

On the Kinetics of the Formation of Small Micelles. 2. Extension of the Model of Stepwise Association

T. Telgmann and U. Kaatz*

Drittes Physikalisches Institut, Georg-August-Universität, Bürgerstrasse 42-44, D-37073 Göttingen, Germany

Received: February 27, 1997; In Final Form: June 23, 1997[®]

The Teubner–Kahlweit theory, which, based on the Aniansson–Wall model of micelle formation, relates the kinetics of stepwise association to the ultrasonic absorption spectrum, has been extended in order to better apply to solutions of short-chain surfactants. In doing so the size distribution of micellar aggregates has been obtained from reasonable assumptions on the forward and backward rate constants of the reaction scheme representing the series of chemical equilibria in the system under consideration. In conformity with experimental spectra, it is found that an ultrafast relaxation process exists that reflects the exchange of monomers between oligomers and the suspending phase. Also in agreement with the characteristics of measured spectra, the slow relaxation process found with long-chain surfactant systems is missing. This turns out to result from the comparatively high oligomer concentration in short-chain surfactant solutions. The fast process of the original model of micelle formation is found to be subject to a relaxation time distribution. Particularly in the cmc range, however, the width of the predicted ultrasonic spectra is nevertheless distinctly smaller than measured. It is suggested that this still remaining discrepancy results from the assumption of discrete rate constants, which may be inappropriate with micelles of rather small size.

1. Introduction

It is aim of this study to establish how existing models of the kinetics of micelle formation can appropriately account for solutions with amphiphile concentration close to the critical micelle concentration (cmc). In the first of these two papers,¹ we reported results from ultrasonic relaxation measurements on aqueous solutions of *n*-heptylammonium chloride (C₇ACl), a short-chain surfactant that had been chosen because of its high cmc of about 0.4 mol/L. With solutions of short-chain surfactants the cmc is a concentration range rather than a single concentration (Figure 3 in ref 1). We therefore aspire to a model that does not proceed from the existence of a well-defined discrete cmc. The spectra measured at concentrations at and above the cmc confirmed previous results for solutions of surfactants with lower critical micelle concentration (Figure 1) in that two relaxation processes emerge in the frequency range between 100 kHz and some a few gigahertz. The process with relaxation frequency at around some a few megahertz has been taken to reflect the mechanism of surfactant monomer exchange between micelles and the suspending solvent. However, in contrast to the accepted theories of micelle kinetics,^{3–8} which predict a discrete relaxation time, in the spectra of C₇ACl solutions this term clearly exhibits a relaxation time distribution. Particularly at concentrations slightly in and above the cmc range the width in the continuous distribution function, which was found to favorably represent the measured spectra, appears to be pronounced. The process with relaxation frequency higher than 100 MHz (Figure 1) had been tentatively attributed to mechanisms of rotational isomerization of surfactant chains in the micellar core.¹ It turned out, however, that neither the relaxation time values nor the values for the amplitude of the high-frequency relaxation term can be unequivocally explained by this assumption. Let the spectra for *n*-decyltrimethylammonium bromide (C₁₀TABr) solutions displayed in Figure 1 also serve as an example. Being an intramolecular process structural isomerization of chains is expected to be controlled by a

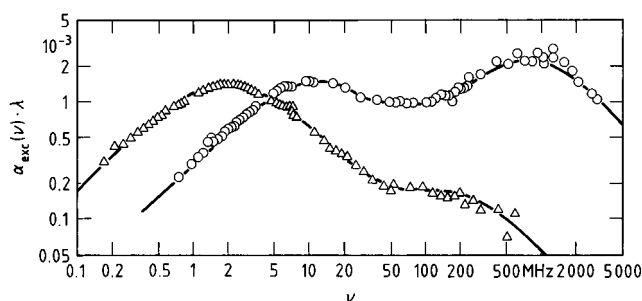


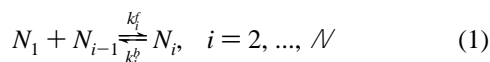
Figure 1. Ultrasonic absorption per wavelength that exceeds the classical part, $(\alpha\lambda)_{\text{exc}}$, displayed vs frequency ν for aqueous solutions of *n*-decyltrimethylammonium bromide at 25 °C and at two different concentrations (Δ , 0.15 mol/L; \circ , 0.5 mol/L (ref 2); cmc = 0.06 mol/L).

relaxation rate that is independent of amphiphile concentration. The relaxation time of the high-frequency relaxation term in the spectra of C₁₀TABr solutions, however, does not show indications of increasing when the solute concentration increases from 0.15 to 0.5 mol/L (Figure 1). In this paper we report results from model calculations that have been performed in order to find out whether the incomplete agreement of the predictions from the Teubner–Kahlweit theory^{7,8} and our experimental findings may result from invalid approximations in the theoretical model. Particularly the size distribution of micelles as assumed by Teubner and Kahlweit in their model may be questioned here. For the systems with high cmc under consideration the mean aggregation number of the micelles is small.¹ On such conditions it may thus be inappropriate to presume, as in the original theory, a negligibly small concentration of amphiphile oligomers in the distribution function.

2. Theoretical Model of Micelle Kinetics

Fundamentals of Existing Theories. Following the ideas of Aniansson and Wall,^{3–6} Teubner and Kahlweit in their treatment of the sonic absorption of micelle solutions^{7,8} proceed from the scheme of coupled reactions

[®] Abstract published in *Advance ACS Abstracts*, September 1, 1997.



where N_i denotes the concentration of micellar aggregates made of i surfactant monomers. The forward and backward rate constants k_i^f and k_i^b , respectively, are assumed to be identical for all molecules undergoing the same step in the reaction scheme defined by eq 1. Hence taking the above series of coupled reactions as a basis of the model it is implicitly assumed that each step in the series is characterized by a well-defined change $\Delta G_i^0 = -RT \ln(k_i^f/k_i^b)$ in the Gibbs free energy. This is a plausible assumption if large micelles are considered. It seems, however, to be less likely true if predominantly small oligomeric aggregates exist in the solution. In the above relation R denotes the gas constant and T the temperature. Assumption of the reaction scheme (eq 1) is also based on the idea that the concentration N_1 of monomers is always substantially higher than that of molecular aggregates ($N_1 \gg N_i, i > 1$) so that direct association of oligomers and higher order micellar structures can be neglected. Omission of reactions $N_i + N_j \rightleftharpoons N_{i+j}, i, j > 1$, may be also questioned if the mean aggregation number is small so that a noticeable amount of oligomers may exist in the solutions.

Let $\xi_i, i = 1, 2, \dots$, denote a suitable set of reaction coordinates and the

$$A_i = -(\partial G / \partial \xi_i)_{p, T, \xi_{j \neq i}} \quad (2)$$

generalized forces. Relaxation of the system in its equilibrium ($\xi = 0$) after a small disturbance is assumed to be controlled by the phenomenological relation

$$\frac{d\xi}{dt} = \frac{1}{T} \mathbf{L} \mathbf{A} \quad (3)$$

where matrix \mathbf{L} contains all coefficients that determine the kinetics of the process at temperature T . Considering small deviations only from the state of equilibrium as characterized by the pressure p , entropy S , and reaction coordinate ξ and looking at the response to periodic variations of the pressure within an externally applied compressional wave, Teubner and Kahlweit derived the relation

$$(\alpha\lambda)_{\text{exc}} = -\frac{\pi}{\kappa_s^\infty VT} \text{Im} \left\{ \bar{H}_p \left(i\omega \mathbf{E} - \frac{1}{T} \mathbf{L} \mathbf{H} \right)^{-1} \mathbf{L} \bar{H}_p \right\} \quad (4)$$

for the excess contribution to the sonic absorption coefficient α per wavelength λ . In this equation, κ_s^∞ denotes the adiabatic compressibility of the solution extrapolated to high frequencies, $i = (-1)^{1/2}$, $\omega = 2\pi\nu$ is the angular frequency, and ν the frequency itself. Furthermore

$$(H_p)_i = \left(\frac{\partial A_i}{\partial p} \right)_{S, \xi} = -(\Delta V_i)_{p, S} \quad (5)$$

is the reaction volume of the i th step and

$$H_{ij} = \left(\frac{\partial A_i}{\partial \xi_j} \right)_{p, S, \xi_{k \neq j}} \quad (6)$$

with $i, j, k = 1, 2, \dots, \mathcal{N}$. \mathbf{E} denotes the identity matrix. If just one uncoupled step of the reaction scheme 1 is considered the matrixes \mathbf{L} and \mathbf{H} and the vectors \bar{H}_p and ξ are scalar quantities and eq 4 reduces to a Debye-type relaxation term⁹ with its discrete relaxation time τ given by $\tau = -(\mathbf{L}\mathbf{H}/T)^{-1}$. Treating the complete reaction scheme, Teubner and Kahlweit, as usual,

took into account the law of mass action

$$k_i^f \bar{N}_1 \bar{N}_{i-1} = k_i^b \bar{N}_i \quad (7)$$

in order to relate the equilibrium concentrations \bar{N}_i of the differently sized species to another. To further reduce the number of parameters they presupposed identical reaction volumes $\Delta V_i = V, i = 1, 2, \dots$ for all steps of the coupled scheme (eq 1). In addition, a nearly Gaussian size distribution of the micelles

$$(k_{i+1}^b \bar{N}_{i+1} - k_i^b \bar{N}_i) / \bar{N}_i = -k^b / \sigma^2 (i - \bar{m}) \quad (8)$$

has been introduced empirically. Herein, \bar{m} is the mean aggregation number and σ^2 the variance of the size distribution. k^b is the mean backward rate constant for micellar sizes at around the mean ($i \approx \bar{m}$)

Extension of the Teubner–Kahlweit Model. Within the framework of the theoretical model outlined above $\mathbf{L}\bar{H}_p$ is an eigen vector of $\mathbf{L}\mathbf{H}$. Hence there exists only one relaxation process. The relaxation rate

$$\tau_1^{-1} = k^b \sigma^{-2} (1 + X \sigma^2 / \bar{m}) \quad (9)$$

of this process is predicted to increase linearly with the ratio of concentrations of associated to monomer molecules given by

$$X = (N_{\text{tot}} - \bar{N}_1) / \bar{N}_1 \quad (10)$$

where $N_{\text{tot}} = \sum_{i=1}^{\mathcal{N}} i \bar{N}_i$. Normally, only monomers are assumed to exist at $c < \text{cmc}$, and, in addition, \bar{N}_1 is identified with the cmc at $c > \text{cmc}$. If this accepted X is given by the relation

$$X = (c - \text{cmc}) / \text{cmc}$$

Hence τ_1^{-1} is expected to increase linearly with the surfactant concentration c . On the above assumption the amplitude A_1 of the relaxation process follows the equation

$$A_1 = A_1(\infty) X \sigma^2 / \bar{m} (1 + X \sigma^2 / \bar{m})^{-1} \quad (12)$$

thus increasing linearly with c at concentrations slightly above the cmc and approaching asymptotically the maximum value

$$A_1(\infty) = \pi (\Delta V)^2 \text{cmc} / (\kappa_s^\infty RT) \quad (13)$$

at high concentrations. The concentration dependence of τ_1^{-1} (eqs 9, 11) and A_1 (eqs 11, 12) have in fact been verified for solutions of long-chain amphiphiles. Substantially different behavior, however, has been found for aqueous solutions of short-chain n -heptylammonium chloride at concentrations slightly above the cmc.¹ The discrepancy between the experimental findings for that micellar system and the predictions from the Teubner–Kahlweit theory are also illustrated by Figure 2 where the dependence of the relaxation time on the relaxation amplitude is displayed. The experimental data significantly deviate from a linear relation

$$\tau_1 = \frac{\sigma^2}{k^b A_1(\infty)} (A_1(\infty) - A_1) \quad (14)$$

as resulting when eq 9 is combined with eq 12. With the aim of obtaining a description of the ultrasonic spectra that also applies for the experimental results of solutions with high cmc (and thus a cmc range), attempts have been made to treat the model on the assumption of more realistic distribution functions of the micellar sizes and also more suitable rate constants. It is

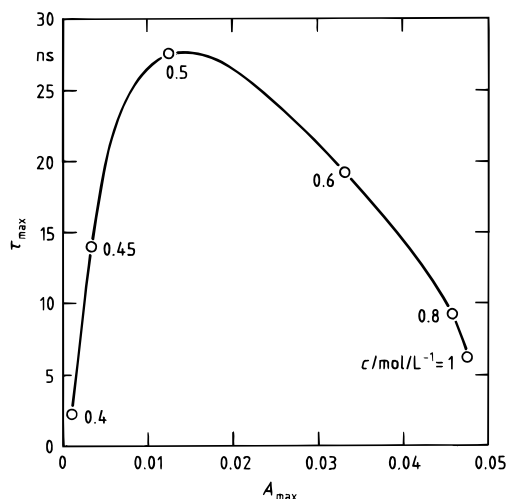


Figure 2. Relaxation time τ_{\max} of the Hill relaxation term in the sonic spectra of C_7ACl solutions at 25 °C plotted vs the relaxation amplitude A_{\max} .

useful for this purpose to realize that eq 4 implies a superposition of Deybe-type relaxations. We therefore expressed the sonic excess absorption by a sum of relaxation terms with discrete relaxation times

$$(\alpha\lambda)_{\text{exc}} = \frac{\pi(\Delta V)^2}{k_s^\infty V RT} \sum_{j=1}^N b_j \tau_j S(\vec{x}_j^E) \frac{\omega\tau}{1 + \omega^2\tau_j^2} \quad (15)$$

Herein \vec{x}_j^E is the eigenvector corresponding to τ_j^{-1} and

$$S(\vec{x}_j^E) = \sum_{i=1}^N A_{ij} \quad (16)$$

where the A_{ij} are the elements of the matrix \mathbf{A} that is formed by the \vec{x}_j^E as column vectors. In eq 15 b_j denote the elements a vector \vec{b} given by

$$\vec{b} = -\frac{R}{\Delta V} \mathbf{A}^{-1} \vec{L} \vec{H}_p \quad (17)$$

Equation 15 adequately relates the ultrasonic excess absorption to the parameters of the reaction scheme of the micellar system (eq 1). The choice of $\Delta V_i = \Delta V$ ($i = 1, 2, \dots$) as in the original model is a simplification since at low i the molar reaction volume is expected to increase with i . The use of a more realistic ΔV_i -versus- i relation, however, would not alter the predictions for the principal relaxation time and relaxation time distribution of the fast process. It might probably alter the relative amplitude of the ultrafast relaxation process in the model, a parameter of minor interest here.

Size Distribution of Micelles. To calculate, with the aid of eq 15, the sonic excess absorption spectra for solutions of C_7ACl , estimates of the size distribution of aggregates and also of the backward rate constants that apply for systems with high and less definitely defined¹ cmc are required. Different from the treatment by Teubner and Kahlweit, we do not presume a particular size distribution of micelles (eq 8) but make assumptions on one concentration only and on the dependence of the forward and backward rate constants on the aggregation number i . The size distribution follows from these assumptions according to eq 7. It is only briefly mentioned that the use of another realistic size distribution would not significantly alter the essential results from this treatment. Various advantages, however, spring from this treatment of the model. First, in

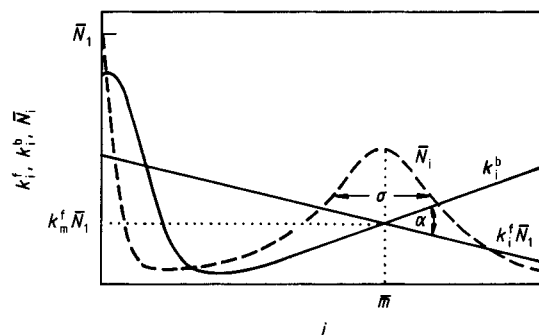


Figure 3. Dependence of the forward (k_i^f) and backward (k_i^b) rate constants (full curves) upon the aggregation number i and the size distribution $\bar{N}_i(i)$ at equilibrium (dashed curve).

conformity with the common idea of the kinetics of micelle formation, the rate constants are treated as fundamental parameters of the system which in turn control the size distribution. Moreover, it is not necessary to suppose a sharp cmc. The concentration dependence of solution parameters, like the monomer concentration, follow from the assumptions on the rate constants. Finally, the mean aggregation number \bar{m} and the variance σ^2 of the model are no longer constants but may depend on the amphiphile concentration, in accordance with experimental data.¹⁰ The concentration dependences of the rate constants that we propose here are based on the following arguments. (1) At small aggregation numbers i the k_i^b have to strongly decrease with i in order to enable the cmc of the system. The k_i^f are assumed to be diffusion controlled and thus only weakly dependent upon i . (2) At large aggregation numbers the k_i^b have to increase and the k_i^f have to decrease with i in order to limit the growth of micellar sizes. (3) Near the relative extrema of the size distribution $\bar{N}_i \approx \bar{N}_{i-1}$ has to follow and consequently $k_i^f \bar{N}_i = k_i^b$ (eq 7). (4) Preference is given to a linear dependence of the k_i^b and k_i^f upon i within the micellar regime because a Gaussian size distribution of micelles follows thereby.⁵ To analytically represent the rate constants, the following simple relations have proven to be adequate:

$$k_{i+1}^f = k_m^f (1 - s_f(i - \bar{m})) \quad (18)$$

$$k_{i+1}^b = k_m^b (1 + s_b(i - \bar{m})) + k_2 \left(1 + \exp\left(\frac{1-i_c}{d}\right) \right) \left(1 + \exp\left(\frac{i-i_c}{d}\right) \right) \quad (19)$$

Using these relations the rate constants of the forward reactions are assumed to linearly decrease with i while those of the backward reactions follows a Fermi distribution function at small i and almost linearly increase with i in the micelle regime (Figure 3). In eqs 18 and 19 parameters k_m^f and k_m^b allow the forward and backward rate constants, respectively, to be matched at $i = \bar{m}$. The slopes $S^f = \bar{N}_1 dk_{i+1}^f/di = k_m^f s_f \bar{N}_1$ and $S^b = dk_{i+1}^b/di (\approx k_m^b s_b$ at $i \geq \bar{m}$ for systems with large \bar{m}) define the point of intersection of the two functions and thus the value \bar{m} . The smaller the angle of intersection α (Figure 3), the broader is the resulting Gaussian distribution of aggregation numbers. It can be shown⁵ that the difference $S^b - S^f$ in the slopes of the k_i^b -vs- i and the $k_i^f \bar{N}_i$ -vs- i relations equals k_m^b/σ^2 . Hence as long as $\bar{N}_1 \approx \text{cmc}$ the variance is given by $\sigma^2 = (s_f + s_b)^{-1}$. To reduce the number of parameters and to also definitely relate the variance (that can be measured) to the slopes S^f and S^b we used $s_f = s_b$ throughout. At least for long-chain surfactant systems parameters k_m^f and k_m^b in eqs 18 and 19, respectively,

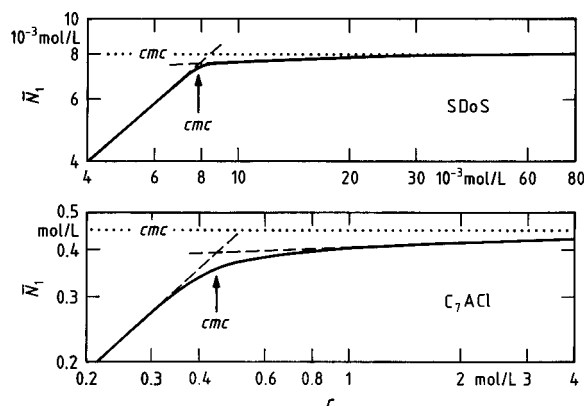


Figure 4. Equilibrium monomer concentration \bar{N}_1 as resulting from the extended Teubner–Kahlweit model at $0.2 \text{ cmc} \leq c \leq 10 \text{ cmc}$ displayed as a function of amphiphile concentration c for simulated sodium dodecyl sulfate (SDoS) and *n*-heptylammonium chloride ($C_7\text{ACl}$) systems.

TABLE 1: Parameters Used in the Numerical Simulation of the Association Behavior in Aqueous Solutions of Sodium Dodecyl Sulfate (SDoS) and *n*-Heptylammonium Chloride ($C_7\text{ACl}$) Using the Extended Model of Micelle Formation

parameter	SDoS	$C_7\text{ACl}$
$k_{\bar{m}}^f, (\text{s} \cdot \text{mol/L})^{-1}$	1.2×10^9	3.3×10^9
$k_{\bar{m}}^b, \text{s}^{-1}$	1×10^7	1.3×10^9
$s_{\bar{f}, \bar{s}b}$	3×10^{-3}	3.3×10^{-3}
k_2^b, s^{-1}	5×10^8	2×10^{10}
d	1	0.6
i_c	2	2
N	100	60

can be derived from ultrasonic relaxation measurements applying the Teubner–Kahlweit theory. The mean aggregation number \bar{m} can be determined by neutron scattering or other methods. The quantities k_2^b , d , and i_c , which model the dependence of k_i^b upon i at small aggregation numbers, are related to the cmc of the system. These quantities are not completely fixed. Under favorable conditions it is, therefore, possible to derive k_2^b from measurements by fitting this extended model to experimental data.

3. Results from Computer Simulations and Discussion

Long-Chain Amphiphiles, Comparison to the Original Model. To test the predictions from the extended version of the theory, we first made numerical simulations of the system sodium dodecyl sulfate/water, which, on one hand, had been intensively investigated by various groups in the past and which, on the other hand, can be also treated appropriately by the original Teubner–Kahlweit model. We used the well-known values¹¹ for the cmc ($8.3 \times 10^{-3} \text{ mol/L}$), the mean aggregation number \bar{m} ($=64$), and the variance of the size distribution σ^2 ($=169$) to get a suitable set of parameter values as displayed in Table 1. The numerical calculations have been done considering the first 100 steps in the scheme of coupled reactions (eq 1). As illustrated by Figure 4, the model predicts the existence of a critical micelle concentration. According to our expectations for a long-chain surfactant system a rather sharp change in the monomer concentration \bar{N}_1 results around a critical concentration and this concentration agrees with the cmc (Figure 4). Different from the common line of reasoning, however, it follows from the plot of \bar{N}_1 versus the amphiphile concentration c that the monomer concentration slightly increases above the cmc to reach the cmc value at high concentrations only. The k_i^b and N_i data derived from the set of parameters given in Table 1 have been also used to calculate^{7,8,12} the elements of the matrixes \mathbf{L} and

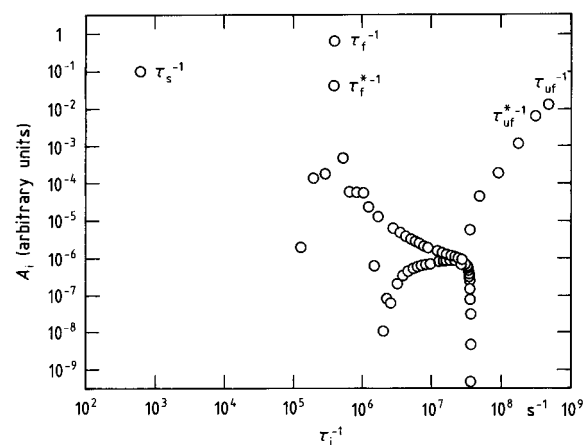


Figure 5. Relaxation amplitudes A_i corresponding with relaxation rates τ_i^{-1} , $i=1, \dots, 100$, in the ultrasonic spectrum of a model system whose parameter values (Table 1) have been chosen to refer to a 0.25 M aqueous solution of SDoS at 25 °C (Figure 4).

\mathbf{H} in eq 4. Utilizing an iteration method,¹³ the eigenfrequencies and amplitudes of the corresponding Debye terms have been derived. To verify the insignificance of errors by rounding and by digital noise in this procedure, the sonic spectrum has been also calculated alternatively using eq 4, which for this purpose has been rewritten to constitute a real relation:

$$(\alpha\lambda)_{\text{exc}} = \frac{\pi}{\kappa_s VT} \omega \bar{H}_p \left(\omega^2 \mathbf{E} + \left(\frac{1}{T} \mathbf{LH} \right)^2 \right)^{-1} \mathbf{LH}_p \quad (20)$$

The development of the excess absorption spectrum of the model into Debye-type contributions is shown by Figure 5, where the relaxation amplitudes A_i are displayed as a function of eigenrates τ_i^{-1} ($i = 1, 2, \dots, N$). The parameters used in this model calculation correspond with those for a 0.025 M aqueous solution of SDoS ($c \approx 4 \text{ cmc}$). There appear to exist three relaxation rate regions in which Debye terms with noticeable amplitude contribute to the spectrum. At low rates ($\tau_i^{-1} < 10^5 \text{ s}^{-1}$) one discrete Debye term emerges. It is taken to represent the slow exchange of monomers between micelles and the suspending phase (Figure 1 in ref 1) with relaxation time τ_s of about 1.6 ms. At distinctly higher frequencies ($10^5 \text{ s}^{-1} < \tau_i^{-1} < 10^6 \text{ s}^{-1}$) two terms are found with relaxation rates that most reasonably reflect the fast response of the size distribution of micelles to external disturbances (Figure 1 in ref 1). The amplitude of one term (relaxation time τ_f , Figure 5) is significantly higher than that of the other one (τ_f^*). Hence the intermediate frequency range ($1 \text{ MHz} < \nu < 10 \text{ MHz}$, Figure 1) of the sonic absorption spectra of long-chain surfactant systems is dominated by one relaxation term with discrete relaxation time τ_f . In the upper part of the range of relaxation rates under consideration additional Debye processes with relaxation times τ_{uf} , τ_{uf}^* , ... result. A more sophisticated investigation of the eigenvalues of the spectrum shows that these ultrafast relaxation processes ($\tau_{uf} = 2 \times 10^{-8} \text{ s}$) are due to monomer/oligomer reactions, the relaxation times of which are predominantly given by k_2^b . Evidence is obtained from our numerical simulation studies that there might exist two ultrafast relaxation processes with comparable amplitudes in the sonic spectra. These processes, however, are just located at the upper limit of the frequency range of measurements (a few gigahertz). It is thus impossible to discriminate these processes in the experimental spectra. This is particularly true since the high-frequency part of the spectra is dominated by the classical contribution (eqs 2, 3 in ref 1) and because the relaxation times

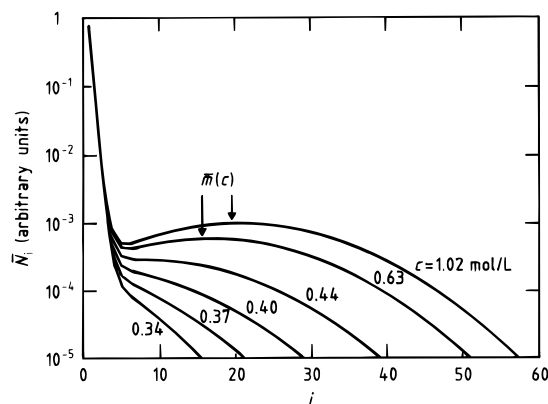


Figure 6. Equilibrium concentration \bar{N}_i of aggregates made of i monomers plotted as a function of aggregation number i as resulting from model calculations of the extended Teubner–Kahlweit theory. The parameters have been chosen in order to correspond to the $C_7\text{ACl}$ /water system at 25 °C and at different surfactant concentrations c .

τ_{uf} and τ_{uf}^* have very similar values. It is only briefly mentioned here that the results from our model calculations for the slow (“s”) and fast (“f”) relaxation process are not only in conformity with experimental findings but also with predictions from the original Teubner–Kahlweit theory.

Short Hydrophobic Chains, Predictions from the Extended Model. Modeling the reaction kinetics of the $C_7\text{ACl}$ /water system, the ultrafast relaxation process representing the formation of oligomers from the beginning has been identified with the high-frequency relaxation (“D”) in Figure 4 of the first part of this study¹ in the sonic absorption spectrum. The rate constant k_2^b is fixed thereby so that there is one less parameter left to be determined from the cmc (≈ 0.45 mol/L). Using the parameter values shown in Table 1, the dependence of the monomer concentration upon the amphiphile concentration as displayed in Figure 4 results. Even for this system with small surfactant chain length and small aggregation number \bar{m} the slope of the \bar{N}_1 -vs- c relation clearly changes in a concentration region around the critical. This change, however, extends over a broad concentration range. Hence the conception of a critical micelle concentration appears to be already washed out with the $C_7\text{ACl}$ /water system. The cmc value determined from the plot of \bar{N}_1 as a function of amphiphile concentration (Figure 4) is 0.45 mol/L, in conformity with the cmc value derived from the principal dielectric relaxation time of the solutions (Figure 3 in part 1 of this study¹). At the cmc the monomer concentration is distinctly smaller ($\bar{N}_1(\text{cmc}) = 0.36$ mol/L) than the cmc. \bar{N}_1 again reaches the cmc value at distinctly higher surfactant concentrations only. In Figure 6 the size distribution of surfactant aggregates is shown for aqueous $C_7\text{ACl}$ solutions at different concentrations. At $c > \text{cmc}$ the shape of the curves resembles those from a thermodynamic model in which the changes in the different contributions to the entropy of the system that accompany the formation of micelles are considered.^{14,15} A special feature of the distribution functions for the $C_7\text{ACl}$ solutions is the less pronounced relative minimum in the oligomer region of aggregation numbers. Hence there exist a noticeable concentration of small supramolecular structures within the liquids. Another remarkable result of the model calculations is the finding that the mean aggregation number increases with amphiphile concentration ($\bar{m} = 16$ at $c = 0.63$ mol/L, $\bar{m} = 19$ at $c = 1.02$ mol/L). At concentrations around the cmc (and smaller than the cmc), the relative maximum in the size distribution function is completely absent. It is also important to notice that even in solutions with $c < \text{cmc}$ there exist small micellar species and oligomeric structures with considerable concentration. The spectrum of eigenrates corre-

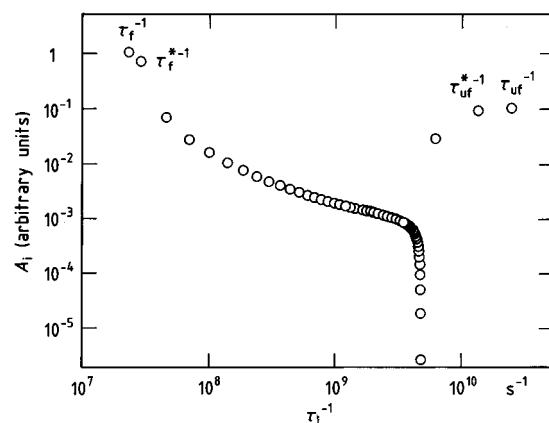


Figure 7. A_i -vs- τ_i^{-1} plot ($i = 1, \dots, 60$) for a model system with parameters (Table 1) corresponding to a 0.45 M aqueous solution of $C_7\text{ACl}$ at 25 °C.

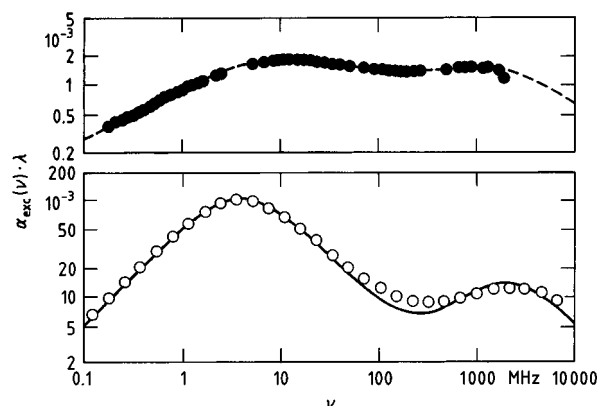


Figure 8. Ultrasonic excess absorption spectrum of the 0.45 M aqueous $C_7\text{ACl}$ solution at 25 °C. The upper diagram gives the measured values (●) and the graph of the $R_{H,D}(\nu)$ relaxation spectral function (dashed curve) used to represent these data analytically.¹ The lower part of this figure shows the spectrum calculated from the extended model using the parameters of this solution (○). The full curve represents the best fit of a sum of two Debye-type relaxation terms to the model spectrum.

sponding with the size distribution at $c = 0.45$ mol/L = cmc is displayed in Figure 7. There does not exist a slow process with relaxation rate $\tau_s^{-1} < 10^7$ in this spectrum. The reason for this unusual result is the aforementioned absence of a relative minimum in the size distribution of micellar species. For that reason no distinction can be made between the slow and fast processes in the response of the size distribution of micelles (Figure 1 in ref 1). The complete absence of an additional slow relaxation process in the $C_7\text{ACl}$ /water system, however, has still to be verified experimentally in the frequency range below 100 kHz. Other methods, like time domain spectrometry, are required for such measurements. It can be shown by model calculations that the different molecular processes lead again to spectral lines that can be separated from another if the amphiphile concentration is enhanced substantially. Another result of these model calculations is the finding of the amplitude of the τ_f^* term to nearly agree with that of the dominating τ_f term. As demonstrated by the model excess absorption spectrum displayed in Figure 8, the simultaneous presence of the τ_f and the τ_f^* term leads to an unsymmetric broadening of the relaxation curve that cannot be adequately represented by a single Debye term. As presumed in the computer model of the $C_7\text{ACl}$ solutions there are also some terms with relaxation frequencies $(2\pi\tau_{\text{uf}})^{-1}$, $(2\pi\tau_{\text{uf}}^*)^{-1}$, ... between about 1 and 4 GHz (Figure 7). Hence the oligomer relaxations are even somewhat faster here than with the aqueous SDoS solutions. It is thus the more

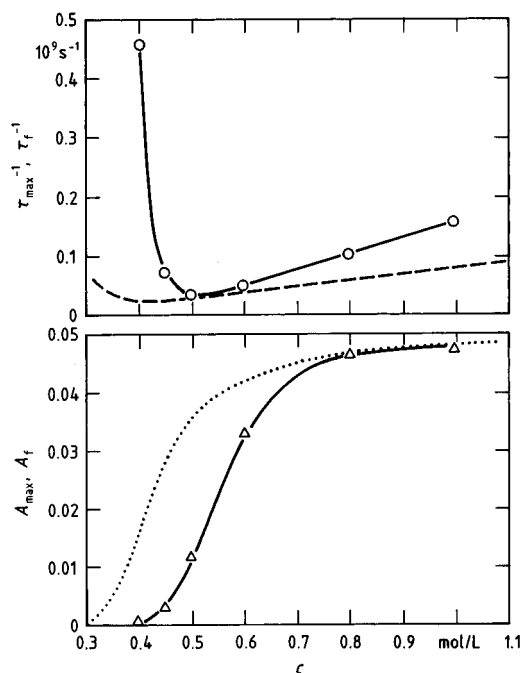


Figure 9. Relaxation rate τ_{max}^{-1} (○) and relaxation amplitude A_{max} (Δ) as derived from the measured spectra¹ as well as the corresponding rate τ_f^{-1} (dashed curve) and amplitude A_f (dotted curve) following from the extended model at 25 °C plotted vs amphiphile concentration c .

difficult to resolve the different high-frequency relaxation terms in the measured ultrasonic spectra.

Measured Spectra in the Light of the Extended Model.

As clearly indicated by Figure 8 the extended theoretical model predicts indeed a relaxation time distribution for the fast relaxation process ($1 \text{ MHz} \leq (2\pi\tau_f)^{-1} \leq 100 \text{ MHz}$). However, the width of the distribution function resulting from the model is still too small to apply for the experimental findings. Hence the extension of the kinetics of micelle formation gives some valuable hints how the ideas of the association mechanisms have to be widened. The same conclusion can be drawn from the dependence of the relaxation rate τ_f^{-1} (Figure 9) upon the amphiphile concentration. As in the experimental data the τ_f^{-1} values from the extended model also show characteristic deviations from the linear behavior predicted by the Teubner–Kahlweit theory. However, the increase in τ_f^{-1} at decreasing c starts at smaller concentration, and it is substantially less steep than measured (Figure 9). At $c > \text{cmc}$ the predicted slope $d(\tau_f^{-1})/dc$ is smaller than resulting from the measurements. This may be taken a reflection of the inappropriateness of using a mean aggregation number \bar{m} independent of c in the model calculations, a presumption that obviously is not fulfilled with the $\text{C}_{7}\text{ACl}/\text{water}$ system (Figure 6). The concentration dependence of the relaxation amplitude A_f as calculated from the extended model nearly agrees with the experimental curve (Figure 9). In correspondence with the τ_f^{-1} -vs- c relation, however, there appears to be also a shift in the cmc for about 0.15 mol/L. The relaxation time τ_{uf} of the ultrafast process in the model, in correspondence with the experimental τ_{D} data (Table 3 in ref 1), is largely independent of the amphiphile concentration. The corresponding relaxation amplitudes A_{uf} , when normalized by the same factor as the A_f data, agree surprisingly well with the A_{D} values extracted from the measured spectra (Figure 10). We thus conclude that the high-frequency Debye-type relaxation term in the ultrasonic absorption spectra of the aqueous solutions of C_{7}ACl predominantly reflects the fast reaction between monomers and oligomeric species within

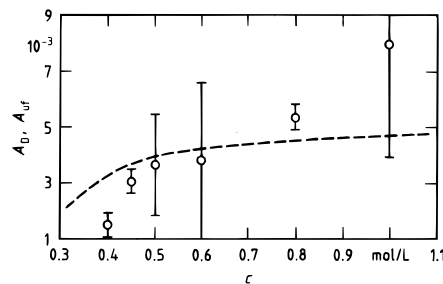


Figure 10. Amplitude A_{D} of the Debye-type relaxation term in the measured spectra (○, ref 1) and the amplitude A_{uf} of the ultrafast relaxation process in the extended model (dashed curve) shown as a function of amphiphile concentration c .

the solution. It is important to notice that a high-frequency Debye term with relaxation time τ_{D} in the order of 10^{-10} s exists also in aqueous solutions of surfactants with distinctly longer hydrocarbon chain (e.g. $(\text{CH}_3(\text{CH}_2)_{n_{\text{C}}-1}\text{N}(\text{CH}_3)_3\text{Br}$, $n_{\text{C}} = 8, 10, 12, 14, 16$;² $n_{\text{C}} = 10$, see also Figure 1). Because of the small concentration of oligomers the contributions from oligomer/monomer reactions to the sonic spectrum will be small. Hence there seems to exist another acoustic relaxation mechanism in this frequency range. It is most probably related to the rotational isomerization of the hydrocarbon chains in the micellar core.² Since a relaxation time independent of concentration is also expected for such unimolecular reaction, a clear-cut analysis of measured spectra in terms of the two different relaxation mechanisms will be impossible.

4. Conclusions

Scenario of the Micelle Formation in Short-Chain Surfactant Systems. The discussion of the sonic spectra of the $\text{C}_{7}\text{ACl}/\text{water}$ system on the basis of the extended model of micelle kinetics results in a rather detailed view of the molecular motions and associations in the micellar solutions. At amphiphilic concentrations c distinctly smaller than the cmc, where the surfactant molecules are predominantly distributed as monomers, only a few oligomeric species are present. In the sonic absorption spectrum the existence of oligomers will result in an ultrafast relaxation process (relaxation time τ_{uf}), an expectation that has still to be verified. At increasing c the growth of oligomers is favored by increasing hydrophobic interactions and at concentrations around the cmc an additional fast relaxation process with relaxation time τ_f develops, indicating the formation of larger micellar species. Due to an increase in the mean aggregation number \bar{m} in this range of surfactant content, τ_f first increases with the amphiphile concentration. At higher c well-defined micelles are formed the size distribution of which nearly follows a Gaussian with almost constant \bar{m} and σ^2 . Consequently, the relaxation time τ_f decreases with c as to be expected on grounds of increasing coreactant concentrations. Relative to that of micelles the concentration of oligomers gets smaller. Unlike long-chain surfactant systems, however, there is never a pronounced relative minimum separating the monomers from the micellar region in the size distribution. For this reason the mechanism of micelle formation is represented by one relaxation process (“f”) in the sonic spectra only. The slow process (“s”) predicted by the original theory is absent. Our model is capable of showing the fusion of both relaxation processes at decreasing chain length of the surfactant. When long-chain surfactant systems are considered, this process is treated in analogy to a diffusion of monomers through a thin pipe connecting two reservoirs. In this figurative picture the pipe is very short in short-chain surfactant solutions so that diffusion through it becomes an insignificant step. Instead of

the usual behavior of long-chain surfactant systems one particular relaxation ("f", "uf") occurs in each reservoir separately.

Limitations of the Extended Model. Many results of our model calculations agree with the experimental findings for the C₇ACl/water system. Even the extended model, however, only inappropriately applies for the broad relaxation time distribution in the fast ultrasonic relaxation process with relaxation frequency between about 1 and 100 MHz. This is especially true for concentrations at around the cmc. The reason may be the assumption of well-defined rate constants k_i^f and k_i^b in the reaction scheme defined by eq 1. This assumption is based on a clear Gibbs free energy profile for the monomer exchange.⁵ To less ordered small micelles this presumption may be inapplicable because the motions of monomers are controlled by quite different structures. Hence even for a given micellar size a distribution of rate constants will govern the relaxation processes and, therefore, lead to a further broadening of the relaxation time distribution. If this is true the width of the frequency range over which the fast relaxation process extends in the ultrasonic spectrum measures the degree of molecular order within (single) micelles. Probably a description of the formation of micellar species that not just proceeds from the idea of stoichiometrically well-defined chemical equilibria but also considers fluctuations in thermodynamic quantities such as the amphiphile concentration might more adequately apply for the short-chain surfactant systems. This idea involves special

contributions to the sonic spectrum near the cmc, at which a somewhat smeared phase transition¹⁶ occurs.

Acknowledgment. We wish to thank Professor R. Pottel for many helpful discussions. Financial support by the Deutsche Forschungsgemeinschaft is also gratefully acknowledged.

References and Notes

- (1) Telgmann, T.; Kaatze, U. *J. Phys. Chem. B* 1997, 101, 7758.
- (2) Kaatze, U.; Lautscham, K.; Berger, W. *Z. Phys. Chem.* **1988**, 159, 161.
- (3) Aniansson, E. A. G.; Wall, S. N. *J. Phys. Chem.* **1974**, 78, 1024.
- (4) Aniansson, E. A. G. *J. Phys. Chem.* **1978**, 82, 2805.
- (5) Aniansson, E. A. G. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, 82, 981.
- (6) Aniansson, E. A. G. *Prog. Colloid Polym. Sci.* **1985**, 70, 2.
- (7) Teubner, M. *J. Phys. Chem.* **1979**, 83, 2917.
- (8) Kahlweit, M.; Teubner, M. *Adv. Colloid Interface Sci.* **1980**, 13, 1.
- (9) Debye, P. *Polare Molekeln*; Hirzel: Leipzig, 1929.
- (10) Chan, S. K.; Herrmann, U.; Ostner, W.; Kahlweit, M. *Ber. Bunsen-Ges. Phys. Chem.* **1977**, 81, 60.
- (11) Hall, D. G.; Wyn-Jones, E. *J. Mol. Liq.* **1986**, 32, 63.
- (12) Telgmann, T. Diploma-thesis, Georg-August-University, Göttingen, 1994.
- (13) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C*; Cambridge University Press: Cambridge, 1992.
- (14) Trachimow, C. Dissertation; Georg-August-University, Göttingen, 1996.
- (15) Trachimow, C.; DeMayer, L.; Kaatze, U. *J. Phys. Chem.*, in preparation.
- (16) Anisimov, M. A. *Critical Phenomena in Liquids and Liquid Crystals*; Gordon and Breach: Philadelphia, PA, 1991.