

Extremely Slow Reaggregation Processes in Micelle Solutions. A Dynamic Light Scattering Study

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Photon correlation measurements were performed on the dodecylpyridinium iodide/water system to yield the mean radius of micelles as a function of the time interval after a change in the temperature from 80 to 25 °C. Depending on the purification procedure applied to the sample, large aggregates, probably with dust particles as nuclei, may be formed after the temperature jump. Simultaneously, large micelles are also formed, the radius of which may reach four times the equilibrium value of the system. The micellar radius exhibits relaxation characteristics with extremely long relaxation times, reaching values up to several hours. Obviously, the nucleation of a sufficient number of micellar aggregates is hindered by the extremely unfavorable equilibrium concentration of submicellar-size intermediates. This leads to a strongly deviating nonequilibrium distribution with an excess of extra large micelles during the 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.

1. Introduction

The study of micelle kinetics is not only of interest in itself, but is also of considerable significance for many biological aggregation and complexation processes. At thermodynamic equilibrium surfactant systems with small critical micelle concentration (cmc) can be represented by the Aniansson–Wall reaction scheme^{1–5} which is widely accepted. It basically considers the equilibria between monomers and all supramolecular species with aggregation number i up to N , assuming a Gaussian distribution of the equilibrium concentrations \bar{N}_i of micellar species ($i \geq 10$). Hence application of this scheme of coupled reactions tacitly implies the presumption that the concentration of monomers is much higher than the concentration of multimers. The Aniansson–Wall model predicts two relaxation processes, the existence of which has been verified experimentally, particularly by pressure jump and temperature jump methods^{6,7} as well as by ultrasonic spectrometry.^{8–12} The slow process with relaxation time τ_s on the order of milliseconds or even seconds is considered to represent that response to a disturbance of the surfactant solution that is related to the formation and decay of micelles. The fast relaxation process with relaxation time τ_f roughly in the range of nanoseconds and microseconds is taken as a response that is accompanied by a change in the mean aggregation number \bar{m} at a nearly constant total number of micelles. It has been shown recently¹³ that in systems with high cmc a considerable amount of oligomers may exist and that it is impossible under such conditions to separate the slow from the fast relaxation process. Instead of the two different responses predicted by the theory of stepwise aggregation, only one is found in the time domain down to 1 ns. In addition, however, an ultrafast relaxation mechanism with

relaxation time τ_{uf} smaller than 1 ns emerges in the measured sonic spectra. By extension of the Aniansson–Wall model, which has been modified to also apply for surfactants with high cmc, evidence shows that the ultrafast relaxation process is due to oligomer/monomer reactions.¹³ Basically, the extended model is founded on a modified distribution function which more adequately describes the sizes of aggregates in short-chain amphiphile systems. A suitable distribution function has been obtained numerically from reasonable assumptions on the forward and backward velocity constants k_f^i and k_b^i ($i = 1, \dots, N$), respectively, in the reaction scheme underlying the Aniansson–Wall model. In this study we look for another extreme. Instead of the ultrafast response, the existence of unusually slow processes in micellar solutions is considered. Evidence for extremely slow relaxation times, τ_{es} on the order of minutes or even hours were reported nearly 20 years ago,¹⁴ but little attention has been given to these experimental findings. The extremely slow relaxation times seem to be characteristic of the approach of micelle solutions toward its new equilibrium after a thermodynamic parameter has been shifted by a considerable amount. In this article we first report experimental conformations of extremely slow relaxation mechanisms. A dynamic light scattering technique was used for this purpose to monitor diffusion properties of the surfactant system after a strong change in its temperature.

2. Experimental Section

Principle of the Method. Following De Rycke,¹⁴ the surfactant system was disturbed by a significant change in the temperature T , which was rapidly shifted from a value at which the amphiphile was molecularly dispersed to a value at which micelles were already formed. The formation of micelles when the cmc was exceeded thereby was visualized by looking for the radius of the supramolecular species, assumed to be spherically shaped. For the mean aggregation number \bar{m} in the

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size distribution of micelles the radius \bar{r} may be simply calculated as

$$\bar{r} = \left(\frac{3}{4\pi} \bar{m} \frac{\phi_v}{N_A} \right)^{1/3} \quad (1)$$

where ϕ_v denotes the molar volume of monomers within a micelle, and N_A is Avogadro's number. According to the Stokes–Einstein relation¹⁵

$$\bar{r} = \frac{kT}{6\pi\eta\bar{D}} \quad (2)$$

where the radius \bar{r} is related to the diffusion coefficient \bar{D} of the micelle and the viscosity η of the suspending phase. In eq 2 k denotes the Boltzmann constant. Using quasielastic light scattering, the diffusion coefficient and hence the radius (eq 2) and aggregation number (eq 1) were continuously monitored during the process of micelle formation, without introducing artificial labels. Diffusion of micelles leads to an additional Lorentzian in the Rayleigh line of the scattered light.¹⁶ The half-width of the Lorentzian can be expressed as

$$\Gamma = \bar{k}^2 \bar{D} \quad (3)$$

where \bar{k} is a wavevector that is selected by the scattering geometry. Assuming $\bar{D} = 10^{-10} \text{ m}^2 \text{ s}^{-1}$ as a typical diffusion coefficient for micelles, a wavelength $\lambda_0 = 500 \text{ nm}$ of the incident light and a scattering angle $\Theta = \pi/2$, a half-width Γ on the order of 10^5 Hz results from eq 3. Hence it is too small to enable the Rayleigh line to be analyzed with the aid of an optical spectrometer. The fluctuations in the scattered light were therefore evaluated in the time domain by applying a photon correlation method.

Surfactant Solutions. Aqueous solutions of *n*-dodecylpyridinium iodide (DoPI, $\text{C}_{12}\text{H}_{25}\text{C}_5\text{H}_5\text{NI}$) were studied, a system for which extremely slow relaxation mechanisms were reported previously.¹⁴ Because of their high electronic polarizability, the iodide ions in the counter-ion layer surrounding the micelle significantly contributed to the amplitude of the scattered light. Because of the resulting enhanced signal-to-noise ratio, preference was given to this anion, though it needed small amounts of $\text{Na}_2\text{S}_2\text{O}_3$ (10^{-4} mol/L , typically) as an additive to prevent the formation of I_2 in the surfactant solutions. Distinctly above the cmc ($5.0 - 5.9 \cdot 10^{-3} \text{ mol/L}$ ^{17,18}) a mean aggregation number $\bar{m} = 87$ and variance $\sigma = 1, \dots, 4$ of the size distribution of micelles was reported.¹ The degree of dissociation of anions was $\beta = 0.13$ ¹⁴, as is characteristic for many ionic surfactants in aqueous solution. Because there exists some variance in the cmc data from the literature, we redetermined the cmc of the DoPI system by measuring the intensity of light scattered from solutions of different surfactant content. As illustrated by Figure 1, cmc = $(5.1 \pm 0.1) \cdot 10^{-3} \text{ mol/L}$ is derived from these measurements at room temperature. A recently developed entropic model of micelle formation predicts the cmc at 80 °C to be 1.7 times higher than at 25 °C.¹⁹ The measured temperatures at which all DoPI in solution is molecularly dispersed (Figure 2) revealed a somewhat smaller temperature effect. Nevertheless it was possible to use a $6.2 \cdot 10^{-3} \text{ molar}$ solution ($c = 1.2 \text{ cmc}$) and a temperature change from 80 °C to 25 °C in our study (Figure 2). At the higher temperature only monomers exist, while at the lower temperature nearly 18% of the surfactant forms micellar aggregates.

Sample Preparation. *N*-dodecylpyridinium bromide (Fluka, Neu-Ulm, Germany, >95%) was dissolved in water and added

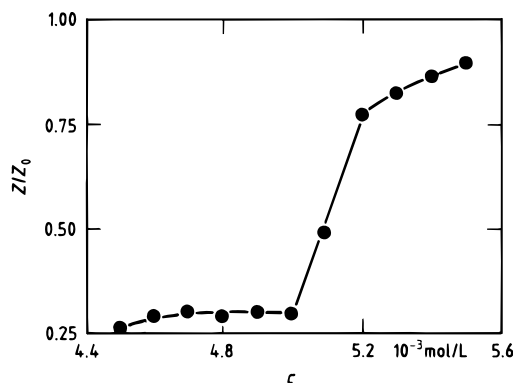


Figure 1. Relative number of photon counts as a function of surfactant concentration for DoPI solutions at 25 °C.

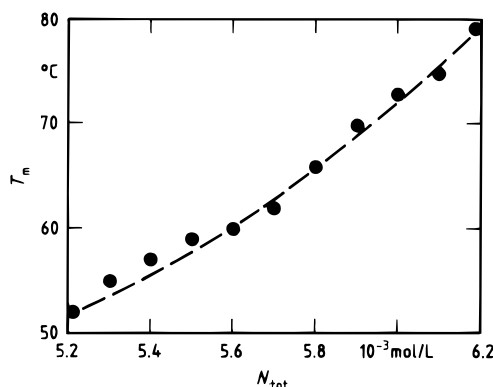


Figure 2. The temperature T_m above which all DoPI is molecularly dispersed displayed against the total concentration $N_{\text{tot}} = c$ of surfactant.

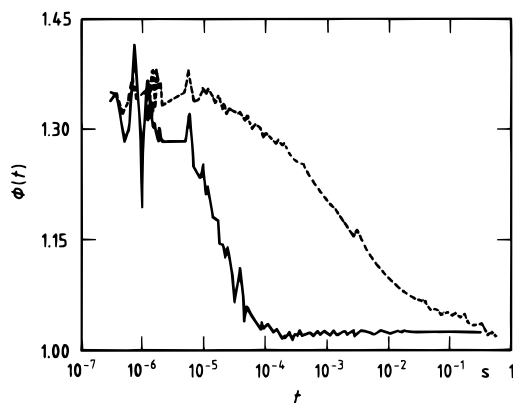


Figure 3. Autocorrelation function $\phi(t)$ of the photon current of the light scattered from an 8 mM DoPI solution at 25 °C when the sample is free of dust (full curve) and when dust particles are present (dashed curve).

to a saturated aqueous solution of potassium iodide. The DoPI salt obtained was recrystallized twice from a saturated KI solution, dried with P_2O_5 in a vacuum chamber, and always stored in the dark. In photon correlation studies severe problems may arise from pollutants capable of scattering light more effectively than the particles under consideration. As shown by Figure 3, even if present only in very small concentration, such pollutants may completely mask the autocorrelation function to be studied. It is therefore of particular importance to prepare samples as free of dust as possible, a difficult undertaking because the high dielectric permittivity of water tends to cause dust particles to be absorbed from the air. Solutions with surfactant concentration $> 10^{-2} \text{ mol/L}$ were cleaned of dust using a method that was successfully applied in the preparation of pure water samples. Dry nitrogen was

used to press the liquid through a filter system (Amicon, Beverley, MA; Sartorius, Göttingen, Germany) directly into the measuring cell. Poly(vinyl chloride) (PVC) tubes were used to fill the cell with the filtrate and to suck out superfluous liquid. Several types of filters were tested. Satisfactory results were obtained using filters made of Teflon with a pore size of 0.1 μm , but also using microfilters designed for molecular weights between 25 000 and 50 000. To remove dust from its walls, the empty cell was cleaned with filtrate which was sucked out afterward and filtered again. Before a measurement was started, this filling procedure has been repeated five times. Nevertheless, dust particles were frequently present in solutions with solute concentration smaller than 10^{-2} mol/L and it became increasingly difficult to remove the dust when the cmc was approached. To increase the proportion of successful preparations it was thus necessary to improve the filter system. Tubes made of Teflon were used throughout at $c > 10^{-2}$ mol/L and a second filter (pore diameter 0.1 μm) was applied to clean the air that was drawn into the cell when the sample was sucked off. Microfilters (molecular weight 50 000) were used which were supported by a Teflon filter with pores of 0.1 μm diameter. Even with these provisions just 20% of the samples were sufficiently free of dust to enable reliable light scattering studies.

Light Scattering Spectrometry. To reduce effects from structure borne sound, the self-beating photon correlation spectrometer was built on a vibration-damped optical table. The central part of the spectrometer was a goniometer system on which the circular cylindrically shaped cell could be precisely positioned. Particular care was always taken to ensure that the axis of the cell coincided with that of the goniometer. The cell was provided with special planar windows that allowed diffraction of the incident and unscattered light passing through the device to be reduced effectively. The temperature of the glass-made cell was controlled by two chambers that were positioned above and below the scattering volume. The temperature of those chambers was kept constant to within ± 0.05 K during measurements by circulating thermostat fluid. Vertically polarized light from an argon-ion laser (Spectra Physics 165-03, maximum output power 150 mW) was focused into the cell. With the aid of an Etalon the laser was operated at a single mode so that the amount of optical noise was small. The wavelength of the laser light (488 nm) was monitored by a Perot-Fabry interferometer to which part of the optical signal was coupled. A microscope objective was used to focus the scattered light onto the photodetector (channeltron, Bendix BX 154) with a 1 mm diameter S20 photocathode, having a very low (< 10 s $^{-1}$) dark photon current. A system of slits and lenses restricting the incident beam, as well as an aperture and a pinhole in front of the photodetector, enabled a high spatial resolution, so that we were able to select a small scattering volume from the sample, and to realize that only a (spatially) coherent part of the scattered light reached the detector. Spatial coherence is necessary for an optimum signal-to-noise ratio and for a maximum accuracy in the correlation function, derived from the time sequence of photons reaching the detector.^{20,21} Following standard routines described in the literature,^{22,23} the analysis of our setup leads to the conclusion that the detector receives light just from one coherent area if an aperture of 0.14 mm is used. In accordance with experiments described previously²⁴ it was found, however, that somewhat larger diameters of the aperture (0.2–0.5 mm) offer more favorable conditions. The scattered light, in addition, passed an interference filter to exclude fluorescent light from the detector. Contributions from orientation correlations were avoided by a pair of carefully

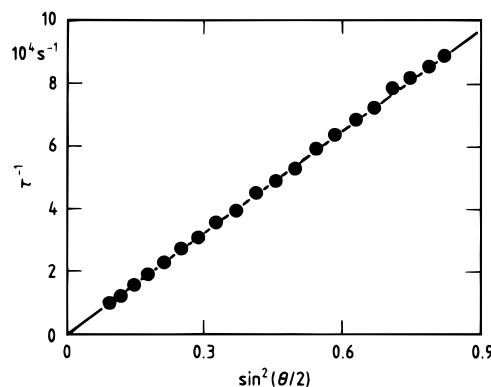


Figure 4. Decay rate τ^{-1} of the photon autocorrelation function displayed versus $\sin^2(\Theta/2)$ for an 8 mM solution of DoPI at 25 °C. Here Θ is the scattering angle (eq 9).

adjusted polarizers. One polarizer was positioned in front of the specimen cell, the other one in the light path to the photodetector. The signal from the detector was fed to a digital correlator (ALV-500/E) that, in combination with a laboratory computer, allows for a real-time determination of the correlation function with a time scale from 200 ns to 3400 s. The correlator, originally developed by Schätzel,^{25–27} is provided with 288 channels which are set in a logarithmic scale. The photodetector is, of course, unable to follow the rapid changes of the optical field. Because of its quadratic characteristic curve, however, it produces a photocurrent $i(\omega)$ which according to the integral

$$i(\omega) = \hat{i} \int_{-\infty}^{\infty} S_E(\omega' - \omega) d\omega \quad (4)$$

is given by the amplitude spectrum $S_E(\omega)$ of the scattered light. In eq 4 \hat{i} denotes an amplitude and $\omega = 2\pi\nu$ is the angular frequency of the optical signal. The Rayleigh line is a Lorentzian. If its half-power width is denoted by Γ , the photocurrent is given by

$$i(\omega) = \hat{i} \frac{2\Gamma}{\omega^2 + (2\Gamma)^2} \quad (5)$$

and the corresponding autocorrelation function $\phi(t)$ reads

$$\phi(t) = \phi \exp(-t/\tau) \quad (6)$$

where $\hat{\phi}$ again denotes an amplitude and where the correlation time τ is given by

$$\tau = (2\Gamma)^{-1} = (2D\vec{k}^2)^{-1} \quad (7)$$

If n denotes the refractive index of the sample liquid

$$|\vec{k}| = 4\pi n \lambda_0^{-1} (\Theta/2) \quad (8)$$

and

$$\tau^{-1} = 2D \left(\frac{4\pi n}{\lambda_0} \right)^2 \sin^2 \left(\frac{\Theta}{2} \right) \quad (9)$$

follows. This relation has been used to test whether the experimental setup was adjusted adequately, and whether effects from multiple reflections and from any isotropy in the arrangement could be neglected. An example for a τ^{-1} versus $\sin^2(\Theta/2)$ relation reflecting the favorable measurement conditions is shown in Figure 4.

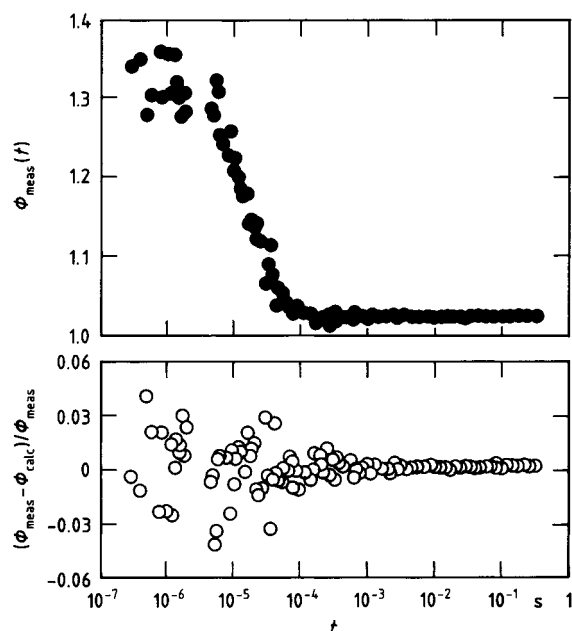


Figure 5. Measured autocorrelation function $\phi_{\text{meas}}(t)$ of the photon current produced by the light scattered from an 8 mM solution of DoPI at 25 °C and relative deviation $(\phi_{\text{meas}} - \phi_{\text{calc}})/\phi_{\text{meas}}$ of the measured data from relation (10) with parameter values found in a nonlinear least-squares regression analysis ($\tau = 21.9 \mu\text{s}$).

3. Results for Nonequilibrium Micellar Systems

The dynamic light scattering data described in the following are based on the determination of the autocorrelation function $\phi(t)$ of the photocurrent either at a fixed scattering angle Θ or as a function of Θ (eq 9). An exponential has been fitted to the measured $\phi(t)$ in order to find the correlation time τ . An example of a measured autocorrelation function is given in Figure 5. In correspondence with the design of the correlator channels a logarithmic time scale $x = \log(t/s)$ is used in the diagram. In doing so, τ is given by the point of inflection of $\phi(t)$. The autocorrelation function is normalized automatically by routines that are implemented on the correlator. Because of the nonperfect scattering geometry, imperfections of the digital electronics, and the finite angle of coherence, $\phi(t)$ does not adopt its ideal values at very short and very long times.²⁶ For this reason the function

$$\phi(t) = \phi(0) \exp(-t/\tau) + \phi(\infty) \quad (10)$$

has been fitted to the experimental data in order to find the relaxation time τ . Figure 5 also illustrates that this function represents the measured $\phi(t)$ appropriately. Using refractive index²⁸ and viscosity^{28,29} data for water, the diffusion coefficients (eq 9) and mean micellar radii (eq 2) corresponding with the relaxation time values were calculated. Figure 6 shows how the radii depend on the amphiphile concentration c . Up to an amphiphile concentration of 10 mmol/L \bar{r} is nearly constant ($\bar{r} = 2.36 \pm 0.05 \text{ nm}$). Above 10 mmol/L the mean micellar radius slightly increases with c to reach $\bar{r} = 2.6 \pm 0.05 \text{ nm}$ at $c = 35 \text{ mmol/L}$. A significant stronger slope $d\bar{r}/dc$ emerges at amphiphile concentrations larger than 35 mmol/L, indicating that this concentration may correspond with the so-called second cmc above which, in addition to globular micelles, nonspherically shaped aggregates are also formed. Results from time-resolved studies of the light scattered from a DoPI solution are displayed in Figure 7. In these measurements the samples have been prethermostated at 80 °C and then rapidly cooled. The change in temperature was provided by switching to a second

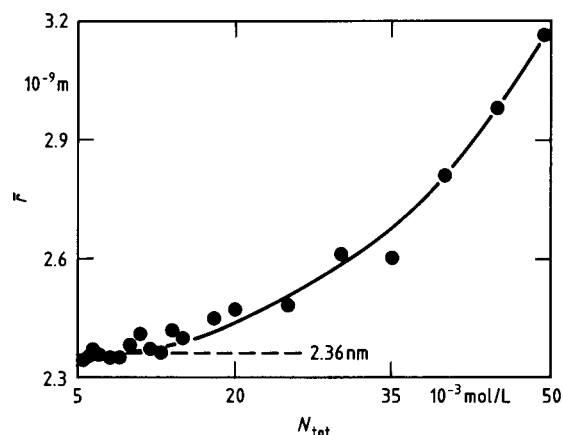


Figure 6. Radius \bar{r} of micelles as found from a τ^{-1} versus $\sin^2(\Theta/2)$ plot (Figure 4) shown as a function of total concentration $N_{\text{tot}} = c$ of surfactant at 25 °C.

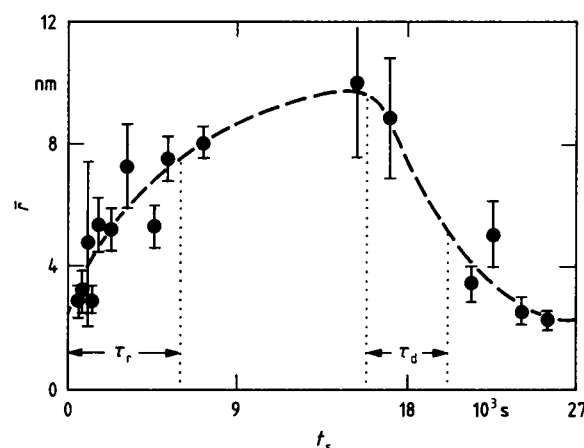


Figure 7. Mean radius \bar{r} of micelles in a 5.5 mM DoPI solution displayed as a function of the interval t_s after application of a temperature jump from 80 to 25 °C.

bath of thermostat fluid which was kept at $25.00 \pm 0.05 \text{ °C}$. Almost 2.5 min after the sample was switched to a second bath, it adopted a temperature of 26 °C. Another 1.5 min later the final temperature was reached within the limits of experimental error. Measurements of the photon correlation function $\phi(t)$ were started 3 min after the bath was switched (Figure 7) when the sample temperature was about 25.5 °C. During the following 8 h $\phi(t)$ was repeatedly recorded at intervals between 2 and 40 min, depending on the time t_s after the thermostat was switched. The dependence upon the time t_s of the mean micellar radius \bar{r} derived from the autocorrelation function of a 5.5 mM aqueous DoPI solution, for the first hours after the change in the temperature, exhibited a characteristic rise process during which \bar{r} reached a value as high as 10 nm. For this particular solution a rise time τ_r of 1.6 h was found. The rise process was followed by a decay in which the micellar radius finally adopted its equilibrium value $\bar{r} = 2.36 \text{ nm}$ again. This latter process was also subject to an unusually long time constant τ_d ($\approx 1.2 \text{ h}$, Figure 7). It is interesting to note that rise times τ_r and decay times τ_d on the order of hours were found at solute concentrations near the cmc only. As illustrated by Figure 8, both τ_r and τ_d significantly decreased with c and adopted values of a few minutes if c exceeded the critical micelle concentration by the amount of 2 mmol/L. Even though at $c \geq 7 \text{ mmol/L}$ the amphiphile was not completely molecularly dispersed at 80 °C, the results for the 7 and 8 mM solutions are included here because after disturbance the time dependence of these systems clearly corresponds with that at lower c . However, the

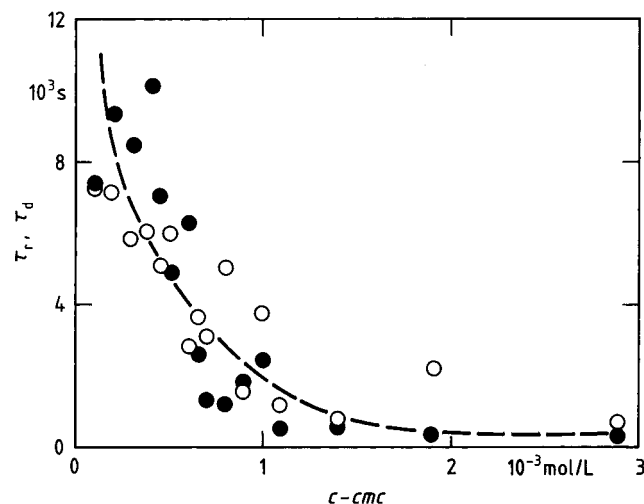


Figure 8. Rise time τ_r (●) and decay time τ_d (○) for the change in the mean radius \bar{r} of micelles after application of a temperature jump from 80 to 25 °C (Figure 7) shown as a function of the total surfactant concentration exceeding the cmc.

comparatively small τ_r and τ_d data at $c > \text{cmc} + 1 \text{ mmol/L}$ were subject to a considerable experimental error because only a few correlation functions could be recorded during the short period of time so that the τ_r and τ_d were based on a small number of \bar{r} values. A similar dependence of τ_r and τ_d upon the surfactant concentration was found if the temperature of the sample, instead of being disturbed by a stepwise change of the temperature, was cooled with a rate dT/dt of 2 K/min only. In these measurements a somewhat smaller maximum value of the rise time resulted ($\tau_r \leq 1.7 \text{ h}$) than in the afore discussed temperature jump experiment (Figure 8). A further series of $\phi(t)$ measurements was performed after a fast enhancement of the sample temperature from 25 to 45 °C. Again two temperature-controlled water baths were used to enable a rapid exchange of the circulating thermostat fluid of the specimen cell. In principle, the same response was found as in the two experiments described before. The maximum relaxation times, however, were somewhat smaller here ($\tau_r \leq 1 \text{ h}$, $\tau_d \leq 1.4 \text{ h}$) than in the previous series of measurements. Nevertheless, even after this comparatively small disturbance of the thermal equilibrium, at concentrations near the cmc extremely slow reaggregation mechanisms take place within the amphiphile solutions.

4. Discussion

The results of our light scattering experiments can be intuitively discussed as follows. After the fast change in the sample temperature from 80 to 25 °C there exists an excessive concentration of surfactant monomers. Tending to reduce this concentration and the areas of contact between hydrophobic parts of the amphiphiles and water molecules, monomers are first deposited at the surface of existing nuclei, as dust particles or micelles that are already present. The excessive monomer content is rapidly cut by this deposition. However, a nonequilibrium size distribution of aggregates with a comparatively small oligomer concentration and a small number of aggregates with an unusually high content of large particles arises. A system with such distorted size distribution needs an uncom-

monly long time to adopt its equilibrium because the process requires the complete reassembly of normal-size micelles from monomers, the concentration of which is buffered by the presence of an excess of large-size micelles. Establishing the final equilibrium after a strong perturbation requires a reorganization of the mean aggregation number and the number density of micelles, as well as of the shape of the micellar size distribution. Hence the equilibration procedure is expected to be governed by three reactions (in normal coordinates), in conformity with the existence of a third relaxation process supplementary to the slow and fast processes with relaxation times τ_s and τ_f , respectively. As will be shown in a future paper, these ideas of micelle kinetics are verified by the evaluation of a nonlinearized isodesmic reaction scheme,³⁰ in conjunction with a recent theoretical model describing the size distribution of micellar systems in terms of known molecular quantities and only a few free parameters.³¹

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