{P}(t_s) = (P(t_s) - P(0))/(P(\infty) - P(0)) \qquad (13)$$

of the following parameters is shown as a function of the time interval t_s after application of the disturbance: the monomer concentration ($P = N_1$), the concentration of all associated molecules ($P = \sum_{i=2}^{N} iN_i = N_{tot} - N_1$), and the concentration of all aggregates ($P = \sum_{i=2}^{N} N_i$). The slow relaxation process of the Aniansson−Wall theory clearly emerges in these parameters. In our model system the corresponding relaxation time τ_s adopts a value ataround 2 ms. The fast process of micelle reformation ($\tau_f \approx 0.3\,\mu$s) appears in the concentration of associated surfactant molecules only. The relative variations $\tilde{P}(t_s)$ are rather small here because the initial size distribution in the simulation differs from the equilibrium distribution function just by slightly altered amplitudes in the micelle regime. The mean aggregation number $\bar{m}$ and the width of the distribution function have been kept constant in the model calculations. At times around 1 ns there is also a small step in the N_1-versus-t_s relation. This ultrafast process becomes significantly more obvious if a stronger disturbance is applied to the model system (Figure 5). It reflects the oligomer/monomer reactions[9] mentioned in the Introduction.

As also briefly mentioned afore, various additional model calculations have been performed varying both the size distribution of aggregates and the k^f_i-versus-i relation significantly. We found the relaxation times τ_{uf} and τ_f of the ultrafast and the fast relaxation process, respectively, to be almost independent of these alterations. Larger changes (up to a factor of 10) have been found in the values of τ_s. It also turned out that the Aniansson−Wall theory (eq 6) predicts τ_s-values which differ by more than a factor of 10^3 from ours. Equation 6 might thus be questioned. It is interesting to notice that Lessner et al.,[20] applying pressure jump techniques to aqueous solutions of ionic surfactants, found τ_s-values up to 10^3 times larger than resulting from equation 6. In addition, their measurements revealed a negative slope in the τ_s-versus-c dependence at concentration slightly above the cmc. These experimental findings have been consistently explained on the basis of the law of mass action

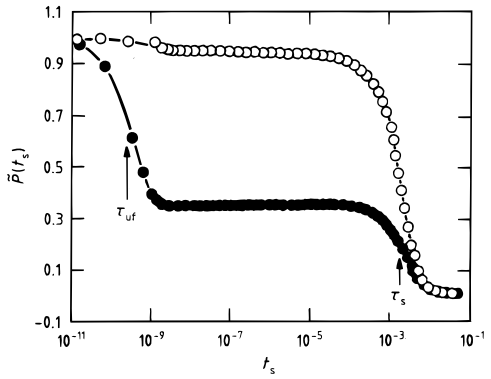

Figure 5. Relative variation $\tilde{P}$ (eq (13)) of the monomer concentration $N_1(=P)$ with the interval t_s after application of a distortion with small (○, Figure 4) and high amplitude (●; $P(0) = 19.6 \times 10^{-3}$ mol/L, $\hat{p} = (P(\infty) - P(0))/P(0) = -8.5 \times 10^{-2}$).

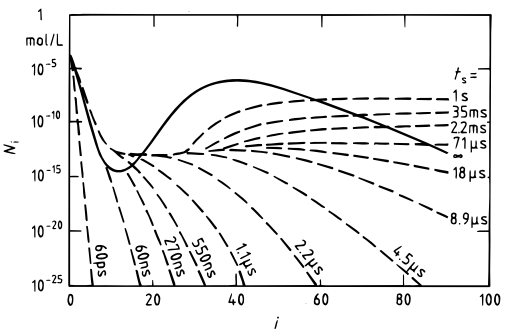

Figure 6. Size distribution function $N_i(i)$ at different time intervals t_s after application of a temperature jump from 80 to 25 °C as resulting from simulation of a model with reduced monomer and dimer concentrations.

by explicitely taking into account the mechanism of counter ion reorganization in the rate equations describing the kinetics of the system.[21] The discrepancy between the predictions of the Aniansson−Wall model and ours, however, is only due to the neglection of nonlinear terms in the analytical treatment of the former approach.

Even the large τ_s-values as resulting from the original nonlinearized kinetic equations, however, cannot account for the extremely slow relaxation process measured in the light-scattering experiments. We therefore again modified the size distribution of aggregates by reducing the concentration of monomers from 1.8×10^{-2} mol/L to 10^{-3} mol/L and the concentration of dimers from 5×10^{-4} mol/L to 10^{-5} mol/L. As shown by the results plotted in Figure 6 this system responds quite differently to an external distortion than the previous ones (e.g., Figure 3). After the period of about 100 μs a size distribution arises which does not exhibit a relative maximum in the micellar region. During the following second all concentrations N_i of micelles with aggregation numbers i larger than about 30 increase continuously. During this period the shape of the distribution function remains nearly unaltered and the surfactant system obviously is still far away from its equilibrium. According to our expectations the velocity of reaggregation is substantially cut down by a reduction in the monomer concentration N_1. Integration of monomers by existing aggregates appears to be less affected by this reduction so that predominantly large micelles are formed. These large micelles cannot be converted sufficiently fast into smaller aggregates to enable the surfactant system to adopt its equilibrium size distribution as rapidly as normally.

5. Conclusions

The results of this model simulation study strongly support the intuitive discussion of our light scattering experiments. After the fast change in the sample temperature from 80 to 25 °C there suddenly exists an excessive concentration of surfactant monomers. Tending to reduce this concentration and thus the effect of hydrophobic hydration, monomers are first deposited at the surface of existing nuclei, like dust particles or micelles that are already present. The excessive monomer content is rapidly reduced by this deposition. However, a nonequilibrium size distribution of aggregates results which is characterized by a comparatively low oligomer concentration. There exists also a small number of aggregates with an unusual high content of large particles. Such an overshoot in the particle size distribution is only possible when the nonlinear terms in the rate equations become dominant. Simulations of the linear equations under similar conditions lead to negative concentration values for the oligomer intermediates during the equilibration process. The model calculations clearly reveal that a system with such distorted size distribution needs an extra ordinary long time to adopt its equilibrium. The process requires the complete reassembly of normal-size micelles from monomers whose concentration is buffered by the presence of an excess of large-size micelles. Establishing the final equilibrium of the size distribution, accompanied by corresponding changes in the total number of micellar aggregates, requires a third relaxation process in excess to those with relaxation times τ_s and τ_f, respectively. This additional extra slow relaxation process reflects a third chemical reaction (in normal coordinates). It becomes obvious by measuring the size distribution after a strong perturbation. The third relaxation time will be hardly observable by experimental methods that are sensitive to monomer concentration, but that scarcely depend on the size distribution of the aggregates.

References and Notes

(1) Tanford, C. *The Hydrophobic Effect*, 2nd ed.; John Wiley and Sons: New York, 1980.
(2) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: New York, 1992.
(3) Gelbart, W. M., Ben-Shaul, A., Roux, D., Eds. *Micelles, Membranes, Microemulsions, and Monolayers*; Springer: Berlin, 1994.
(4) Aniansson, E. A. G.; Wall, S. N. *J. Phys. Chem.* **1974**, *78*, 1024.
(5) Aniansson, E. A. G. *J. Phys. Chem.* **1978**, *82*, 2805.
(6) Aniansson, E. A. G. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 981.
(7) Aniansson, E. A. G. In *Techniques and Applications of Fast Reactions in Solution;* Gettins, W. J., Wyn-Jones, E., Eds.; Reidel: Amsterdam, 1979; p 249.
(8) Aniansson, E. A. G. *Prog. Colloid Poly. Sci.* **1985**, *70*, 2.
(9) Telgmann, T.; Kaatze, U. *J. Phys. Chem.* **1997**, *101*, 7758.
(10) Trachimow, C.; DeMaeyer, L.; Kaatze, U. *J. Phys. Chem. B* **1998**, *102*, 4483.
(11) Telgmann, T.; Kaatze, U. *J. Phys. Chem.* **1997**, *101*, 7766.
(12) Dormand, J. R.; Prince, P. J. *J. Comput. Appl. Math.* **1980**, *6*, 19.
(13) Fehlberg, E. *Computing* **1969**, *4*, 93.
(14) Fehlberg, E. *Computing* **1985**, *34*, 265.
(15) Heinzel, G. *c't Mag. Computertechnol.* **1992**, *8*, 172.
(16) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes in C*; Cambridge University Press: Cambridge, 1988.
(17) DeMaeyer, L.; Trachimow, C.; Kaatze, U. *J. Phys. Chem.* In press.
(18) Labhart, H. *Einführung in die Physikalische Chemie*, Part 2; Springer: Berlin, 1975.
(19) Einstein, A. *Ann. Phys.* **1905**, *17*, 549.
(20) Lessner, E.; Teubner, M.; Kahlweit, M. *J. Phys. Chem.* **1981**, *85*, 1529, 3167.
(21) Kahlweit, M. *Pure Appl. Chem.* **1981**, *53*, 2069.