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Micellar Catalysis and Concept in Apolar Media*

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The active interest aroused by catalytically affected reactions in apolar surfactant solutions requires one to look for a relation to micelle formation and solubilization in an effort to attain a more unified description of phenomena peculiar to apolar surfactant systems.

Since these catalytic phenomena are usually summarized by the notion »micellar catalysis« the present paper wants to contribute towards a sound abstraction of this concept. This was done by analyzing a particular catalyzed reaction (the catalyzed hydrolysis of *p*-nitrophenylacetate in the presence of dodecylammoniumpropionate in cyclohexane) in the frequently investigated apolar solutions of cationic surfactants. A quantitative description of the overall reaction was obtained which was found in satisfactory agreement with experimental details. It was concluded that micellar and multiple association patterns are reflected also in the relationships obtained by examining catalytically influenced reactions in these systems.

Catalysis in quaternary liquid mixtures, i. e. substrate, water, apolar solvent, and surfactant, has been investigated very intensively in recent years, starting probably with the first observation of this kind by Friberg and coworkers[1] in 1971. The possibility to solubilize certain amounts of substrate and water in the polar environment of reversed micelles appeared to be very promising in view of several aspects: For example, the role of water as reactant in the rate determining step can be investigated under these conditions. Many other effects due to the existence of reversed micelles have been anticipated. In a number of instances, however, the interpretation is apparently influenced by assumptions with regard to structural details of the expected micellar aggregate which actually may not even be formed.

The numerous experimental results derived from such investigations were collected by Fendler and Fendler[2] in their comprehensive monograph on this subject. It appears that in general the interest has been focussed — apart from the remarkable catalytic effects observed in some of these systems — on apparent differences in the action of the so called anionic, cationic and nonionic surfactants. Moreover, one seems to assume (as far as the term »micellar catalysis« is concerned) that (a) these aggregates are formed by surfactants

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in the presence of water (or aqueous substrate solutions) and (b) that they can be considered to be micellar aggregates, in particular, reversed micelles.

Due to the importance of reversed micellar aggregates as model systems for the study of encymatic and membrane interactions, reaction mechanism in organic solvents, and pharmaceutical applications as, for example, the microencapsulation (i. e. solubilisation phenomena of polar solubilisate), considerations of the supposed mutual relation between stability and catalysis appears to be tempting in two respects:

(1) It could serve to elucidate and characterize the concept of a lipophilic micelle from a different point of view and (2) to define the idea of the »micellar catalysis«, i. e. in which way it is related to the well known concepts of homogeneous and heterogeneous catalysis. If homogeneous catalysis considers the entire reaction to occur in a single phase, while heterogeneous catalysis at interphases, the introduction of the new concept of micellar catalysis appears to be justified only if the catalysis within a micellar aggregate is related to the proper association process of the surfactants, i. e. if the micellar catalysis is due to a cooperative phenomenon. Occasionally such cooperative phenomena produced by the micellization process in apolar solvents were reported, for example, the modified properties of solubilized water of the so-called aqueous pseudophase[3,4]. One should realize, however, that this pseudophase concept itself is not satisfactorily defined. Actually, it does not appear possible to offer a general definition since this should be based on well reproducible experiments. There are a number of experimental techniques, for example, NMR, viscosity, density, and IR-measurements which permit one to distinguish roughly between strongly bonded solubilized molecules (for example, water) usually in the first hydration shell of the cations and more loosely attached or »free« molecules of the solubilizate. It is thus evident that a certain ambiguity is unavoidable when the concept »pseudophase« is justified. Considering this one has to decide in every particular case as to the usefulness of this notion. AOT in *n*-octane or isooctane, is a suitable example where the application of the pseudophase concept is acceptable since this anionic surfactant may solubilize up to ~ 120 mol H_2O/mol AOT[3,5]. The corresponding situation with nonionic surfactants is even more favorable since these systems solubilize considerably larger amounts of water. Within the class of ionic surfactants the anionic amphiphilic molecules predominantly tend to form lipophilic aggregates which take up well defined amounts of water. The obvious connection between pure lipophilic micelles of this kind and their solubilizing capacities is stressed frequently[6,7]. Somewhat contrary to this class with regard to their solubilizing capacity is the catalytically interesting and often investigated group of cationic surfactants[8]. Proton and electron transfer were reported repeatedly especially on surfactants containing alkylammonium cationic groups combined with anions of monocarbonic acids[8–10].

As has been mentioned above it has become customary to use the notion »micellar catalysis« quite generously as soon as catalytic phenomena in the above defined surfactant systems are considered. It will be shown that this concept should be used with more caution since it might be concluded from the following discussion that it is quite questionable whether, in the many instances cited in the literature, micelles (or micellar aggregates containing water) have formed at all — even in the presence of water.

Since there is still some discussion as to the existence of lipophilic micelles, it appears to be necessary to remember some of the facts known about micellization in apolar solvents. After that the catalytic effects which are ascribed to the existence of such micelles can be analyzed in the light of some new experimental results. The micellization of surfactants in aqueous and nonaqueous media is a particular pattern of the generally known association phenomenon, exhibited by a large number of organic molecules in the dissolved state. Micelle formation is considered to be characterized by a spontaneous, reversible, rather monodisperse and relatively ordered aggregation above a certain critical concentration (CMC). Figure 1. shows for two typical anionic (AOT) and cationic (DAP) surfactants the mono- and polydispersity of the surfactant aggregates in cyclohexane, respectively. The evaluation of this diagram followed the procedure given by Adams et al.[11]. Other typical features of reversed micelles in apolar solvents were discussed elsewhere in greater detail[7,12]. Summarizing, all experimental details on apolar surfactant solutions demonstrate unambiguously that reversed micelles exist according to the above mentioned criteria. Furthermore, as is shown in Figure 1. for DAP/C_6H_{12}, many so-called amphiphilic molecules do not exhibit the tendency (or exhibit only a weak tendency) to form relatively ordered and individualized concentration independent aggregates. On the contrary they exhibit concentration dependent sizes of the aggregates and varying distributions of the apparent molecular weights. In predicting micellar or non-micellar aggregational patterns of amphiphilic molecules one often refers to the still somewhat uncertain

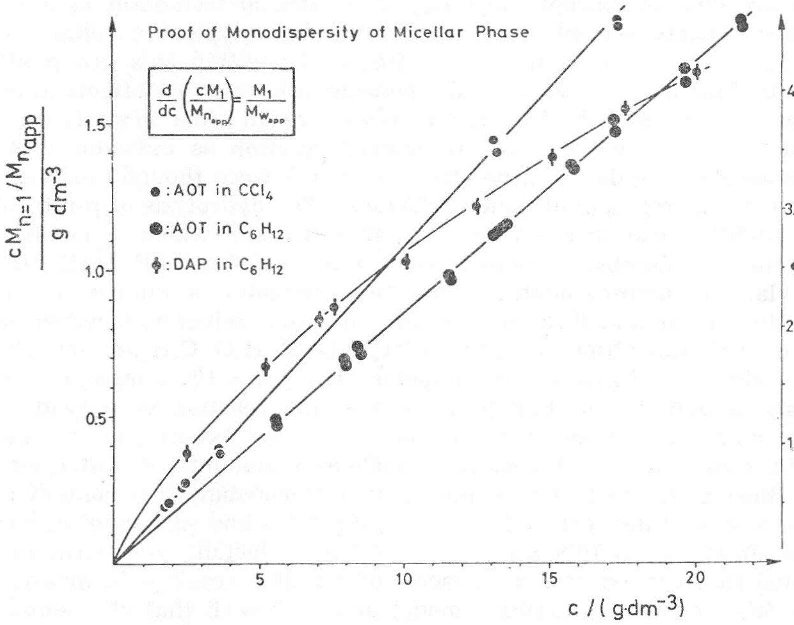

Figure 1. Aggregational behaviour of DAP and AOT in cyclohexane. The diagram has been plotted according to the procedure of Adams et al[11]

intuitive concept of the »hydrophile-lipophile-balance« (HLB). However, the frequently observed tendency to distinguish between cationic and anionic surfactants according to their aggregational behaviour is certainly unjustified. It can be positively stated that both anionic and cationic surfactants form reversed micelles. Due to very recent experimental results[13] the relation between spatial requirements of the lipophilic molecular parts and the molecular structure of the surfactant, i. e. the structurally caused feasibility of intramicellar dispersion interaction which were already considered in earlier discussions[14], proves again to be an essential prerequisite for micellization. The micellar stability, however, depends on enthalpic and entropic contributions to the free energy of micellization.

Turning now back to a more detailed investigation of a possible relation between the micellar concept and catalysis cationic surfactants in apolar media appear particularly suitable since deviations from typical micellar patterns according to experience is met more frequently within this group of ionic surfactants. Furthermore, they exhibit considerable catalytic effects in quaternary liquid mixtures of the kind mentioned above. In order to study the above supposed relation, a catalytically influenced reaction as indicator was used. Hence molecular details could be analyzed which were thought relevant with respect to the aggregation of ionic surfactants. The hydrolysis of *p*-nitrophenylacetate (*p*-NPA) was selected as a suitable reaction which is catalyzed by proton donors. A number of cationic surfactants, as e. g. DAP, DAB, DAF etc. (=dodecylammoniumpropionate, -benzoate, -formiate) is known to catalyze this reaction. Their micellization tendency in apolar solvents, however, is controversial. It is thus observed in the *p*-NPA, DAP, H_2O, C_6H_{12}-system that the reaction velocity is increased by a factor of $1 - 2 \times 10^2$ compared with the hydrolysis in bulk water. Furthermore, that the reaction velocity decreased with larger amounts of added water, and, to a lesser extent, with the increase of *p*-NPA concentration at constant weighed-in amounts of water and surfactant. Raising the surfactant concentration at constant H_2O content accelerates the reaction rate. Although the ratio of *p*-NPA and surfactant concentrations was about 10^{-3} to 10^{-2}, an increase in the surfactant concentration by 10 accelerated the reaction rate by a factor of 4.2. This result is in disagreement with the idea of the pseudophase model and thus with that of a solubilizing micellar aggregate. The experimental results are plotted in Figure 2. The overall reaction scheme which explains satisfactorily the mutual relationships between the reaction velocity and the reactants resembles a catalytical reaction superimposed by a competitive side reaction, i. e. the hydration of DAP:

$$\begin{gathered} \mathrm{S + C \rightleftharpoons SC \rightarrow C + P} \\ \mathrm{C + n\,(H_2O) \rightleftharpoons C\,(H_2O)_n} \end{gathered} \tag{1}$$

where S is the substrate, C the catalyst(=surfactant), and P the product. Introducing the extent of reaction (ξ) with respect to both equations, the mass balance yields for the three essential variables

$$\begin{gathered} [s] = s_0 - \xi_1 \\ [C] = c_0 - \xi_1 - \xi_2 \\ [H_2O] = w_0 = n\xi_2 \end{gathered} \tag{2}$$

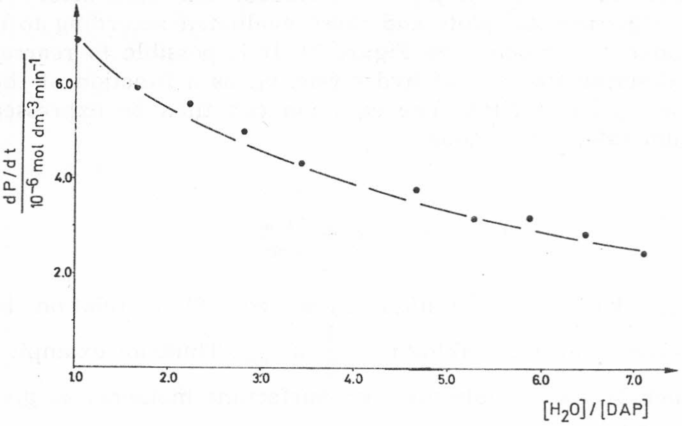

Figure 2. Velocity of the catalyzed hydrolysis of p-NPA versus the $[H_2O]/[DAP]$-ratio in cyclohexane. Parameter: $[DAP] = 1.5 \times 10^{-2}$ mol dm^{-3}, $[p\text{-}NPA]_0 = 1.6 \times 10^{-4}$ mol dm^{-3}. Temp. = 25.00 °C.

Accordingly, by applying the mass action law to both reactions (eq. 1), one obtains

$$K = \frac{s_0 - \xi_1}{(s_0 - \xi_1)(c_0 - \xi_1 - \xi_2)}$$

and

$$K' = \frac{\xi_2}{(c_0 - \xi_1 - \xi_2)(w_0 - n\xi_2)^n} \tag{3}$$

It can be shown that with suitable approximations the reaction velocity of the hydrolysis of the *p*-NPA, i. e. according to eq. (1)

$$\frac{dP}{dt} = k' [SC],$$

is given by

$$\frac{dP}{dt} = k' \frac{s_0 c_0^2}{\frac{s_0 w_0}{n^2} + c_0^2 + s_0 c_0} \tag{4}$$

k' is found to be an apparent first order rate constant which depends on the weighed-in water concentration. Thus in order to find the true second order rate constant the right hand side of eq. (4) has to be multiplied by w_0, i . e.

$$\frac{dP}{dt} = k \frac{s_0 c_0^2 w_0}{\frac{c_0 w_0}{n^2} + c_0^2 + s_0 c_0} \tag{5}$$

where k is of the order of 4×10^{-2} dm^3 mol^{-1} s^{-1}. Equation (5) expresses the fact that small water concentrations (at a given substrate amount) increase the reaction velocity. This situation is always fulfilled experimentally since small amounts of water, due to the hydration tendency of the polar parts of the surfactant cannot be completely excluded. The satisfactory coincidence between the experimental plots and those evaluated according to eq. (4) confirms the underlying model (see Figure 2). It is possible to rearrange eq. (5) in order to describe the rate of hydrolysis, v_h, as a function of the substrate concentration, s_0, i. e. *p*-NPA. The equation can then be expressed in terms of a maximum rate, $v_{h,\,max}$, thus

$$v_h = \frac{v_{h,\,max}\, s_0}{s_0 + \dfrac{v_{h,\,max}}{k\, w_0}} \tag{6}$$

where $v_{h,\,max} = k\, n^2 w_0 c_0^2/(w_0 + n^2 c_0)$. From eq. (6) a relation between s_0, w_0, c_0, and n can be derived taking $v_h = \frac{1}{2}\, v_{h,\,max}$. Thus, for example, the aggregation number of water molecules per surfactant monomer is given by $n = (s_0 w_0/(c_0^2 - s_0 c_0))^{1/2}$.

The effect of added benzene to a *p*-NPA, DAP, H_2O, C_6H_{12}-liquid mixture is also notable (Figure 3) with regard to the proposed investigation, since it has been reported that remarkable differences of the catalytic effect of DAP in cyclohexane and benzene were observed[15]. Decreasing reaction velocities in changing from C_6H_{12} to C_6H_6 can be quantitatively understood by assuming a competitive reaction between benzene and water. The actual calculations of the velocity of hydrolysis of *p*-NPA as a function of the volume fraction of benzene in a C_6H_{12}/C_6H_6-mixture starts with eq. (1) substituting benzene for water, i. e. keeping the H_2O concentration constant. Also in this context effects

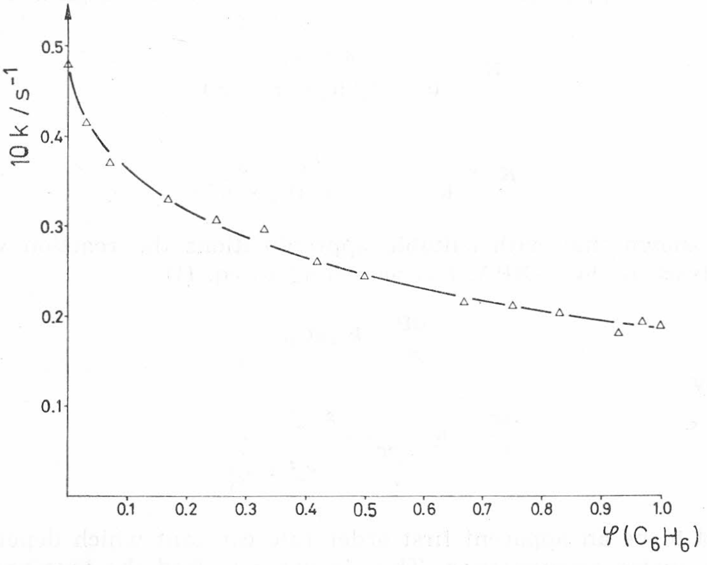

Figure 3. Pseudo-first-order rate constant of the catalyzed hydrolysis of p-NPA in the system: *p*-NPA, DAP, H_2O, C_6H_{12}/C_6H_6 versus the volume fraction of benzene $\varphi\, C_6H_6$. Parameter: [DAP] = 1.5 × 10^{-2} mol dm^{-3}, [H_2O] = 2 × 10^{-2} mol dm^{-3}, Temp. = 25.00 °C, [*p*-NPA]$_0$ = 1.6 × 10^{-4} mol dm^{-3}.

of polar solvents as, for example, chloroform or apolar solvents like carbon tetrachloride, which is known to be catalytically hydrolized[16] by reversed micelles, should be mentioned. The first can decompose micellar aggregates, the latter is seen to be a potential reactant. These observations may explain phenomena otherwise attributed to geometrical parameters of reversed micelles[4]. Some supplementary investigations, for example, the effect of water on the density of the binary system DAP/C_6H_{12} and AOT/C_6H_{12} appeared to be relevant for the present discussion. These density determinations were based on high precision measurements with a seven digits displaying Parr densitometer. The initial slopes of the density (ϱ_{exp}) versus weighed-in amount of water (ω = $[H_2O]/[surfactant]$)-plots, i. e.

$$\lim_{\omega\to 0}\left(\frac{1}{\varrho_{calc}}\,\frac{d\,\varrho_{exp}}{d\omega}\right),\ \varrho_{calc} = \frac{n_{surf}M_{surf} + n_{solv}M_{solv} + n_{H_2O}\,M_{H_2O}}{10^3\,V_{solution}}\ [\mathrm{g\ ml^{-1}}]$$

differed characteristically for the DAP/C_6H_{12}- and AOT/C_6H_{12} system, namely 2.09462×10^{-4} and 1.31594×10^{-4}, respectively. Two additional curves are plotted in both diagrams (Figures 4 and 5), assuming additivity of the added amounts of water. The difference is small but significant. Starting with hydrated surfactant monomers these results point to different mechanisms determining the solubilizing capacities of the surfactants. I. e., surfactants which form micelles in the pure state (or in the hydrated state) are less sensitive with respect to water compared with amphiphilic molecules which form micellar aggregates *only* in the presence of water as is probably the case with DAP.

These observations are confirmed by the aggregational patterns of DAP and AOT in cyclohexane discussed above (see Figure 1). The evaluation of the curves indicated that the associational behaviour of DAP in this solvent is better represented by a multiple association model.

Although it is well known that the presence of water (or an aqueous substrate solution) not only stabilizes the solubilizing aggregates but initiates also their formation according to a model developed earlier[17], the stabilization of the solubilizing aggregates to be formed may not be sufficient compared with

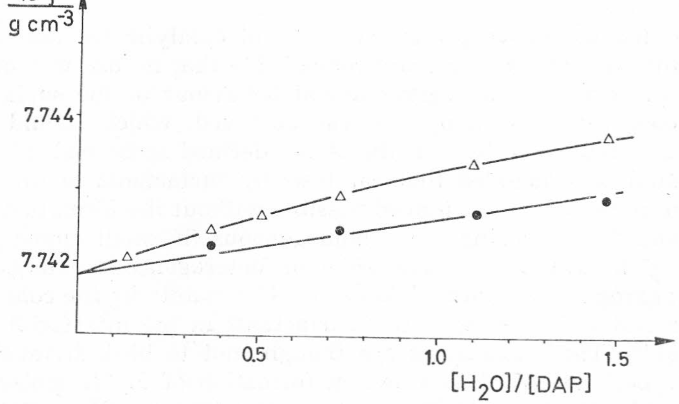

Figure 4. Density of a 0.15 mol/dm³ solution of DAP in cyclohexane versus $[H_2O]/[DAP]$ -ratio (△). (●) calculated density assuming additivity of weighed-in amount of water. Temp. = 25.00 °C.

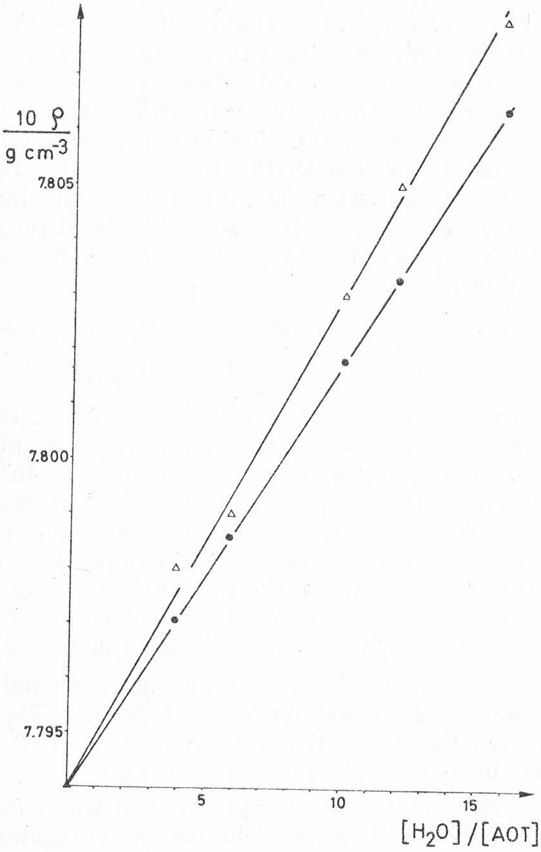

Figure 5. Density of a 0.2 mol/dm^3 solution of AOT in cyclohexane versus $[H_2O]/[AOT]$ -ratio (△). (●) calculated density assuming additivity of weighed-in amount of water. Temp. = 25.0 °C.

kT. Actually, this situation prevails in many cases, i. e., very probably also in the present one.

Reexamining the above presented model of catalytic reaction in the light of these additional details it appears remarkable that no use was made of any property characteristic of an aggregational behaviour of the surfactants. Moreover, no cooperative phenomenon was observed, which should have been expected if a micellar catalysis in the above defined sense had occurred. Therefore it should be concluded that catalysis by surfactants in the system described in the present paper is indeed possible without the formation of micellar aggregates and thus occuring via a homogeneous (if small amounts of water (e. g. water of hydration) are available) or heterogeneous catalysis (if loose cluster-like aggregates are formed, held together mainly by the cohesive energy of the water and stabilized by a few surfactants in the interfacial region (see Fendler et al.[18]). These associates are thought not to be individualizable and are probably best described as a swarm formation of dipole molecules in the sense reported by Hartmann[19]. The presence of a true micellar catalysis, however, should be detected by a suitable selection of molecules with the same active groups, relevant for the proposed experiment but with different aggregational features.

In this line of reasoning, the formation of solubilizing micellar aggregates and micellar catalysis are thought to depend upon one another. There does not exist, apparently, much material on true micellar catalysis in apolar media. Thus, it is hoped that more suitable examples will be collected in order to confirm this interdependence of micellar catalysis and the micellar concept.

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SAŽETAK

Micelarna kataliza i predodžba u nepolarnoj sredini

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Izraziti interes za katalitičke reakcije u nepolarnim otopinama tenzida zahtijeva pregled odnosa nastajanja micela i topljivosti u smislu postizanja jedinstvenog opisivanja pojava. Kako su te katalitičke pojave obično poznate pod pojmom »micelarna kataliza« prikazani rad želi pridonijeti jasnijoj predodžbi tog pojma. To je napravljeno analiziranjem naročito katalizirane reakcije (katalizirana hidroliza *p*-nitrofenilacetata u nazočnosti dodecilamonijeva propionata u cikloheksanu) u često istraživanim nepolarnim otopinama kationskih tenzida. Kvantitativni opis ukupne reakcije slaže se s eksperimentalnim pojedinostima. Zaključeno je da se micelarni i višestruko-asocijacijski modeli odrazuju također i u odnosima dobivenim istraživanjima katalitičkih reakcija u tim sistemima.

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