# WHAT DO WE KNOW ABOUT MICELLES AND WHICH QUESTIONS ARE STILL OPEN ?

M. KAHLWEIT

MAX-PLANCK-INSTITUT FÜR BIOPHYSIKALISCHE CHEMIE,
POSTFACH 968, D-3400 GÖTTINGEN, F.R.G.

Abstract - An analysis of the time constants and amplitudes
of the relaxation processes in aqueous micellar solutions is
presented. Ionic micelles are considered as charged colloidal
particles. At low counterion concentration the electrostatic
repulsion prevents coagulation of the submicellar aggregates
so that micelles grow by incorporation of monomers only. At
high counterion concentration, however, this reaction path
is bypassed by a reversible coagulation of submicellar aggre-
gates. With nonionic systems, both reaction paths compete
right from the cmc on.The results are compared with the pre-
dictions of the DLVO theory and discussed with respect to the
structure and the equilibrium properties of micelles.

## INTRODUCTION

We shall consider aqueous solutions of nonionic and ionic detergents, the
latter in the presence of an electrolyte with the same counterion. The free
molecules of the detergent as well as those of the added electrolyte are
assumed to be completely dissociated. The size distribution of the aggre-
gates in such a solution is assumed to have the shape schematically shown
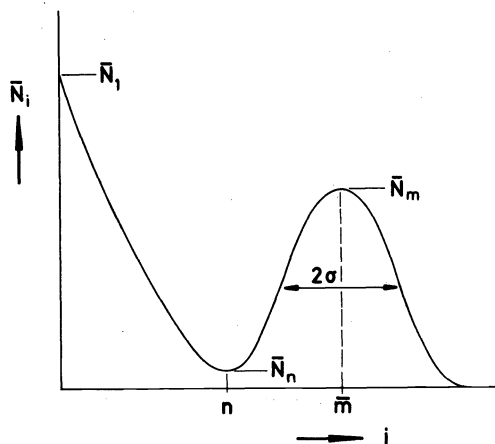in Fig. 1, where i denotes the number of detergent molecules per aggregate,



Fig. 1. Size distribution of aggregates in a
micellar solution (schematically).

and $N_i$ the number density of aggregates of class (i). The aggregates on the
left hand side of the minimum will be called submicellar, those on the
right hand side (proper) micelles.

The shape of the size distribution is thus characterized by the following
quantities:
$N_1$, the number density of free monomers
$n$ , the position of the minimum
$N_n$, the number density of aggregates at the minimum
$m$ , the mean aggregation number of the micelles

$\sigma$ , the width of their size distribution
$N_m$, the number density of aggregates at the maximum
We shall further use the following notations:
$N$ , the total number density of detergent molecules
$Z$ , the total number density of micelles
$N_e$, the number density of electrolyte molecules
$N_g$, the number density of free counterions
$N_\gamma$, the number density of monomers at the cmc.

The equilibrium values of all quantities will be denoted by a bar ($^-$). For reasons of convenience we shall further introduce the dimensionless concentration variable

$$X \equiv (N - \bar{N}_1)/\bar{N}_1 = \bar{m} \, \bar{Z} \, / \, \bar{N}_1$$

The cmc as well as the mean aggregation number of the micelles can be determined by static measurements. The dependence of the cmc on T and p yields the mean reaction enthalpy and reaction volume, respectively, of the aggregation reactions. Static measurements further indicate, that ionic micelles are incompletely dissociated. Their effective degree of dissociation, $\alpha_m$, can be determined by a number of methods, e.g., by measuring the dependence of $N_\gamma$ on $N_e$. By making use of the law of mass action and the mass balance one can then compute $\alpha_m$, $\bar{N}_1$, $\bar{N}_g$, and $\bar{Z}$.

The shape of the size distribution is a function of the variables T, p, N, and $N_e$. To study the kinetic processes in the solution, one may, therefore, perturb the system by a rapid change of one of these variables and then follow its reequilibration by means of an appropriate detection method. If one does so, one finds, in general, two relaxation processes, the time constants of which are about three orders of magnitude apart.


A BRIEF RETROSPECT

The first successful attempt to analyse the time constants of the two relaxation processes was published by Aniansson and Wall (1) in 1974. It was based on the assumption that micelles can grow by incorporation of monomers only, according to the equation

$$N_{i-1} + N_1 \rightleftharpoons N_i \quad , \tag{1}$$

but was restricted to nonionic detergents. In view of Fig. 1 the authors assumed the association reactions near the minimum of the size distribution to be rate determining for the formation of micelles. Correspondingly, the first relaxation process arises from a rapid redistribution of the proper micelles. During this process the mean aggregation number of the micelles changes, whereas their total number remains unchanged. In the following slow process then both the total number of micelles and their mean aggregation number approach their final equilibrium values. These two processes are schematically shown in Fig. 2.

For the time constant $\tau_1$ of the fast process Aniansson and Wall derived

$$1/\tau_1 = (b_m/\sigma^2) \; [1 + (\sigma^2/\bar{m}) \; X] \tag{2}$$

where $b_m$ is the mean rate constant for the dissociation of a monomer from a micelle. Eq. (2) predicts a linear increase of $1/\tau_1$ with X, the intersection with the ordinate giving $(b_m/\sigma^2)$, the slope $(b_m/\bar{m})$. Since $\bar{m}$ can be determined by static measurements, the concentration dependence of $1/\tau_1$ thus yields

$$1/\tau_1 : \quad \sigma \quad \text{and} \quad b_m \approx N_\gamma \, a_m$$

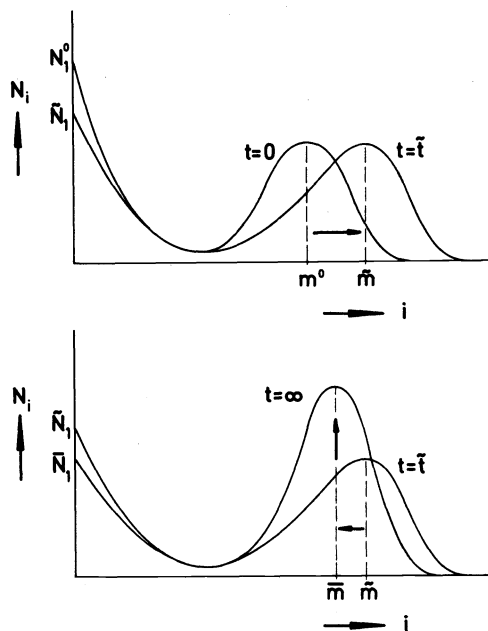where $a_m$ is the corresponding association rate constant.

Fig. 2. Physical nature of the two relaxation processes
in micellar solutions (schematically).
Above: first process;    below: second process.

Although derived for nonionic detergents, this result was compared by quite
a number of research groups in the following years mainly with experiments
on ionic systems, apparently because the relaxation processes are much
easier to detect in such systems than in nonionic ones. The agreement
between theory and experiment was, in general, satisfactory.

For the time constant for the formation of micelles, $\tau_2$, Aniansson and Wall
derived

$$1/\tau_2 \sim X^{n/\bar{m}} [1 + (\sigma^2/\bar{m})\ X]^{-1} \tag{3}$$

where the proportionality constant includes the mean rate constant for the
dissociation reactions in the rate determining region, i.e., at the minimum
of the size distribution, the effective width of this minimum as well as
law of mass action constants.

In this case the agreement between theory and experiments on ionic systems
was qualitative only: at intermediate and high detergent concentrations,
eq. (3) predicts a monotonous decrease of $1/\tau_2$ with X. The experiments con-
firmed this prediction, in general, but the decrease was found to be consi-
derably steeper than predicted. It was soon recognized that this discrepancy
had to be attributed to the ionic nature of the detergents, in particular,
to the influence of their counterions.

In 1978 Teubner et al. (2,3) supplemented the analysis of the time constants
by an analysis of the corresponding amplitudes. This analysis was again
based on reaction equation (1), again treating the micelles as being non-
ionic. It turned out that the equations for the relative amplitudes can be
split into a detection term and a perturbation term:

$$A_1 = f \cdot (x_1^o - \tilde{x}_1) \tag{4}$$

and

$$A_2 = g \cdot \tilde{x}_1 \tag{5}$$

The detection term of f and g, resp., are functions of the parameters which
are followed in order to detect the relaxation process, such as electric

conductivities or extinction coefficients, as well as of X.

$x_1^o$ and $\tilde{x}$ denote the relative deviations of the monomers at the beginning of the fast and of the slow process, resp., and are functions of the derivatives of the equilibrium properties of the micellar system with respect to the intensive variable which is changed in the relaxation experiment, as well as of X.

The agreement between theory and experiments on ionic systems was satisfactory. Fig. 3 shows as an example the concentration dependence of $A_2$ for the
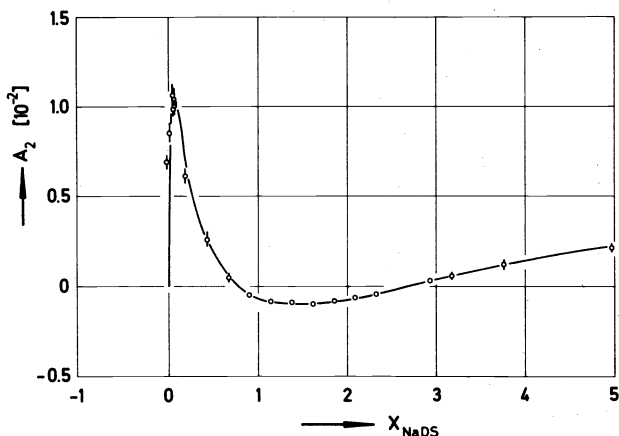


Fig. 3. Relative amplitude $A_2$ versus X for
$H_2O$ - NaDS. $25^{\circ}C$; p-jump/conductivity; ref.(2).

system $H_2O$ - NaDS at $25^{\circ}C$, perturbed by means of a p-jump and detected by following the electric conductivity. The full line shows the fit of the theoretical equation to the experimental results: the amplitude rises from zero at the cmc, passes through a maximum, changes sign, passes through a minimum, changes sign again, and appears to approach a plateau with further increasing concentration.

The first zero is readily understood: as Fig. 1 illustrates, monomers and micelles can be looked at as communicating tubes. As the number density of monomers decreases, that of the micelles increases, and vice versa. Since, however, both species have different equivalent conductivities, at a certain concentration the change of the contribution of the monomers to the total conductivity will compensate the change of the contribution of the micelles. The first zero thus represents a zero of the detection term and appears only if the relaxation process is detected by following the conductivity. The slow process itself does take place at this concentration, but becomes indetectable by this particular detection method.

The position $X_K$ of this first zero is a function of the equivalent conductivities of the species as well as of $(\sigma^2/\bar{m})$. Since the conductivities can be determined by static measurements, the determination of $X_K$ thus represents an additional method for the determination of $(\sigma^2/\bar{m})$:

$$X_K \quad : \quad (\sigma^2/\bar{m})$$

The second zero arises from a zero of the perturbation term and is of a more fundamental nature: As it can be shown (4), the relative deviation of the monomers at the beginning of the slow relaxation process is related to the dependence of the cmc and $\bar{m}$ on the intensive variable y by

$$\tilde{x}_1 \sim (\partial \ln Z/\partial y) \cdot \delta y \tag{6}$$

where

$$\partial \ln Z/\partial y = - [(1/X) (\partial \ln N_\gamma/\partial y) + (\partial \ln m/\partial y)] \tag{7}$$

Consequently, if $(\partial \ln N_\gamma/\partial y)$ and $(\partial \ln m/\partial y)$ are of opposite sign, $(\partial \ln Z/\partial y)$ will change sign at a certain concentration, as will $\tilde{x}_1$. At this particular concentration, the change of the cmc is compensated by the change of $\bar{m}$. $\bar{Z}$ remains unchanged,i.e., the first process leads to the final equilibrium, the second process does not take place. If, however, $(\partial \ln N_\gamma/\partial y)$ and $(\partial \ln m/\partial y)$ are of equal sign, this second zero will not appear.

Since the determination of the dependence of the cmc, and, in particular, of $\bar{m}$ can be tedious, a fit of eq. (5) to the experimentally determined concentration dependence of $A_2$ represents a convenient method for the determination of $(\partial \ln N_\gamma/\partial y)$ and $(\partial \ln m/\partial y)$:

$$A_2: \quad (\partial \ln N_\gamma/\partial y) \quad \text{and} \quad (\partial \ln m/\partial y)$$

Besides of these two zeros, Fig. 3 shows another important feature of the concentration dependence of $A_2$: between the two zeros the amplitude is rather small, with further increasing concentration, however, it approaches a plateau which represents a measure for $(\partial \ln m/\partial y)$. Thus, as long as the dependence of $\bar{m}$ on the corresponding intensive variable is different from zero, the concentration range of the experiments can be extended to high detergent concentrations.

In 1980 Herrmann et al. (5) published the results of relaxation experiments on the nonionic system $H_2O$ - Triton X-100. Fig. 4 shows $A_2$ as well as $1/\tau_2$ versus X. The system was perturbed by means of a T-jump, the process detected by following the change of the fluorescence of an indicator.
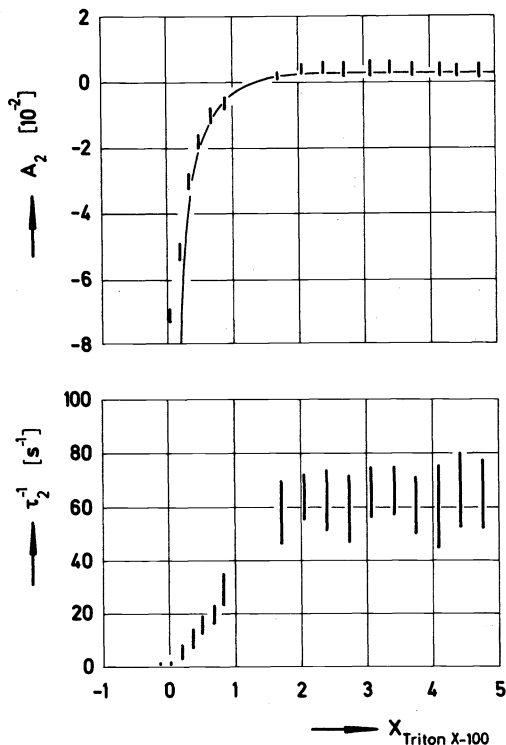


Fig. 4. Relative amplitude $A_2$ and inverse time
constant $1/\tau_2$ versus X for $H_2O$ - Triton X-100 - NaCl.
$10^\circ C$; T-jump/indicator; ref. (5).

In this case, $A_2$ shows only one zero, which stems from the zero of the perturbation term. The concentration dependence of the amplitude agrees well

with the predictions of the theory (full line), whereas that of the time constant shows a qualitative discrepancy: $1/\tau_2$ increases from zero at the cmc to apparently approach a plateau with further increasing concentration, whereas eq. (3) predicts a monotonous decrease.

This discrepancy is the more surprising, since the analysis of the time constants by Aniansson and Wall on the basis of eq. (1) should be valid in particular for nonionic systems. In the meantime, this characteristic shape of the $1/\tau_2$ curve has been confirmed for two other nonionic systems, namely $C_{12}E_8$ and $C_8E_6$ (6).

In 1981, finally, Leßner et al. (7) succeeded in improving an earlier attempt by Chan et al. (8) to take into account the ionic nature of detergents and presented a consistent theory of the amplitudes and the time constants of the two relaxation processes, being valid for ionic and nonionic systems.

The two main results of this analysis were the following:
i) the amplitudes can be analysed without detailed information about the reaction path, along which the system approaches its equilibrium, by merely applying the law of mass action and the mass balance. With respect to the amplitudes an agreement between theory and experiment thus only confirms the law of mass action in its explicit form, but not the underlying reaction equation.

ii) the analysis of the time constants, on the other hand, has to be based on a particular reaction equation. If one again assumes eq. (1), the analysis yields that for ionic systems at intermediate and high concentrations, the concentration dependence of the time constant of the slow process is mainly determined by the concentration of the counterions:

$$1/\tau_2 \sim (\bar{N}_g/\bar{N}_1)^{-q} \qquad (8)$$

where q is a function of n, $\alpha_m$ and the mean degree of dissociation of the aggregates at the minimum of the size distribution, $\alpha_n$.

For nonionic systems the result reduces to eq. (3). For ionic systems, however, it predicts a considerably steeper decrease of $1/\tau_2$ with increasing detergent concentration. Eq. (8) further predicts that if relaxation experiments are performed on ionic systems in the presence of different amounts of an added electrolyte with the same counterion, at intermediate and high counterion concentrations all $1/\tau_2$ curves should coincide if plotted versus
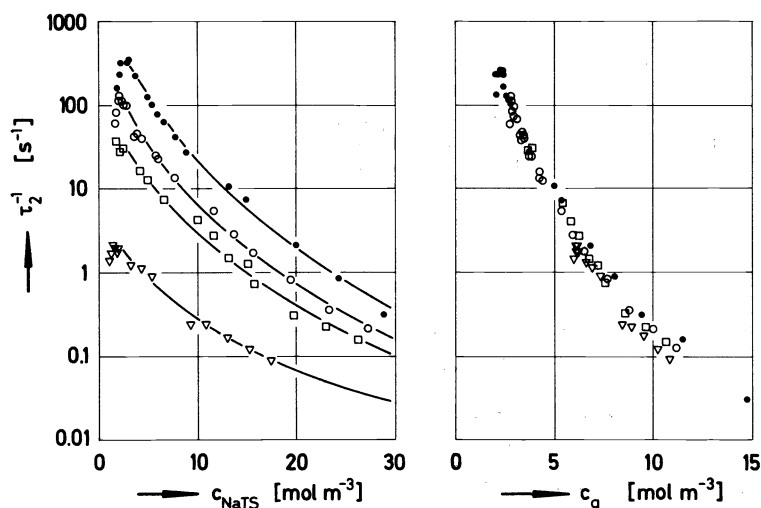


Fig. 5. Inverse time constant $1/\tau_2$ for $H_2O$ – NaTS – $NaClO_4$. 35°C; ref. (7). $NaClO_4$ in mol m$^{-3}$: (●) 0; (o) 1; (□) 2; (▽) 5.

the concentrations of the (free) counterions instead of detergent concentration. This was confirmed by experiments on the system $H_2O$ - NaTS. Fig. 5 shows $1/\tau_2$ for this system with different amounts of $NaClO_4$. The left part shows the results plotted versus the detergent concentration with the electrolyte concentration as parameter, the right part shows the same results plotted versus the counterion concentration.

### PROPOSAL OF A MODEL

Leßner et al. (9) then extended the measurements to higher detergent concentrations on the system $H_2O$ - NaDS. Fig. 6 shows $A_2$ and $1/\tau_2$ at $25^{\circ}C$. With
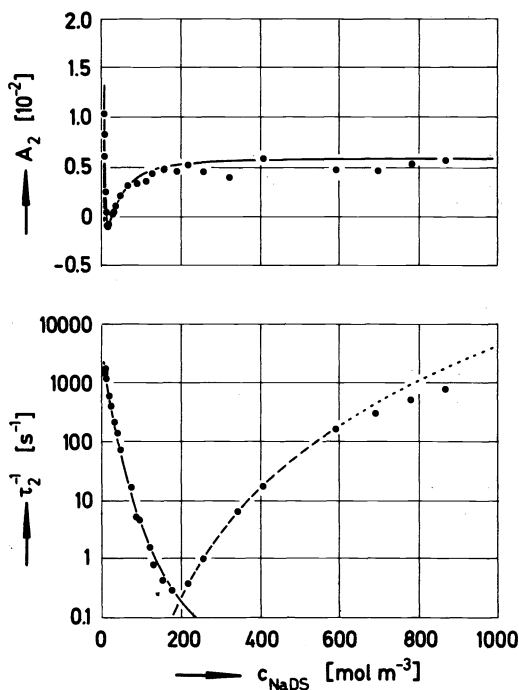


Fig. 6. Relative amplitude $A_2$ (above) and inverse time
constant $1/\tau_2$ (below) for $H_2O$ - NaDS at $25^{\circ}C$; ref. (9).
Full lines: fits of eq. (5) and (8), resp.
Broken line: fit of eq. (16).

respect to the amplitude, the experimental results agree well with the theory (full line), indicating that the law of mass action in its explicit form is valid over the entire concentration range, and that, in particular, no new species appear.

The same is true for the time constant at low and intermediate concentrations: $1/\tau_2$ decreases monotonously as predicted by eq. (8) (full line). At $c_{NaDS} = 1.8 \cdot 10^2$ mol m$^{-3}$, however, it passes through a minimum and increases again, apparently approaching a plateau at high concentrations, in qualitative contradiction to the theory.

The observation that in some ionic systems $1/\tau_2$ first decreases, then passes through a minimum to increase again, has already been reported by other authors (10). Also known was the fact that the addition of electrolytes leads to a shift of the minimum towards lower detergent concentrations.

In their attempt to interpret this behaviour, Leßner et al. (9) then measured the temperature dependence of $1/\tau_2$ below and above the minimum and

found the dependence below the minimum to be about twice as strong as that above. This indicates that the reaction path for the formation of ionic micelles is different below and above the minimum. Since it further occured to them that the detergent concentration at the minimum is of the order of the socalled "flocculation value" of dispersion colloids, they proposed the following model:

Ionic micelles, including the submicellar aggregates, can be looked at as charged particles. Below the minimum of the $1/\tau_2$ curve, these particles are stable with respect to coagulation due to the repulsive electrostatic forces. Consequently, they can grow by subsequent incorporation of monomers only according to reaction equation (1).

With increasing counterion concentration, however, the electric double layer around the particles becomes increasingly compressed, so that the attractive dispersion forces can lead to a coagulation according to the reaction equation

$$N_k + N_1 \rightleftharpoons N_i \quad ; \quad k + 1 = i \tag{9}$$

where (k) and (l) denote classes of submicellar aggregates, i.e. on the left hand side of the minimum of the size distribution (Fig. 1), whereas (i) denotes a class of the proper micelles, i.e. on the right hand side of the minimum.

To preserve microscopic reversibility this implies an important consequence with respect to the properties of the micelles, since it requires the possibility of dissociation of a proper micelle into two submicellar units.

One can then represent the reaction path for the formation of micelles by two parallel resistors $R_1$ and $R_2$, where $R_1$ refers to reaction path eq. (1) and $R_2$ to reaction path eq. (9).

At low counterion concentrations $R_2$ is very high due to the electrostatic repulsion between the submicellar aggregates. In that concentration range, therefore, $R_1$ determines the rate of formation of micelles. $R_1$, however, increases with increasing counterion concentration as $(\bar{N}_g)^q$ (eq. (8)), whereas $R_2$ decreases due to the compression of the electric double layer around the particles, until both resistors become comparable: $1/\tau_2$ passes through a minimum. With further increasing counterion concentration $R_1$ becomes so high that from then on, $R_2$ determines the rate of formation of the micelles.

One can thus write

$$- \dot{x}_1 = [(\tau_{21})^{-1} + (\tau_{22})^{-1}] \, x_1 \tag{10}$$

where $1/\tau_{21}$ is given by eq. (8) and $1/\tau_{22}$ has to be evaluated from the theory of reversible coagulation, using the results of the DLVO theory.

Based on reaction equation (9) one finds

$$1/\tau_{22} = \beta \, \bar{m} \, X \, [1 + (\sigma^2/\bar{m}) \, X]^{-1} \tag{11}$$

where $\beta$ is a measure for the mean dissociation rate constant of reaction equation (9).

For nonionic detergents, the electrostatic repulsion being absent, $R_2$ should be low already at the cmc, so that with nonionic micelles both reaction paths should compete right from the cmc on. By combination with eq.(3) one thus finds for the concentration dependence of the time constant of the slow relaxation process in nonionic systems

$$1/\tau_2 = (M \, X^{n/\bar{m}} + \beta_o \, \bar{m} \, X) \, [1 + (\sigma^2/\bar{m}) \, X]^{-1} \tag{12}$$

where $\beta_o$ denotes the mean dissociation rate constant of the reaction eq. (9)

in the absence of a potential barrier.

The shape of the $1/\tau_2$ curve then depends on the values of M and $\beta_o \bar{m}$, respectively. For M >> $\beta_o \bar{m}$, i.e., if the nonionic micelles grow mainly by incorporation of monomers, eq. (12) reduces to eq. (3). If, however, M << $\beta_o \bar{m}$, i.e., if the nonionic micelles form mainly by coagulation of sub-micellar aggregates, eq. (12) becomes

$$M << \beta_o \bar{m}: \quad 1/\tau_2 = \beta_o \bar{m} X [1 + (\sigma^2/\bar{m}) X]^{-1} \tag{13}$$

which has the shape of an adsorption isotherm, in accord with Fig. 4.

For ionic detergents, on the other hand, $\beta$ should be a function of the counterion concentration. To obtain this dependence one makes use of Fuchs' (11) theory of slow coagulation, which yields for the association rate constant

$$a = a_o / f$$

where $a_o$ is the association rate constant for rapid coagulation, and f is the socalled retardation factor. Since the law of mass action requires $\beta$ to have the same concentration dependence as the association rate constants, one may thus set

$$\beta = \beta_o / f \tag{14}$$

Following the procedure outlined by Reerink and Overbeek (12) one finds

$$f = (\bar{N}_g/N_{go})^{-s} \tag{15}$$

where $N_{go}$ is the flocculation value, and s is a function of the surface potential and the radius of the particles, as well as of the valency of the counterions. With these results eq. (11) becomes

$$1/\tau_{22} = \beta_o \bar{m} X [1 + (\sigma^2/\bar{m}) X]^{-1} (\bar{N}_g/N_{go})^s \tag{16}$$

for $\bar{N}_g \leq N_{go}$.

Fig. 6 shows the fit of this equation to the experimental curve (broken line). The fit yields:

$$\beta_o = 20 \text{ s}^{-1}, \quad c_{go} = 3 \cdot 10^2 \text{ mol m}^{-3} \quad \text{and} \quad s = 6$$

which are of the expected order of magnitude. The same is true for the Hamaker constant, which can be evaluated from $c_{go}$:

$$A = 6 \cdot 10^{-20} \text{ J}$$

According to the DLVO theory the addition of an electrolyte with the same counterion should enhance the rate of coagulation. Fig. 7 shows $1/\tau_2$ of the system $H_2O$ - NaDS at $25^{\circ}C$ in the presence of different amounts of $NaClO_4$.
In accord with the prediction, increasing counterion concentration leads to a shift of the minimum towards lower detergent concentrations, until, at high electrolyte concentrations, $1/\tau_2$ appears to increase right from the cmc on, resembling the concentration dependence of $1/\tau_2$ in nonionic systems (Fig. 4).

For high X, eq. (16) reduces to essentially
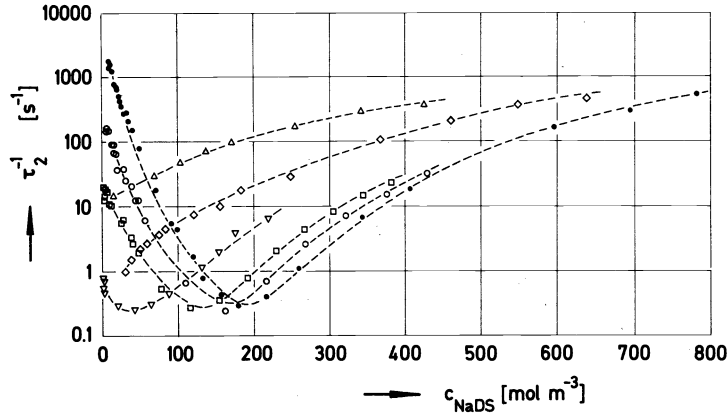
$$1/\tau_2 \sim (\bar{N}_g/N_{go})^s \tag{17}$$

Fig. 7. Inverse time constant $1/\tau_2$ for $H_2O$ - NaDS - $NaClO_4$
at $25^{\circ}C$ versus detergent concentration, ref. (9).
$NaClO_4$ in mol $m^{-3}$: ($\bullet$) 0; (o) 10; ($\square$) 20; ($\triangledown$) 50; ($\Diamond$) 100; ($\triangle$) 200.

By combination with eq. (8) one then finds for the concentration dependence
of the time constant of the slow relaxation process in ionic systems at
intermediate and high counterion concentrations

$$1/\tau_2 = C_1 \, (\bar{N}_g/\bar{N}_1)^{-q} + C_2 \, (\bar{N}_g/N_{go})^{s} \tag{18}$$



Eq. (18) predicts that if the curves in Fig. 7 are plotted versus the counterion concentration instead of detergent concentration, they should coincide. Furthermore, if plotted on a double logarithmic scale, the resulting curve should be represented by two straight lines, the slope below the minimum being -q, that above the minimum +s. Fig. 8 shows this plot.
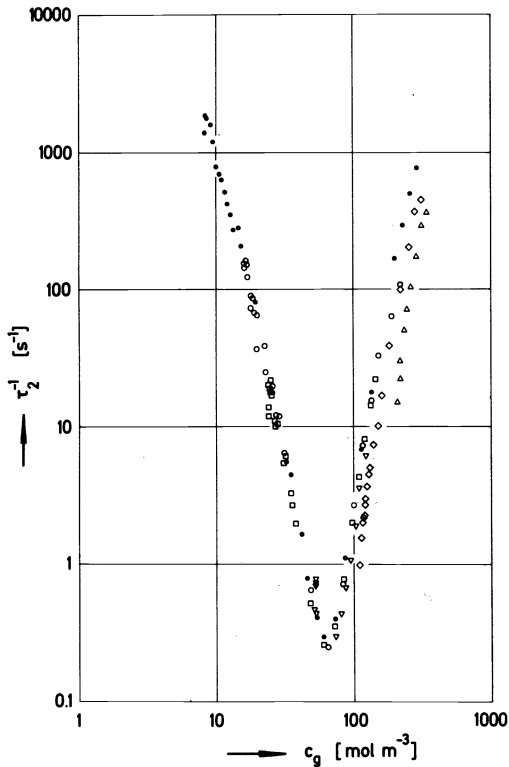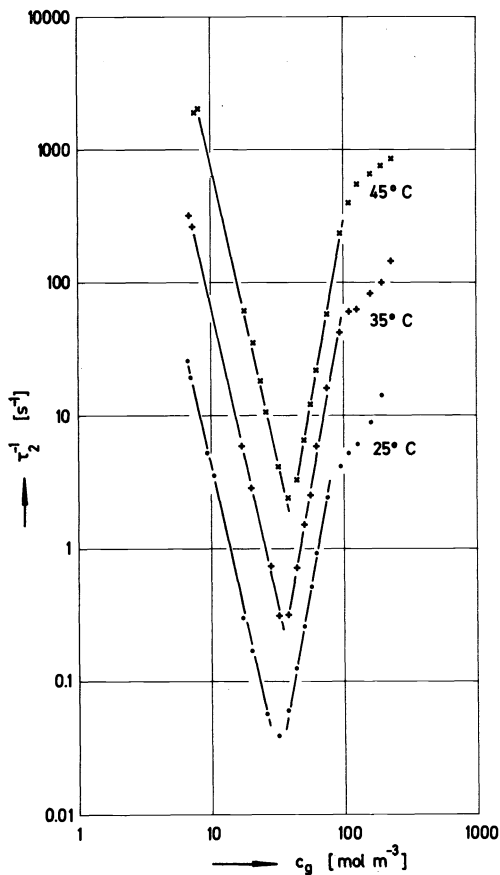
Fig. 8 . Inverse time constant $1/\tau_2$ for $H_2O$ - NaDS - $NaClO_4$ at $25^{\circ}C$ versus counterion concentration (double logarithmic plot), ref. (9). Symbols as in Fig. 7.

To further support the proposed model, Klar and Leßner (13) have studied the temperature dependence of the slope s and that of the flocculation value $N_{go}$. The DLVO theory predicts (12) the temperature dependence of s to be much weaker than that of $N_{go}$:

$$s \sim T, \quad \text{whereas} \quad N_{go} \sim T^5 \qquad (19)$$

Fig. 9 shows $1/\tau_2$ for the system $H_2O$ – CsDS versus counterion concentration at different temperatures, plotted again on a double logarithmic scale. In qualitative agreement with the theory the temperature dependence of s is indeed rather weak, whereas the minimum – being a measure for $N_{go}$ – is considerably shifted towards higher concentrations with increasing temperature.

Fig. 9. Inverse time constant $1/\tau_2$ for $H_2O$ – CsDS versus counterion concentration at different temperatures (double logarithmic plot), ref. (13).
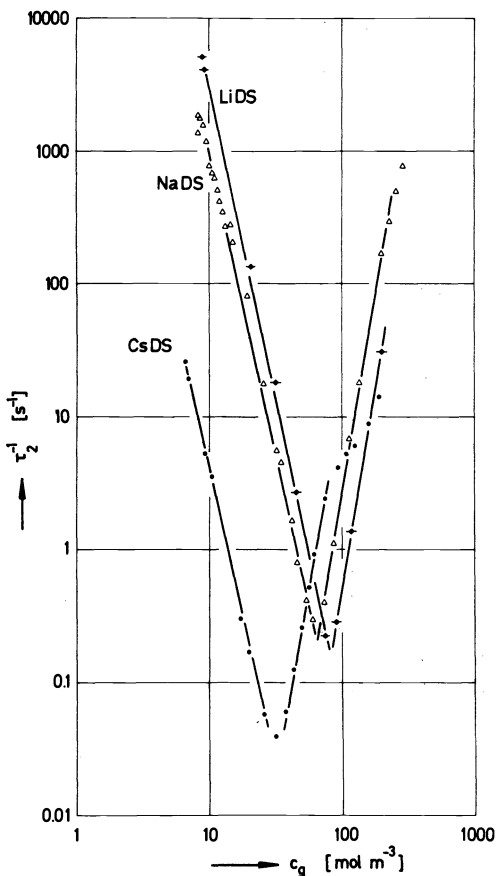


Experience tells that with dispersion colloids the order of the flocculation value is

    Li > Na > Cs

Klar and Leßner have, therefore, compared the positions of the minima for LiDS, NaDS and CsDS, all at 25°C. Fig. 10 shows the result. As one can see, the positions of the minima do follow the same order. We note that the same is true for the cmc's of these detergents.

Fig. 10. Inverse time constant $1/\tau_2$ for LiDS, NaDS and CsDS at 25°C versus counterion concentration (double logarithmic plot), ref. (13).

The question then arises, whether or not cationic detergents show a similar behaviour. The answer is positive: Fig. 11 shows the V-curve for the system $H_2O$-DTABr (dodecyltrimethylammonium bromide) at $10^\circ C$.
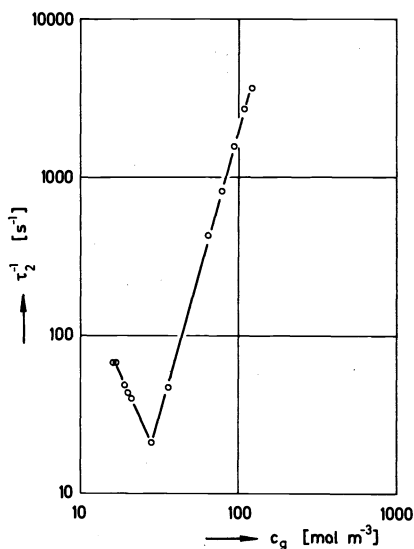


Fig. 11. Inverse time constant $1/\tau_2$ for DTABr at $10^\circ C$ versus counterion concentration (double logarithmic plot).


CONSEQUENCES AND OPEN QUESTIONS

The major question, of course, is that with respect to the structure of the micelles. In that connection we wish to draw the attention of the reader to considerations by Fromherz (14) who suggested a surfactant-block model for micelles. According to his model, originally developed to solve the antago- nism between earlier models, a micelle is essentially constructed out of eight subunits of ordered detergent molecules. If this model was an approach to reality, one could conceive a proper micelle to dissociate into submicel- lar aggregates.

The model further predicts that a fully assembled micelle is rather stable with respect to further incorporation of monomers. It permits, however, the association of proper micelles to large rod shaped micelles. Since our model claims that at a sufficient high counterion concentration submicellar aggre- gates associate to form micelles, the question arises at which concentration the proper micelles start to associate. To answer this question we have extended the measurements to even higher detergent concentrations. Fig. 12 shows the results for the system $H_2O$ - CsDS at different temperatures. As one can see, the amplitudes remain constant over a wide concentration range. At very high detergent concentrations, however, they rise, pass through a maximum and decrease again. The effect decreases with rising temperature. It indicates that the explicit form of the law of mass action, as used in the analysis of the amplitudes at lower concentrations, may no longer be valid, in particular, that new species appear.

In this connection we recall that other authors (15) have found a sudden increase of the molecular weight of NaDS micelles after adding a sufficient amount of $Na^+$ counterions to a diluted NaDS solution. To obtain the same counterion concentration with NaDS alone, one would have to apply $1.5 \; 10^3$ mol $m^{-3}$ NaDS, which is impossible due to the limited solubility of NaDS at this temperature. Whether or not the two effects are correlated, has thus still to be clarified.

Another question to be studied is the transition from the isotropic to the anisotropic phases at high detergent concentrations, i.e., the appearance of a long range order in micellar solutions.
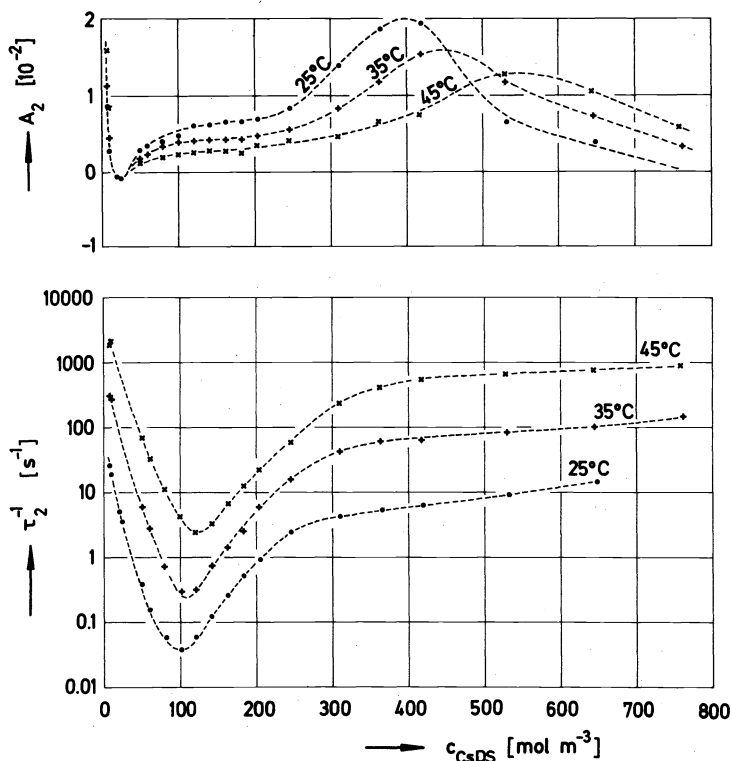
Fig. 12. Relative amplitude $A_2$ and inverse time constant $1/\tau_2$
for $H_2O$ - CsDS at different temperatures.


Last but not least we wish to mention the consequences of these results for
the processes in micellar catalysis, since one is now in the position to vary
the lifetime of the micelles over several orders of magnitude as well as the
reaction mechanism of their formation by an appropriate choice of the chain
length of the detergents and the chemical nature of the counterions.

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