J. Phys.: Condens. Matter 6 (1994) A351–A356. Printed in the UK

Simulating surfactant self-assembly

S Karaborni, K Esselink, P A J Hilbers and B Smit
Shell Research BV, Koninklijke/Shell-Laboratorium, Amsterdam, PO Box 3003, 1003 AA Amsterdam, The Netherlands

Received 24 September 1993

Abstract. This paper briefly reviews simulations of a simple model oil/water/surfactant system. The model describes only the most characteristic elements of oil/water/surfactant mixtures: oil and water do not mix, and a surfactant is an amphiphilic molecule; one side of the molecule likes oil more than water, and the other side likes water more than oil. Molecular dynamics simulations have been performed on this simple model to study the effects of surfactant chain length on the oil/water interfacial tension, the relation between micellar shape and surfactant structure, and the solubilization of an oil droplet in an aqueous micellar solution.

1. Introduction

A surfactant consists of a hydrophobic fragment chemically connected to a hydrophilic one. The amphiphilic nature of such molecules gives surfactants their unique properties. For example, when added to water, surfactants reduce the surface tension and solubilize oil [1]. Besides their practical applications, surfactants are also of fundamental interest as model systems for the study of self-assembly.

Despite significant experimental and theoretical work, many aspects of surfactant self-assembly remain poorly understood on the molecular level. Even for the simplest structures, micelles in water, elementary questions such as the extent of water penetration into the core of a micelle [2], the nature of the hydrocarbon/water interface [32], the types of interaction essential for the formation of micelles [4], and the qualitative molecular structure of a micelle remain unanswered. In this short review of our work, we describe the use of computer simulations in addressing qualitative aspects of these complex systems.

From a molecular simulation point of view, surfactant dynamics are extremely difficult to study. This becomes clear if we consider that it is estimated to take 10^{-9}–10^{-2} s for a surfactant to leave or enter a micelle, and 10^{-2}–1 s for the breakup of a micelle [5]. If we recall that a computer simulation, using the molecular dynamics technique, is limited to several nanoseconds [6], it becomes obvious that drastic assumptions have to be made to study the self-assembly of micelles.

There have been two approaches to studying micelles. (1) Using a realistic model of water and surfactant molecules, a micelle is constructed *a priori*, and its evolution is studied [7–12]. These simulations yield important information on the detailed structure and dynamics within a micelle, but cannot be used, at present, to study the self-assembly of micelles [13]. (2) Using a very simple oil/water/surfactant model, one tries to simulate the self-assembly of surfactants into micelles or different structures. In this work, we focus on the second approach. Using such an approach, it was possible to observe the self-assembly process of micelles [14, 15], vesicles [16], and the solubilization of an oil droplet [17].

0953-8984/94/SA0351+06$19.50

2. A simple 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 as follows: what features of this system are responsible for the characteristic behaviour as observed experimentally for these systems? Widom and co-workers were among the first to address this question [18]. Two simple observations constituted their starting point: oil and water do not mix, and a surfactant is an amphiphilic molecule. Continuum models, based on the Widom model, have been developed by Stillinger [19], Telo da Gama and Gubbins [20], and Wu *et al* [21].

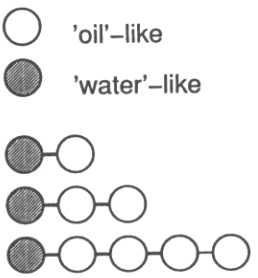

Figure 1. Schematic drawing of the oil/water/surfactant model.

The present model uses the same ingredients as the Widom model. The existence of four types of particles is assumed: o particles, w particles, h particles, and t particles. These particles are used to model three types of molecule, 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 springs. The four types of particle interact with truncated and shifted Lennard-Jones potentials with energy parameter ϵ_{ij}, distance parameter σ_{ij}, and cut-off radius R_{ij}^{c}. It is 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 dependent on the type of interaction. The w–w and o–o interaction is 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 the same interactions for the t particles as for the o particles. The only difference between an o particle and a t particle is that the t particles are connected with harmonic forces to other t or h particles (see figure 1). The interactions of the h particles are 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 a temperature $T = 1.0\epsilon/k_{B}$ and a density $\rho = 0.7\sigma^{3}$, the oil and water do not mix and form a stable liquid/liquid interface [22].

3. Results

The model introduced in the previous section contains many simplifications. It is therefore important to test whether this model still captures the essential properties of surfactants: do the model surfactants lower the interfacial tension of the bare oil/water interface and do they self-assemble to form micelles?

3.1. The oil/water interface

Figure 2 shows the effects of adding various types of model surfactants on the interfacial tension of the bare oil/water interface [22, 23]. It can be seen that the model surfactants indeed lower the interfacial tension. Furthermore, increasing the tail length of the surfactants makes them more effective in reducing the interfacial tension, in agreement with experimental data [23]. Our simulations demonstrate that the surface tension decreases linearly with surfactant concentration. Experimentally, a characteristic break in the interfacial tension is observed at high surfactant concentrations. This break is caused by the formation of micelles in the water phase. The simulations, on relatively small systems ($\simeq$ 1000 particles), did not show the formation of micelles, and thus the absence of a break in the calculated interfacial tension curve.

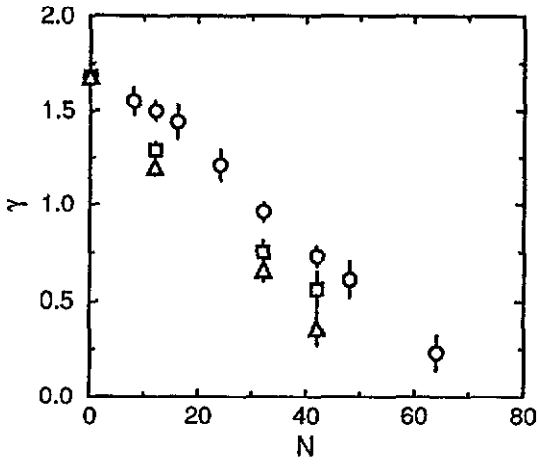

Figure 2. Surface tension γ as a function of the total number of surfactants N for various linear surfactants (the model of figure 1) as obtained from the simulations. The number of chain segments is ○: 1, □: 3, and △: 5. Details on the simulations can be found in [22, 23].

Similar model systems of a liquid–liquid interface have been used to study the dynamics of adsorption of amphiphilic molecules by Mareschal and co-workers [24]. The adsorption was considered as a 'chemical reaction' in which the distance from the interface was considered as a one-dimensional reaction coordinate. The diffusion was analysed by calculating the potential of mean force. Benjamin used a similar model to study the transport of ions across a liquid–liquid interface [25] and to study electron transfer reactions at the liquid–liquid interface [26].

3.2. Self-assembly

The study of self-assembly of micelles requires the use of very large systems. [14] and [15] report that simulations on 40 000 particles were performed on a parallel computer using an efficient parallel molecular dynamics algorithm [27]. In figure 3, a snapshot of a part of the system is shown. It is important to note that these simulations were started from a random distribution of surfactants and the monolayer and micelles were not constructed *a priori*. This figure shows that simulations on a simple surfactant model can be used to study the self-assembly of micelles. The micellar size distribution, a test for the system indeed being of micellar nature, has been calculated in [15]. Furthermore, it is shown that in these simulations one can observe surfactants entering/leaving a micelle, the fusion of micelles,

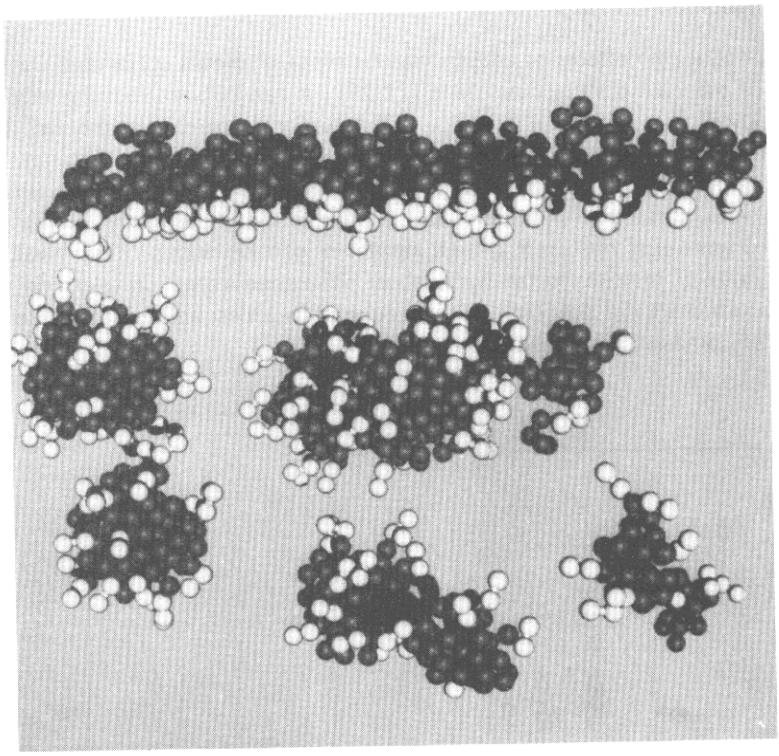

Figure 3. Typical example of a configuration of surfactants in an oil/water system for 1.5% surfactants. The total number of particles was $\approx 40\,000$. The snapshot shows only the surfactants that form a monolayer at the oil/water interface and the surfactants in the water phase. For clarity, the surfactants in the oil phase and the oil and water particles are not shown. The hydrophilic segments are white and the hydrophobic segments grey. Further details on these simulations can be found in [14, 30].

and even the breakdown of a micelle. Similar processes have been observed experimentally [5].

The micelle morphology as a function of surfactant shape has been studied [28]. These simulations show that, depending on the size of the head group, one can observe bilayers, tubular micelles, or spherical micelles. The behaviour of amphiphilic comb molecules in oil/water surfactant mixtures was studied by Balazs *et al* [29] using a similar model. These calculations show the formation of intramolecular polymer micelles. The self-assembly of vesicles has been studied by Drouffe *et al* [16] who focused on thermal fluctuations in vesicles.

3.3. Oil solubilization

From a technological point of view, the rate at which surfactants solubilize oil droplets is very important and has been studied extensively. The rational design of efficient surfactants requires a detailed understanding of the mechanism of oil solubilization. To obtain more understanding at a molecular level, Karaborni *et al* [17] used molecular dynamics simulations to study the solubilization of an oil droplet in an aqueous surfactant solution. This study, using the simple oil/water/surfactant model, revealed three mechanisms for the

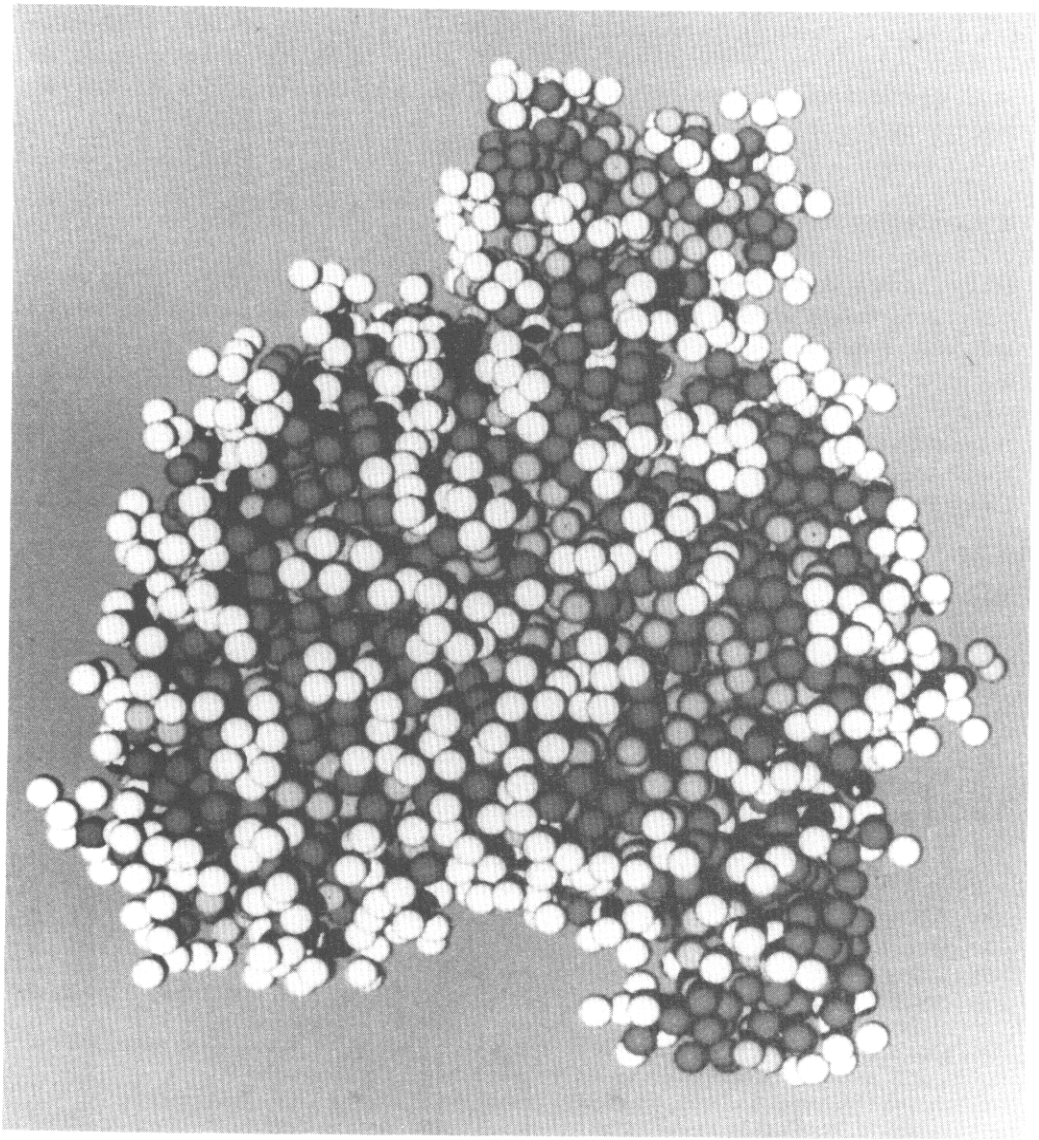

Figure 4. Instantaneous configuration of an oil droplet in water before the collective desorption of 47 surfactants and 27 oil molecules. Oil molecules are drawn in light grey, and surfactant molecules are drawn in dark grey (tails) and white (head–groups). The water molecules are not shown. This figure is an illustration of mechanism (3) by which oil solubilization in micellar solutions proceeds. Details of mechanism (3) are mentioned in the text. Further details on these simulations can be found in [17].

transfer of oil molecules from the droplet to the water phase: (1) individual oil molecules leave the oil droplet and are trapped by micelles in the vicinity of the droplet; (2) the collision of the droplet with micelles causes the exchange of oil between the droplet and the micelle; and (3) because of the low interfacial tension between the oil droplet and the water, caused by the adsorption of surfactants, the oil droplet shows large fluctuations. During such

a fluctuation part of the oil droplet, together with a large number of surfactant molecules, can desorb (see figure 4). Furthermore, it is shown in [17] that the extent to which either of these mechanisms prevails depends on the size of the oil molecules. For example, for small oil molecules mechanism (1) is more likely, while for large molecules the other two mechanisms are dominant.

4. Concluding remarks

In this review, some recent results on computer simulations using very simple model oil/water/surfactant systems are presented. Molecular dynamics simulations have shown that, with a very simple model, the characteristic phenomena of surfactant systems, such as the reduction of surface tension, the self-assembly of micelles or vesicles, and the solubilization of an oil droplet, can be observed. The simplicity of the model makes it possible to perform systematic studies, which may lead to a better understanding of surfactant-dependent processes such as cleaning, enhanced oil recovery, and transport through biological membranes.

References

[1] Mittal K L and Lindman B 1984 *Surfactants in Solution* (New York: Plenum)
[2] Menger F M 1979 *Accounts Chem. Res.* **12** 111
[3] Chen S-H 1986 *Ann. Rev. Phys. Chem.* **3** 351
[4] Beesley A H, Evans D F and Laughlin R G 1988 *J. Phys. Chem.* **92** 791
[5] Lang J and Zana R 1987 *Surfactants in Solution: New Methods of Investigation* ed R Zana (New York: Dekker) ch 8
[6] Allen M P and Tildesley D J 1987 *Computer Simulation of Liquids* (Oxford: Clarendon)
[7] Haan S W and Pratt L R 1981 *Chem. Phys. Lett.* **79** 436
[8] Haile J M and O'Connell J P 1984 *J. Phys. Chem.* **88** 6363
[9] Karaborni S and O'Connell J P 1990 *Langmuir* **6** 905
[10] Jönsson B, Edholm O and Teleman O J 1986 *J. Chem. Phys.* **85** 2259
[11] Watanabe K and Klein M L 1989 *J. Phys. Chem.* **93** 6897
[12] Shelly J C, Sprik M and Klein M L 1993 *Langmuir* **9** 916
[13] Smit B 1993 *Computer Simulation in Chemical Physics (NATO ASI)* ed M P Allen and D J Tildesley (Dordrecht: Kluwer) pp 2025–8
[14] Smit B, Hilbers P A J, Esselink K, Rupert L A M, van Os N M and Schlijper A G 1990 *Nature* **348** 624
[15] Smit B, Esselink K, Hilbers P A J, van Os N M and Szleifer I 1993 *Langmuir* **9** 9
[16] Drouffe J-M, Maggs A C and Leibler S 1991 *Science* **254** 1353
[17] Karaboni S, van Os N M, Esselink K and Hilbers P A J 1993 *Langmuir* **9** 1175
[18] Wheeler J C and Widom B 1968 *J. Am. Chem. Soc.* **90** 3064
[19] Stillinger F H 1983 *J. Chem. Phys.* **78** 4654
[20] Telo da Gama M M and Gubbins K E 1986 *Mol. Phys.* **59** 227
[21] Wu D, Chandler D and Smit B 1992 *J. Phys. Chem.* **96** 4077
[22] Smit B 1988 *Phys. Rev.* A **37** 3431
[23] Smit B, Schlijper A G, Rupert L A M and van Os N M 1990 *J. Phys. Chem.* **94** 6934
[24] Mareschal M, Meyer M, and Turq P 1991 *J. Phys. Chem.* **95** 10723
[25] Benjamin I 1992 *J. Chem. Phys.* **96** 577
[26] Benjamin I 1991 *J. Phys. Chem.* **95** 6675
[27] Esselink K, Smit B and Hilbers P A J 1993 *J. Comput. Phys.* **106** 101
[28] Smit B, Hilbers P A J and Esselink K 1993 *Tenside Surfact. Detergents* **30** 287
[29] Balazs A C, Zhoe Z and Yeung C 1992 *Langmuir* **8** 2295
[30] Smit B, Hilbers P A J, Esselink K, Rupert L A M, van Os N M and Schlijper A G 1991 *J. Phys. Chem.* **95** 6361