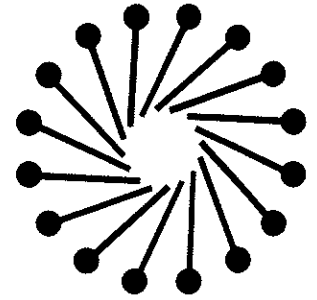


**TENSIDE**  
**SURFACTANTS**  
**DETERGENTS**



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# Computer Simulations of Simple Oil/Water/Surfactants Systems

*Die Selbstorganisation von Tensiden wird am Beispiel eines einfachen Öl/Wasser/Tensid Modells untersucht. Im Modell werden nur die eindeutigen, auf der Hand liegenden Eigenschaften erfaßt: Öl und Wasser sind nicht mischbar, und, ein Tensid ist ein amphiphiles Molekül, d. h. eine Seite verträgt sich mit Öl, aber nicht mit Wasser, die andere Seite verträgt sich mit Wasser, aber nicht mit Öl. Computersimulationen an ausgedehnten Öl/Wasser/Tensid Systemen geben eine überraschende Fülle struktureller Einzelheiten wieder. Mizellen bilden sich spontan in der wäßrigen Phase, an der Grenzfläche bildet sich ein Monolayer von Tensiden. Simulationen an Wasser/Tensid Systemen zeigen, daß sich bei einer bestimmten Tensid-Konzentration scheibchenförmige oder sphärische Mizellen bilden, je nach Gestalt der Kopfgruppe. Die Simulationen liefern eine vollständige Verteilungsfunktion der Größe der Mizellen. Darüber hinaus betrachten wir (im Gleichgewicht) dynamische Prozesse, wie z. B. das Ein- und Austreten von einzelnen Tensidmolekülen in Mizellen, die Fusion zweier Mizellen und das langsame Zusammenbrechen einer Mizelle. Mit unseren Ergebnissen geben wir eine Antwort auf kontrovers diskutierte Fragen, z. B. die Wechselwirkungen zwischen Tensidmolekülen, die für ihre Selbstorganisation wesentlich sind.*

*A simple oil/water/surfactant model is used to study the self-assembly of surfactants. The model contains only the most obvious elements: oil and water do not mix, and a surfactant is an amphiphilic molecule i. e. one side of the molecule likes oil but dislikes water, the other side likes water but dislikes oil. Computer simulations on large oil/water/surfactant systems show a surprisingly rich structural detail. Micelles are formed spontaneously in the water phase and a monolayer of surfactants is formed at the interface. Simulations on water/surfactant systems show that, depending on the shape of the head-group, disk-like or spherical micelles form at a particular surfactant concentration. The simulations yield a complete micellar size distribution function. Furthermore, we observe (equilibrium) dynamical processes such as the entering of single surfactants into micelles, single surfactants leaving micelles, the fusion of two micelles, and the slow breakdown of a micelle. We use our results to answer some controversial questions concerning the interactions that are essential for surfactant self-assembly.*

## 1 Introduction

An important property of surfactants is that dissolved in water or other solvents they can self-assemble to form ordered structures. Depending on, for example, the structure of a surfactant, the salt concentration, or the presence of co-surfactants, they form spherical micelles, rod-like micelles, bi-layers or other self-assembled structures [1].

Over the last few years, several computer simulation studies have been reported [2–22]. O'Connell and co-workers [5, 7, 17, 18] studied the structure of a micelle by confining the surfactants in a sphere and connecting the heads with a force to the surface of this sphere. This force models the water. In this model, the number of surfactants in a micelle and the radius of the hydrocarbon core of the micelle has to be chosen a priori, rather than "measured" in the course of a simulation. The effect of water is explicitly taken into account in [6, 10, 13]. Watanabe et. al. [10, 13] simulated a sodium octanoate micelle in an aqueous solution for 0.2 ns. With these realistic models a simulation of the time-evolution of such a system during 0.2 ns requires a sizable amount of computer time. Yet, 0.2 ns turns out to be too short to observe the spontaneous formation of micelles. Therefore, in these studies, the micelle is constructed a priori and the behaviour of these "postulated" micelles is studied. An obvious question is whether it is possible to study the spontaneous formation of micelles using a simple model.

In section 2, we present a simple oil/water/surfactant model. Since simulations on this model require a large system and a large amount of computer time, we have used a parallel computer for most of our simulations. In order to make optimal use of the capacity of a parallel computer a special algorithm has been developed. This model is used in section 3 to calculate the effect of the surfactants on the interfacial properties of the bare oil/water interface. In particular, we are interested in the effects of changes in the chemical structure of the surfactant. These simulations were done on a relatively small system. It turns out that this system is too small to observe the formation of micelles. A much larger oil/water/surfactant system is studied in section 3.2. In this system we observe the formation of micelles.

Experimentally one observes that the shape of a surfactant determines to a large extent the micelle morphology [23]. In section 4, we investigate the relation between the shape of the head group of a surfactant and the micellar structure.

## 2 Oil/Water/Surfactant Model

An important question one has to answer before one can construct a simple model of an oil/water/surfactant system is: what features of this system are responsible for the characteristic behaviour as is observed experimentally in these systems? Widom and co-workers were among the first to ask this question [24, 25, 26]. Two simple observations constituted their starting point: oil and water do not mix, and a surfactant is an amphiphilic molecule, i. e. a molecule of which one side is hydrophilic and dislikes oil and the other side is hydrophobic and likes oil. Using these ingredients they constructed a lattice model that predicted three-phase equilibria and ultra low surface tensions. Since then various other lattice models have appeared in the literature. A recent review of the results ob-

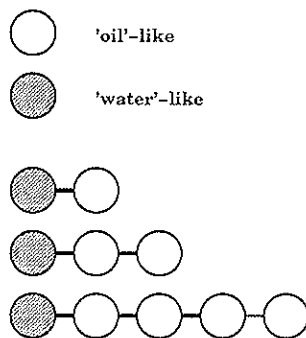


Fig. 1. Schematic drawing of the oil/water/surfactant model. Some surfactant structures are shown which are studied in the remainder of this article

tained by these lattice models is given in ref. [27]. Continuum models, based on the *Widom* model, have been developed by *Stillinger* [28] and *Telo da Gama and Gubbins* [29].

In our model, which uses the same ingredients as the *Widom* model, we assume the existence of four types of particles: o particles, w particles, h particles, and t particles. These particles are used to model three types of molecules, namely oil molecules, water molecules and surfactant molecules. An oil molecule consists of a single o particle, and a water molecule consists of a single w particle. A surfactant molecule is made up of one or more t particles and one or more h particles; these are joined together by harmonic potentials

$$U_{ij} = \frac{1}{2} k (|r_i - r_j| - \sigma)^2, \quad (1)$$

where the value of the force constant is made sufficiently large such that at any instant 98% of the connected units have length that is within 2% of the average value  $\sigma$ .

The four types of particles are truncated and shifted *Lennard-Jones* potentials with energy parameters  $\epsilon_{ij}$ , distance parameter  $\sigma_{ij}$ , and the cut-off radius  $R_{ij}^c$

$$\Phi_{ij} = \begin{cases} \phi_{ij}(r) - \phi_{ij}(R_{ij}^c) & r \leq R_{ij}^c \\ 0 & r > R_{ij}^c \end{cases}, \quad (2)$$

and

$$\phi_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right], \quad (3)$$

where  $i, j$  indicates the type of atom (w, o, h, or t) and  $r$  is the distance between the atoms.

Of course, the use of a *Lennard-Jones*-type potential is a drastic simplification. Therefore, we have not tried to op-

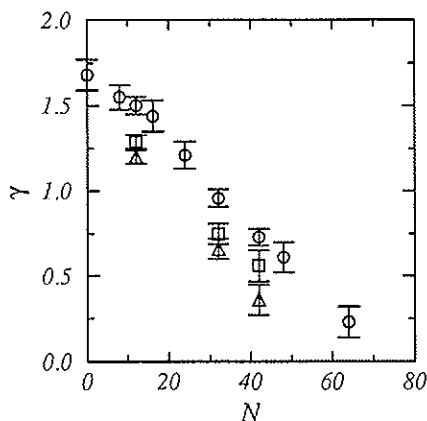


Fig. 2. Surface tension  $\gamma$  (reduced units) as a function of the total number of surfactants  $N$  for various linear surfactants (the model of fig. 1) as obtained from the simulations. The number of chain segments is  $\circ$ : 1,  $\square$ : 3, and  $\triangle$ : 5

imize the *Lennard-Jones* parameters for the various interactions. We have assumed that for all interactions  $\epsilon_{ij} = \epsilon$  and  $\sigma_{ij} = \sigma$ . In order to make the o-o and w-w interactions different from the w-o interaction, the truncation of the potential ( $R_{ij}^c$ ) is made depending on the type of interaction. The w-w and o-o interactions are truncated at  $R_{ij}^c = 2.5\sigma$  and the o-w interaction at  $R_{ij}^c = 2^{1/6}\sigma$ , which makes the latter interaction completely repulsive. Furthermore, we have used for the t particles the same interactions as for the o particles. Therefore, the only difference between an o particle and a t particle is that the t particles are connected with harmonic forces (equation (1)) to other t or h particles (see figure 1) The interactions of the h particles is for most surfactants identical to the interactions of the w particles. In order to study the effects of changing the interactions between head groups, we have used  $R_{ij}^c = 2^{1/6}\sigma$  for the h-h interactions of some surfactants.

With these interactions, it turns out that at temperature  $T = 1.0\epsilon/k_B$  and density  $\rho = 0.7\sigma^{-3}$ , the oil and water do not mix and form a stable liquid-liquid interface [9]. The surfactant molecules are of an amphiphilic nature, one end is hydrophilic (and dislikes oil), the other end is hydrophobic (and likes oil). With this model it is simple to mimic different chemical structures. For example, addition of oil-like particles to the tail allows us to study the influence of increasing the tail length [14] or branching of a surfactant [16].

### 3 The Oil/Water Interface

In this section we investigate whether our model captures some of the essential features of a surfactant system such as: are our model surfactants surface active, do they reduce the interfacial tension, and can the effects of changes in the chemical structure of a surfactant be predicted? Since our model contains many simplifications, we restrict ourselves to a qualitative comparison with experiments.

Since we are mainly interested in the behaviour of the surfactants at the interface rather than in the behaviour of surfactants in the bulk, we have performed simulations on a relatively small number of particles. It turns out that such a system is too small to observe the formation of micelles. Micelles do form in systems with a much larger number of particles.

#### 3.1 Small systems

The most simple surfactant that we can study with our model is a dumbbell surfactant (see fig. 1). We have performed simulations with a system of 512 particles, half of these were water particles and the other half oil. The size of the simulation box was  $7.15\sigma \times 7.15\sigma \times 14.30\sigma$ . The computational aspects of these simulations are described in detail in refs. [9, 16]. The results for the surface tension as a function of the number of surfactants on the interfacial tension are shown in Fig. 2.

From a practical point of view one is interested in relating the capacity of a surfactant in reducing the interfacial tension to the structure of the surfactants. In order to obtain such an insight, the effect of chain length in reducing the interfacial tension has been studied experimentally in ref. [14]. In our model we can mimic changes in the surfactant structure as well. For example, by adding more hydrophobic segments to the tail (see Fig. 1) we can study surfactants with different chain lengths.

We have compared surfactants with a chain length of one, three, and five hydrophobic segments. In these simulations we have used a system of 256 w particles and 512 o particles placed in a periodic box of size  $7.15\sigma \times 7.15\sigma \times 21.45\sigma$ . Further details can be found in refs. [14, 16, 30].

The effect of the chain length of surfactants on the interfacial tension of the bare oil/water interface is shown in Fig. 2. The results show that as the chain length increases the surfactants are more efficient in reducing the interfacial tension, i.e. one needs less surfactants in order to reduce the interfacial tension of the bare oil/water interface by the same amount. This is exactly what is found experimentally [14].

The simulations demonstrate that the surface tension decreases linearly as the number of surfactants increases. In the experimental curves, a characteristic break in the interfacial tension curves is observed at high concentrations of surfactants. This is due to the formation of micelles in the water phase. In our simulations we did not observe the formation of micelles. A possible explanation is that our system is too small to observe the formation of micelles or that our model is unable to predict the formation of micelles.

### 3.2 Large systems

In the previous section we have demonstrated that our simple oil/water/surfactant model captures some of the essential features of a real system. We could not observe, however, the formation of micelles. To test whether this is due to the small system size, we performed simulations on a very large system.

The simulations were started with 39,304 particles which were placed on an fcc-lattice with size  $30.4\sigma \times 30.4\sigma \times 60.8\sigma$ . Surfactants were placed on this lattice such that a spatially random distribution of surfactants was guaranteed. All the remaining particles in one half of the periodic box were water and those in the other half oil. The surfactant concentration ranged from 0.75 to 3%. The system was equilibrated for at least 100,000 time steps ( $\Delta t = 0.005 \tau_0$ ), followed by a production run of at least another 100,000 time steps. The simulations were performed on a parallel computer using the algorithm described in ref. [31].

In most of the simulations we studied a surfactant with a hydrophilic part consisting of two h particles and a linear hydrophobic chain with five t particles (see Fig. 3). For comparison, some simulations were performed with the dumbbell surfactants (see Fig. 1).

A typical example of the instantaneous arrangement of the surfactants is shown in Fig. 4. In the water phase micelles have formed spontaneously. In the oil phase (not shown) some clustering of surfactants can be observed. This clustering was much more irregular and was not investigated in detail. For comparison, a simulation of dumbbell surfactants at the same concentration with the same system size was performed. In this simulation the formation of micelles could not be observed.

## 4 Micelle Formation

In the previous section we have found that our model predicts the formation of micelles in the water phase. We have observed that once the micelles are formed they are stable for a relatively long time and the number of surfactants in a micelle remains constant. Since the total number of micelles is very small (ca. 8) it is impossible to obtain sufficient statistics to calculate a complete micelle size distribution.

In this section, we study micelle formation in more detail. We focus our attention on the formation of micelles in the water phase. The simulations were performed at constant temperature ( $T = 1.0\epsilon/k_B$ ) and density ( $\rho = 0.7\sigma^{-3}$ ). The temperature was kept constant by coupling to a heat bath. Periodic boundary conditions were imposed in all three directions. Initially, 32,000 particles were placed on an fcc-lattice with size

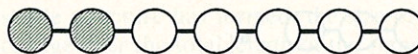


Fig. 3. Schematic drawing of the surfactant structure

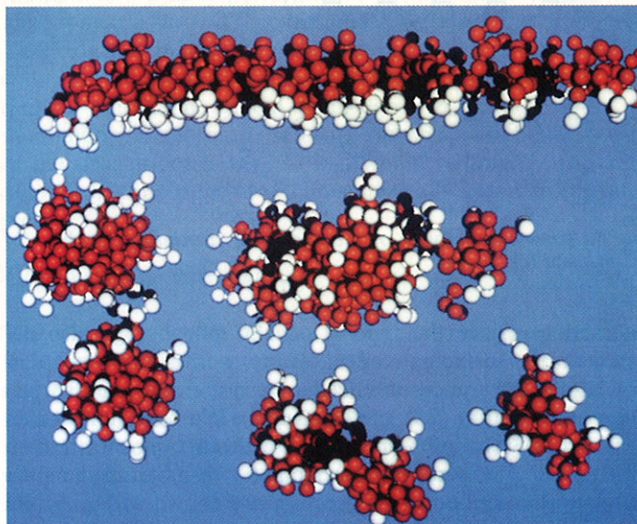


Fig. 4. Typical example of a configuration of surfactants in an oil/water system for 1.5% surfactants. The snapshot shows only the surfactants at one of the monolayers and the surfactants in the water phase. For clarity the surfactants in the oil phase and the oil and water particles are not shown. The hydrophilic segments are white and the hydrophobic segments red

$35.8\sigma \times 35.8\sigma \times 35.8\sigma$ . We started our simulations with a spatially random distribution of surfactants. The concentration of surfactants was 2%. We continued our simulations at least  $5 \times 10^5$  time steps, some simulations were continued up to  $10^6$  time steps. The first  $10^5$  time steps were used for equilibration and not used to evaluate average properties (see table 1 for some details).

### 4.1 Micelle morphology

Experimentally it is well known that depending on the type of surfactant molecule different micellar aggregates are stable at particular surfactant concentrations [23]. In this section, we use our model to study some aspects of the relation between the shape of a surfactant and the morphology of the micellar aggregate. In particular we are interested in how the shape of the head group of a surfactant influences the micelle structure. Furthermore, we investigate the influence of the head group

Table 1. Computational details and summary of the surfactant structure and interactions. "nr" is the number of the simulation, Surf is the notation for the surfactant structure, "(h)<sub>2</sub>ht<sub>5</sub>" means that the central "h" particle is connected to two other "h" particles and a (linear) chain of 5 "t" particles (see also Fig. 5). In order to distinguish head groups with attractive "h-h" interaction from those with repulsive interactions an "H" symbol is used for the latter " $R_{h-h}^i$ " gives the distance (in units  $\sigma$ ) at which the potential that describes the interaction between two "h" particles is truncated, and " $N_{tot}$ " is the total number of time steps

nr	Surf	$R_{h-h}^i$	$N_{tot}$
1	h <sub>2</sub> t <sub>5</sub>	2.50	$5 \times 10^5$
2	(h) <sub>2</sub> ht <sub>5</sub>	2.50	$1 \times 10^6$
3	(h) <sub>3</sub> ht <sub>5</sub>	2.50	$1 \times 10^6$
4	H <sub>2</sub> t <sub>5</sub>	1.12	$5 \times 10^5$
5	(H) <sub>3</sub> Ht <sub>5</sub>	1.12	$1 \times 10^6$

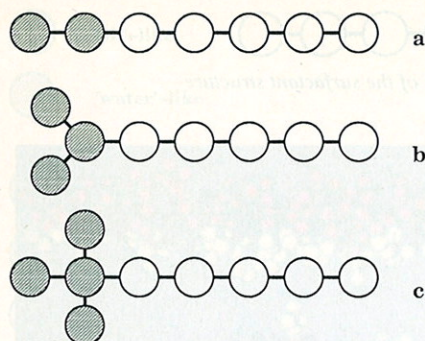


Fig. 5. Schematic drawing of the surfactant structures (a)  $hht_5$ , (b)  $(h)_2ht_5$ , and (c)  $(h)_3ht_5$

interactions. Since the type of micelle morphology also depends on the surfactant concentration, we focused our attention on the differences in micellar structure at a fixed surfactant concentration (2% of surfactants). We have not studied systematically the influence of the surfactant concentration on the results. The particular surfactants we have used in the simulation described in this section are shown in Fig. 5. We have made the head of the surfactant increasingly bulky by connecting more head groups to a central head group.

It is interesting to compare the surfactants  $h_2t_5$ ,  $(h)_2ht_5$ , and  $(h)_3ht_5$ . Simple geometric arguments [23] suggest that it is easier to pack  $h_2t_5$  surfactants in a bilayer,  $(h)_2ht_5$  surfactants in a cylinder, and  $(h)_3ht_5$  surfactants in a sphere. In a simulation one would therefore expect that at sufficiently high concentrations of surfactants, the first two surfactants will give very large clusters and  $(h)_3ht_5$  gives a distribution of cluster sizes. Such a trend is indeed observed in our simulations.

Fig. 6 shows snapshots of the largest cluster in the system with  $h_2t_5$  surfactants (system 1, see table 1). The surfactants organize in a bilayer structure. The surfactant concentration is too small to observe a "real" bilayer. It would therefore be interesting to perform these simulations at higher concentrations. The structure of the micelles of the  $(h)_2ht_5$  surfactants

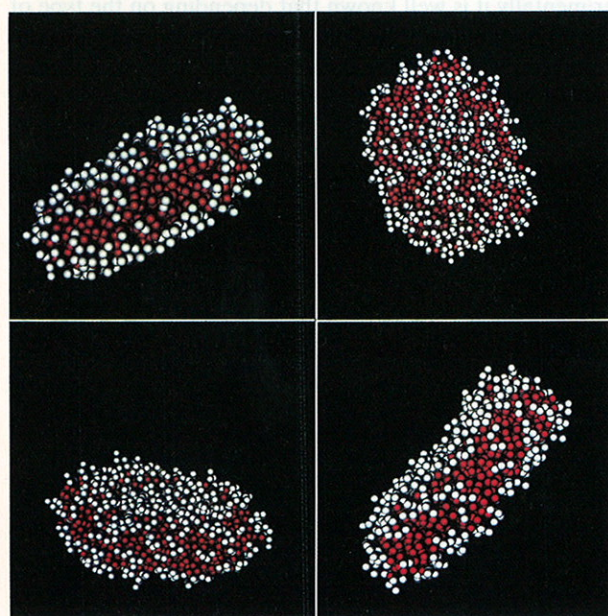


Fig. 6. Snapshots of the aggregate formed by the  $h_2t_5$  surfactants. The white spheres represent the  $h$  particles and the dark spheres the  $t$  particles. Note that for clarity the water particles are not depicted. The four pictures show the aggregate at different angles

(system 2) is less clear. We observe that these surfactants neither form a proper bilayer like structure nor a spherical micelle. A more or less cylindrical shape can be observed but it would require much longer simulations to elucidate this. The  $(h)_3ht_5$  surfactants form spherical micelles.

The influence of the type of interaction between the head groups is striking. If we make the h-h interactions repulsive, the system with  $H_2t_5$  surfactants (system 4) forms at the given concentration spherical micelles instead of a bilayer structure. This suggests that in the case of the surfactant with repulsive interactions water particles surround the H particles and it is for the surfactants not favourable to have H segments in direct contact. This makes the effective shape of a surfactant with repulsive interactions similar to a surfactant for which (attractive) h particles are connected with harmonic springs (surfactant  $(h)_3ht_5$ , system 3) and the micelle shape will be similar.

If we consider a  $(H)_3Ht_5$  surfactant with repulsive H-H interactions (system 5), we also obtain spherical micelles. The average micelle size is significantly smaller than for  $(h)_3ht_5$  surfactants with attractive h-h interactions. This can also be understood by considering again the effective size of the surfactants. In the case of repulsive H-H interactions water hydration makes the effective size of a surfactant larger, than for surfactants where h-h interactions are identical to h-w interactions. Thus one can expect smaller spherical micelles to be more favourable.

It is interesting to compare these results with the experimental data of Nusselder and Engberts [32], who studied the micelle structure of various 1-alkyl-4-( $C_{12}$ -alkyl)pyridinium iodides. These authors show that variation of the 1-alkyl substituent leads to remarkable differences in aggregation behaviour. For example, the sphere-to-rod like micelle transition occurs at a significantly higher surfactant concentration for a small 1-alkyl ( $CH_3$ ) substituent than for a bulky branched ( $CH(CH_2)_2$ ) substituent.

In our simulation, we observe a similar trend, more bulky head groups favour spherical micelles. This agreement with our model calculation supports the conclusion of Nusselder and Engberts that the aggregate morphology is indeed primarily determined by the shape of the surfactant molecule. Furthermore, our simulations show that it is not sufficient to consider only the shape of the surfactant. Comparison of the surfactants with attractive and repulsive head group interactions shows that the hydration by water can have a dramatic effect on the aggregation behaviour. Therefore it is important to consider the effective shape of a surfactant and include the influence of possible hydration.

#### 4.2 Dynamics

The molecular dynamics technique has as an advantage that one can study the dynamics. In our simulations we started with a completely random distribution of surfactants. This allows us to monitor the formation of micelles. First we discuss the formation of the bilayer like micelles, then we describe the dynamics of the spherical micelles.

We observe that the formation of a bilayer like micelle is a two stage process. The first stage is that spherical micelles (pre-micelles) are formed from a random distribution of surfactants. This is a relatively fast process which occurs in the first 50,000 time steps. The next stage is the growth of the bilayer. The growth of the bilayer is shown in Fig. 7. In this figure the size of the bilayer is given as a function of time. We observe that the growth occurs in discrete steps. Fig. 8 shows a snapshot of the bilayer just after one of these growth steps. This figure indicates that the steps are due to the subsequent

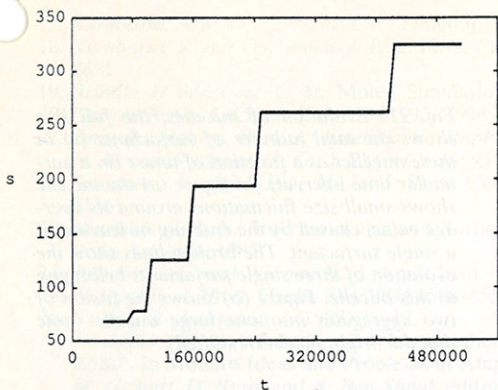


Fig. 7. The size of the bilayer ( $s$ ) as a function of the number of time steps ( $t$ )

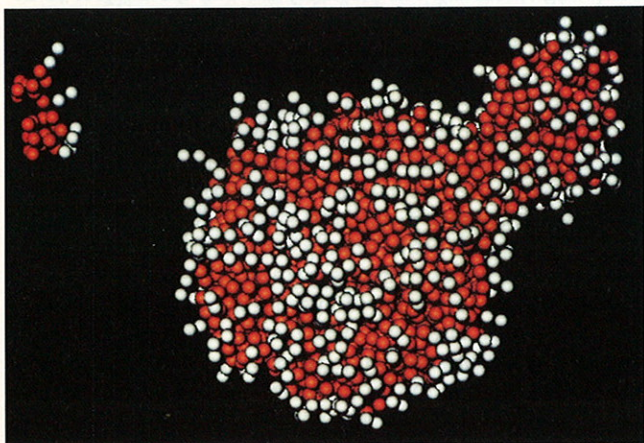


Fig. 8. Snapshots of a bilayer micelle just after the addition of a pre-micelle

addition of pre-micelles. It is interesting to note that this pre-micelle attaches at the edge of the bilayer, which can be understood from an energetic point of view. Fig. 7 also demonstrates that the growth of the micelles is a much slower process than the initial formation of micelles. The latter process involves the diffusion of micelles, while the first process involves the diffusion of pre-micelles.

We have not continued our simulations to see whether all surfactants present in the system would end up in this bilayer. But Fig. 7 does not indicate that the aggregate has stopped growing, we therefore expect that if we would continue the simulations almost all surfactants would be in this aggregate.

Initially, the formation of spherical micelles (system 3) also involves the formation of pre-micelles. After their formation, these pre-micelles do not fuse (in general), but slowly adjust their size until they have reached a stable structure. Once this

stable structure has formed, the size of the micelles does not change over the total length of the simulation.

An important question is whether we can use our simulations to determine a complete micelle size distribution. In the simulations we have performed so far the number of monomers is nearly zero. Only occasionally we see a free monomer. This indicates that at the particular conditions the critical micelle concentration (c.m.c.) is very low. It would therefore require a very large system to have a significant number of monomers. Furthermore, since the dynamics on the time scale of the simulations is very slow it would require a very large number of time steps to obtain statistically independent samples.

### 4.3 Micelle size distribution

The system for which we have studied the formation of micelles is at conditions where the c.m.c. is too low to observe single monomers in our system. Furthermore, the dynamics is so slow that it takes a large number of time steps to determine a micelle size distribution. In order to enhance the dynamics, we have studied our system at a higher temperature. At these conditions it can also be expected that the c.m.c. will be significantly larger.

In order to obtain good statistics, it is favourable to use surfactants which form relatively small micelles. In the previous section we have observed that  $(H)_3(H)_5$  surfactants (repulsive interactions between the head groups) form the smallest micelles. We have investigated a range of temperatures,  $T = 2.2\epsilon/k_B$  gave optimal results. For more computational details see ref. [33].

The particular surfactant structure we have studied is depicted in fig. 9. The bulky head and relatively short chain favour the formation of micelles with a relatively small aggregation number as observed in typical surfactant systems [1].

A solution containing micelles can be described quantitatively by the size distribution of aggregates [34]. We can determine this distribution by counting the clusters at regular intervals. The distribution as obtained from our simulations is shown in fig. 10. This figure shows a maximum in the micellar distribution function, indicating the presence of an optimum micellar size.

In order to test whether equilibrium has been reached, we prepared a system with an entirely different initial condition at a much lower temperature. At this condition *all* surfactants were in aggregates. The temperature was then increased to  $T = 2.2\epsilon/k_B$  and after equilibration the obtained micellar distribution function was indistinguishable from the one obtained starting from a completely random distribution of surfactants (Fig. 10). This strongly suggests that the obtained micellar distribution is an equilibrium property.

The cluster distribution function shown in Fig. 10 has an optimum cluster size of 22 to 23 surfactants. We observe mi-

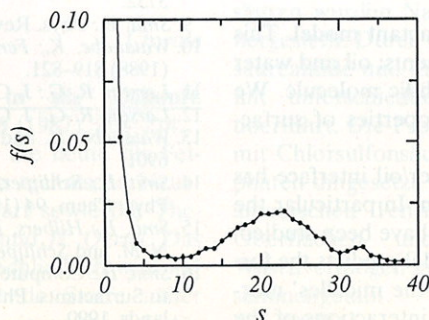
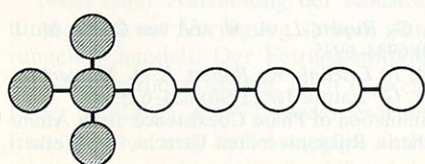


Fig. 9. (left) Schematic drawing of the surfactant structure

Fig. 10. (right) Micellar size distribution function  $f(s)$ .  $s$  is the number of surfactants in an aggregate. The figure has been obtained by averaging over approximately 200 configurations taken every 4000<sup>th</sup> time step and normalized by dividing by the total number of clusters

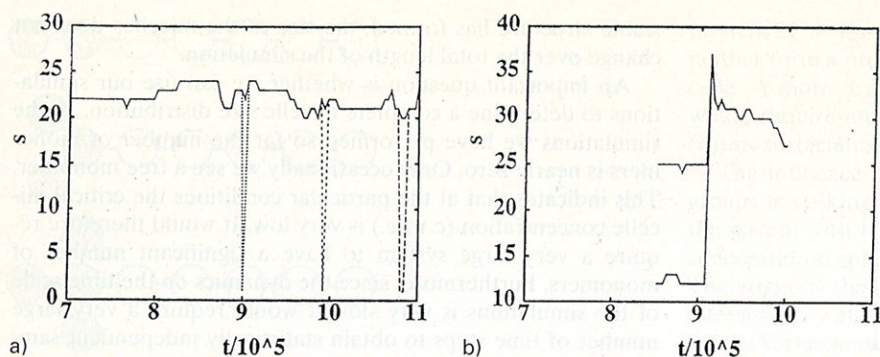


Fig. 11. Evolution of micelles; the full line shows the total number of surfactants ( $s$ ) in these micelles as a function of time  $t$  (in a particular time interval). In figure (a) the micelle shows small size fluctuations around its average value, caused by the entering or leaving of a single surfactant. The broken lines show the evolution of three single surfactants belonging to this micelle. Figure (b) shows the fusion of two aggregates into one large micelle (note that the origin has been shifted)

celles with sizes ranging from 15 to 30 surfactants, indicating a significant polydispersity. An important aspect is that in the distribution function we observed a maximum, and a minimum between the (proper) micelles and the oligomers. Such a shape of the distribution function has been predicted by various mass-action models [35, 36] and is one of the basic assumptions in the theory of the dynamics of micelle formation [37]. These results demonstrate that a simple molecular surfactant/water model gives rise to such a distribution and therefore confirms the basic assumptions of these theories.

Having established that our model shows the same behaviour as an equilibrium micellar solution, we can now study the dynamics. In our simulations we observe that monomers leave a micelle and enter another micelle, that two micelles fuse, and occasionally that a micelle that looks initially stable falls apart. To obtain a quantitative description of these phenomena it is useful to look at the evolution of typical micelles and of some individual surfactants. This is shown in Fig. 11. In fig. 11 (a) the size evolution of a micelle, with roughly an optimum number of surfactants, is shown. This micelle shows small fluctuations in size when an individual surfactant leaves or enters a micelle, but nothing dramatic happens. A different behaviour is observed when we follow two micelles which have a size which is not optimum as is shown in Fig. 11 (b). These two micelles fuse and form one big micelle. According to Fig. 10 it can be expected that this big micelle is not very stable, which is reflected in Fig. 11 (b) since its size rapidly decreases towards a more optimum micellar size. Furthermore, we see occasionally (not shown) the complete breakdown of a micelle, which is a much slower process than the leaving or entering of a single surfactant. These dynamical processes are exactly what is observed experimentally in systems with strongly screened electrostatic interactions [37], to which our model closely corresponds. The simplicity of our model allows us to use a larger time step, requires less cpu-time, and has faster intrinsic dynamics than simulations of realistic models [3, 5, 6, 13]. As a result the relevant dynamical processes in this model occur on a time scale accessible to a simulation.

## 5 Concluding Remarks

We have presented a simple oil/water/surfactant model. This model contains only the most obvious elements: oil and water do not mix and a surfactant is an amphiphilic molecule. We have used this model to study various properties of surfactants.

The behaviour of surfactants at the water/oil interface has been studied using a relatively small system. In particular the effects of changes in the chemical structure have been studied. If we use a sufficiently large system our model predicts the formation of micelles. We demonstrated that the micelles' morphology is very sensitive to the shape and interactions of the

head groups. The simulations also yielded a complete micellar size distribution.

The molecular interactions that play an essential role in promoting surfactant self-assembly are still the subject of debate. For a long time it was the general belief that aggregation is driven by the release of "structured" water from around the hydrocarbon chains [38]. Reexamination of thermodynamic data showed that even at high temperatures, where the unique structural properties of water are almost completely negligible, aggregation can occur. Furthermore, micelle formation has also been observed in other liquids such as hydrazine [39, 40], ethyl-ammonium nitrate [41, 42, 43], formamide [44, 45] and various glycols [46]. Striking is that all these liquids can form hydrogen bonds. This observation motivated *Beesly et al.* [47] to study the formation of micelles in non hydrogen-bonding polar fluids. They observed that in 3-methylsyrone no self-aggregation of surfactants occurs. From this observation they concluded that for cooperative interaction between amphiphilic molecules, hydrogen bonding is essential.

In our model the interactions between head groups is short-ranged repulsive, and it is therefore not essential to have long-ranged repulsive interactions for the formation of micelles, as is suggested in ref. [4]. Our conclusions are in line with recent work on lattice models of surfactant systems. In most of these models no specific hydrogen bonding or long-ranged interactions are assumed, yet these lattice models predict a very large number of (self-assembled) phases [11, 25, 27].

## Bibliography

- Mittal, K. L. and Lindman, B. eds.: Surfactants in Solution. Plenum, New York, 1984.
- Haan, S. W. and Pratt, L. R.: Chem. Phys. Lett. 79 (1981) 436-440.
- Van der Ploeg, P. and Berendsen, H. J. C.: Molec. Phys. 49 (1983) 233-248.
- Owenson, B. and Pratt, L. R.: J. Phys. Chem. 88 (1984) 2905-2915.
- Haile, J. M. and O'Connell, J. P.: J. Phys. Chem. 88 (1984) 6363-6366.
- Jönsson, B.; Edholm, O. and Teleman, O. J.: J. Chem. Phys. 85 (1986) 2259-2271.
- Woods, M. C.; Haile, J. M. and O'Connell, J. P.: J. Phys. Chem. 90 (1986) 1875-1885.
- Egberts, E. and Berendsen, H. J. C.: J. Chem. Phys. 89 (1988) 3718-3732.
- Smit, B.: Phys. Rev. A, 37 (1988) 3431-3433.
- Watanabe, K.; Ferrario, M. and Klein, M. L.: J. Phys. Chem. 92 (1988) 819-821.
- Larson, R. G.: J. Chem. Phys. 89 (1988) 1642-1650.
- Larson, R. G.: J. Chem. Phys. 91 (1989) 2479-2488.
- Watanabe, K. and Klein, M. L.: J. Phys. Chem. 93 (1989) 6897-6901.
- Smit, B.; Schlijper, A. G.; Rupert, L. A. M. and van Os, N. M.: J. Phys. Chem. 94 (1990) 6934-6935.
- Smit, B.; Hilbers, P. A. J.; Esselink, K.; Rupert, L. A. M.; van Os, N. M. and Schlijper, A. G.: Nature 348 (1990) 624-625.
- Smit, B.: Computer Simulation of Phase Coexistence: from Atoms to Surfactants. PhD thesis, Rijksuniversiteit Utrecht, The Netherlands, 1990.

17. Karaborni, S. and O'Connell, J. P.: Langmuir, 6 (1990) 905.
18. Karaborni, S. and O'Connell, J. P.: J. Phys. Chem. 94 (1990) 2624–2631.
19. Brindle, D. and Care, C. M.: Molec. Simulations, 5 (1990) 345–351.
20. Larson, R. G.: J. Chem. Phys. 96 (1992) 7904–7918.
21. Smit, B.; Hilbers, P. A. J.; Esselink, K.; Rupert, L. A. M.; van Os, N. M. and Schlijper, A. G.: J. Phys. Chem. 95 (1991) 6361–6368.
22. Watanabe, K. and Klein, M. L.: J. Phys. Chem. 95 (1991) 4158–4166.
23. Israelachvili, J. N.: Intermolecular and Surface Forces. Academic Press, London, 1985.
24. Wheeler, J. C. and Widom, B.: J. Am. Chem. Soc. 90 (1968) 3064.
25. Widom, B.: J. Phys. Chem. 88 (1984) 6508–6514.
26. Widom, B.: Langmuir 3 (1987) 12–17.
27. Gompper, G. and Schick, M.: "Lattice theories of microemulsions". In Modern Ideas and Problems in Amphiphilic Science, W. M. Gelbart, D. Roux and A. Ben-Shaul, editors, 1991.
28. Stillinger, F. H.: J. Chem. Phys. 78 (1983) 4654–4661.
29. Telo da Gama, M. M. and Gubbins, K. E.: Molec. Phys. 59 (1986) 227–239.
30. Smit, B.; Hilbers, P. A. J. and Esselink, K.: "Computer simulations of surfactants at a liquid/liquid interface". In Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution, S-H Chen, J. S. Huang and P. Tartaglia, editors. Proc. NATO ASI, 1992.
31. Esselink, K.; Smit, B. and Hilbers, P. A. J.: J. Comp. Phys. 106 (1993) 101–107.
32. Nusselder, J. J. and Engberts, J. B. F. N.: J. Am. Chem. Soc. 119 (1989) 5000–5002.
33. Smit, B.; Esselink, K.; Hilbers, P. A. J.; van Os, N. M. and Szejfer, I.: Langmuir 9 (1993) 9–11.
34. Chevalier, Y. and Zemb, T.: Rep. Prog. Phys. 53 (1990) 279–371.
35. Wennerström, H. and Lindman: Physics Reports 52 (1979) 1–86.
36. Hoeve, C. A. J. and Benson, G. C.: J. Phys. Chem. 61 (1957) 1149–1158.
37. Lang, J. and Zana, R.: "Chemical relaxation methods". In Surfactants in Solution: New Methods of Investigation, R. Zana, editor, 1987.
38. Evans, D. F. and Ninham, B. W.: J. Phys. Chem. 90 (1986) 226–234.
39. Ramadan, M. Sh.; Evans, D. F. and Lumry, R. W.: J. Phys. Chem. 87 (1983) 4538–4543.
40. Ramadan, M. Sh.; Evans, D. F.; Lumry, R. and Phillion, S.: J. Phys. Chem. 89 (1985) 3405–3408.
41. Evans, D. F.; Yamauchi, A.; Roman, R. and Cassassa, E. Z.: J. Colloid Interface Sci. 86 (1982) 89.
42. Evans, D. F.; Yamauchi, A.; Wei, G. J. and Boomfield, V. A.: J. Phys. Chem. 87 (1983) 3537.
43. Evans, D. F.; Kahler, E. W. and Benton, W. J.: J. Phys. Chem. 87 (1983) 533.
44. McDonald, C. J.: J. Pharm. Pharmacol. 22 (1970) 148–150.
45. Ray, A.: Nature 231 (1971) 313.
46. Vasil'eva, V. F. and Yashunskii, V. G.: J. Gen. Chem. USSR (Eng. Transl.) 32 (1962) 2845.
47. Beesley, A. H.; Evans, D. F. and Laughlin, R. G.: J. Phys. Chem. 92 (1988) 791–793.

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11448

#### Beiträge zur Theorie des Fettlickerns. G. Reich und H. Oertel; Das Leder 38 (1987) 41–47.

In Bezug auf die Wirkungsweise des Fettlickerns sind 3 Hauptfaktoren zu nennen: die Zusammensetzung des Lickerfettes, die Bedingungen des Lickervorganges und die Merkmale des zu fettenden Leders.

Theoretische Überlegungen gehen von den Strukturelementen des Kollagens aus – Molekül, Mikrofibrille, Fibrille, Elementarfaser, Faser –, sowie den Möglichkeiten, die Zwischenräume zwischen diesen Elementen auszufüllen bzw. diese Elemente zu umhüllen.

Ausgehend von diesen Überlegungen wurden Berechnungen angestellt und Messungen durchgeführt, aus denen sich ableiten läßt, daß sich die optimale Fettung im Bereich der Fibrillen abspielt. Aus dieser Erkenntnis ergeben sich die Kriterien für die Auswahl der Fettstoffe und die Optimierung des Fettlickerns: Durch Steuerung der Teilchengröße des Lickerfettes kann das Eindringen in den Fibrillenbereich optimiert werden; das Fett muß sich so an den Kollagen-Chrom-Komplex anlagern, daß es seine Fibrillen-isolierende Wirkung voll entfalten kann; die gebundenen Fettstoffe müssen optimale Gleitmittel sein, um die Beweglichkeit der isolierten Fibrillen gegeneinander zu gewährleisten. Die diesen Erfordernissen entsprechenden Fettmengen liegen unter den in der Praxis zu meist eingesetzten.

D 2 (90360)

Chwala

#### Lederfettungsmittel – ein Ausblick in die Zukunft. H. Lohmann und H. Strijbos; Das Leder 38 (1987), 208–214.

Nach einer Aufzählung der Rohstoffe, die heute für Fettungsmittel zur Verfügung stehen, werden technische Neuerungen behandelt. Der Fettungsmittelbedarf sowie die Theorie des Fettlickerns (vgl. auch G. Reich und H. Oertel. Das Leder 38 (1987), 41–47) werden erörtert. Schließlich wird auf Emulgatoren und OH-Gruppen enthaltende Stoffe näher eingegangen und festgestellt, daß sich hier ein weites Feld

für Fettungsmittel mit Tensideigenschaften als weichmachende Lederfettungsmittel eröffnet (Fettalkoholpolyglykoläther, sulfonierte Carbonsäureester, Alkylglycoside, Polyester, Polycarbonate u. v. a.).

Mit Nachdruck wird zum Schluß die klassische Naturstoffgruppe der tierischen und pflanzlichen Öle besprochen, d. Säugetierfette, Fischöle und Pflanzenöle. Es wird darauf hingewiesen, daß vor allem ölproduzierende Pflanzen eine stets erneuerbare Rohstoffquelle für die industrielle Verwendung darstellen. Die landwirtschaftliche Öl- und Fettproduktion nimmt schon heute kräftig zu. Gezielte chemische Umwandlungen dieser Rohstoffe führen zu neuen Grundstoffen, die sich zur Weichmachung von Leder einsetzen lassen.

D 2 (90363)

Chwala

#### Some Synthetic Detergents from Petroleum Products. S. A. Fam, M. M. A. El-Sukkary and F. El-Dib; J. Amer. Oil Chem. Soc. 63 /11, 1475–1479.

Petroleum Fraktionen mit einem Siedepunkt von 200 bis 270°C aus ägyptischem Erdöl, entparaffiniert und geruchfrei gemacht, mit einem Anteil von 34% Naphthenen und 16% Isoparaffinen, wurden einer Oxydation in flüssiger Phase mit Cobalt-Acetat als Katalysator bei verschiedenen Temperaturen unterworfen. Aus den dabei gewonnenen Naphthensäuren wurden Naphthensäureamide und Naphthenalkohole hergestellt. Durch Oxäthylierung wurden sowohl die Naphthensäureamide als auch die Naphthenalkohole in Ethylenoxidaddukte mit unterschiedlicher Anzahl an Ethylenoxid-Einheiten überführt. Die Produkte mit 5 Ethylenoxid-Einheiten wurden mit Chlorsulfonsäure zu den Sulfaten, mit P<sub>2</sub>O<sub>5</sub> zu den Phosphaten umgesetzt. Von den so erhaltenen nichtionischen und anionischen Tensiden wurden Löslichkeit, Trübungspunkt, Oberflächen- und Grenzflächenspannung, Schaum- und Waschvermögen geprüft. Die Meßwerte sind in Tabellen zusammengefaßt.

D 1 (90356)

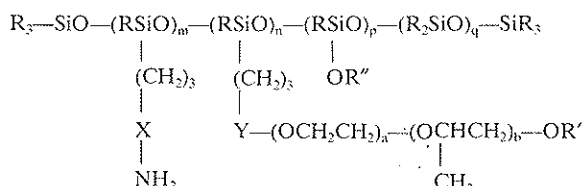
Chwala



**Europäische Patentanmeldungen**

**Amin und polyoxyalkylenfunktionalisierte Polydiorganosiloxane**

Als Antischaummittel in speziellen Waschmitteln und Textilhilfsmitteln werden Polydiorganosiloxane der Formel I beansprucht



I

R = C<sub>1-4</sub>-Alkyl, Phenyl oder 3,3,3-Tri-fluorpropyl (mit mind. 80 % CH<sub>3</sub>)  
X = —O—CH<sub>2</sub>CH(OH)CH<sub>2</sub>NH—W— (II) oder X enthält und NH<sub>2</sub> ist direkt gebunden

Y = —O—CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> (III) oder Y entfällt und die Polyglykolgruppen sind direkt gebunden, wenn p = 0 und X entfällt, dann ist Y = (III)

m, n = 1–25, vzw. 1–10

p = 0–15, vzw. 1–5

q = 5–500, vzw. 10–400

a, b = 0–150 a + b = 5–200

W = C<sub>1-6</sub>-Alkylen

R' = H, C<sub>1-6</sub>-Alkyl, C<sub>1-6</sub>-Acyl oder Phenyl

R'' = C<sub>1-6</sub>-Alkyl

Vorzugsweise ist R = R' = CH<sub>3</sub> und W = —(CH<sub>2</sub>)<sub>2</sub>—

Die Produkte sind leicht herzustellen.

EP 404698 v. 19. 06. 90/27. 12. 90; FR-Prior. 22. 06. 89 (8581) B 01d-19/04, C 08g-77/46, C 081-83/12, D 06m-15/64 Rhone-Poulenc Chim., Erf.: J. Kirk 90783 EP

**Polyacrylsäureester mit langkettigen Kohlenwasserstoff- und Polyoxyalkylen-Gruppen und deren Verwendung als grenzflächenaktive Substanzen**

Die Herstellung von Polyacrylsäureestern mit langkettigen Kohlenwasserstoff- und Polyoxyalkylen-Gruppen durch Umesterung von durch Radikalpolymerisation hergestellten Polyacrylsäureestern mit C<sub>1-4</sub>-Alkyl-Gruppen mit einer Mischung von a) Alkoholen und b) Polyoxyalkylenmonoolen der Formel R<sup>1</sup>—O—(C<sub>n</sub>C<sub>2n</sub>O)<sub>x</sub>—H wird beansprucht.

R<sup>1</sup> = KW-Rest des Ausgangsalkohols R<sup>1</sup>OH

n = 2–4 (2–3)

x = 4–50

Als Alkohole (a) setzt man gesätt. aliph. C<sub>4-22</sub>-Alkohole, ungesätt. aliph. C<sub>8-22</sub>-Alkohole, Alkylphenole mit 8–20 C-Atomen in der Alkylgruppe oder Alkoxyate mit 1–3 EO oder PO ein. Die Umesterung findet bei 70–160 °C ggf. in einem Lösungsmittel in Gegenwart eines üblichen Umesterungskatalysators und Anwendung eines Molverhältnisses von (a):(b) 1:11 bis 28:1

bis zu einem Umsatz von 70 % statt.

Beansprucht wird die Verwendung von Polyacrylsäureestern als W/O-Emulgatoren für natürliche oder synthetische Öle.

Mit nur geringen Mengen Tensid läßt sich Wasser in Dieselöl emulgieren, z. B. für Dieselöl-getriebene Gasturbinen.

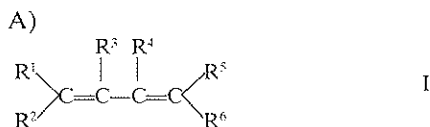
Bis zu 50 % der Alkylacrylate lassen sich durch Alkyl-Methacrylate ersetzen. Als Alkohole (a) verwendet man vzw. Stearyl-, Talgfett- oder Oleylalkohol. Vzw. verwendet man für (b) ein Alkoxyat mit R<sup>1</sup> = CH<sub>3</sub>, n = 2 oder 3 und x = 6–20 mit einem Molverhältnis von 1:10 bis 10:1.

Die Polyacrylsäureester haben gute Tenseideigenschaften und gute physiologische Eigenschaften. Die enge Molgewichtsverteilung des Ausgangspolymeren wird bei der Umesterung erhalten.

EP 386507 v. 17. 02. 90/12. 09. 90; DE-Prior. 03. 03. 89 (DE 3906702), C 08f-8/14, C 11d-1/00 Th. Goldschmidt AG, Erf.: J. Fock, E. Esselborn u. D. Schäfer. 90818 EP

**Sulfonierungsprodukt von konjugierten Dienen, Polymere des Sulfonierungsproduktes sowie dispergierende Zusammensetzung, die das Sulfonierungsprodukt und/oder das Polymer enthält**

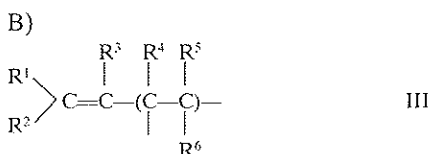
Als Dispergiermittel werden Sulfonierungsprodukte von A) konjugierten Dienen der Formel I und B) deren Polymere und Copolymere beansprucht.



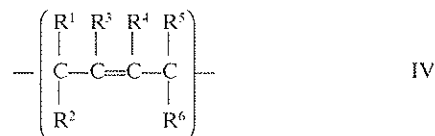
I

R<sup>1</sup>–R<sup>6</sup> = H, C<sub>1-8</sub>-Alkyl, C<sub>6-20</sub>-Aryl oder —SO<sub>3</sub>X

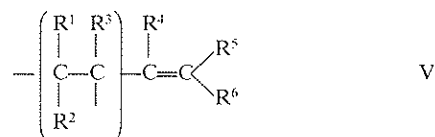
X = H, Metall, NH<sub>4</sub> oder quart. NH<sub>4</sub>



III



IV



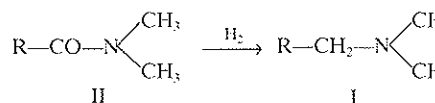
V

Die sulfonierten Produkte sind stark sauer und werden als Dispergiermittel für die Herstellung fester Brennstoffe, Zement, Farbstoff/Pigment oder Metalloxid-Dispersionen, für Faser- oder Wasser-Behandlungsmittel, Galvanisierbäder oder Viskositätsregler für Bohrschlämme verwendet. Die Polymere von I sind einfach zu verwenden. Sie sind auch Harze mit hoher Ionenaustauschkapazität.

EP 337738 v. 11. 04. 89/18. 10. 89; JA-Prior. 15. 04. 88 (91286) C 07c-143/00, C 07c-143/16, C 07c-139/00, C 088f-28/02, B 01f-17/00 u.a. Japan Synth. Rubber Co., Ltd., Erf.: H. Ono, K. Ito, T. Uekawa u. K. Ishikawa. 90814 EP

**Verfahren zur Herstellung von N,N-Dimethyl-N-alkylaminen**

N,N-Dimethyl-N-alkylamine der Formel I mit weniger als 1 % Alkanol werden durch Hydrierung von N,N-Dimethylalkylamiden hergestellt. Katalysator ist ein Kupferchromit-Typ, der CuO, Cu(CrO<sub>2</sub>)<sub>2</sub> und MnO<sub>2</sub> enthält. Der Wasserstoff wird in einem molaren Verhältnis H<sub>2</sub>:Dimethylalkylamid von 2–20 bei einem Gesamtdruck von 10–100 Bar und bei einer Temperatur von 220–280 °C im Kreis durch die Lösung gepumpt.



II

I

R = C<sub>12-24</sub>-Alk(en)yl

Vzw. ist II ein N,N-Copradimethylamid und R = C<sub>12-14</sub>-Alk(en)yl. Der Katalysator besteht aus (ber. als Oxide) 10–75 (45–49) Gew.-% CuO, 10–75 (45–49) Gew.-% Cr<sub>2</sub>O<sub>3</sub> und 2–20 (2–10) Gew.-% MnO<sub>2</sub>. Der H<sub>2</sub> im Kreislauf enthält 1 Vol.-% Dimethylamin, das man zugibt, wenn die Alkalität 75 % des erwarteten theoretischen Wertes erreicht hat.

Die Produkte werden bei der Herstellung von quart. Ammoniumsalz-Tensiden, Bactericiden und industriellen Desinfektionsmitteln verwendet.

EP 357470 v. 05. 07. 89/07. 03. 90; FR-Prior. 08. 07. 88 (9280) B 01j-23/86, C 07c-209/50, C 07c-211/08 CECA S.A., Erf.: R. Brouard u. C. Forquy. 90822 EP