3775

Mechanism of Aggregation of Oil-in-water Microemulsion Droplets Stabilized by Dodecyl Pentaoxyethylene Alcohol, $C_{12}E_5$

Michael M. Kozlov†
Freie Universität Berlin, FB Physik, WE 2, Arnimallee 14, 1000 Berlin 33, Germany

Modern experimental data allow us to analyse the mechanical and structural properties of a surfactant mono-layer covering a microemulsion droplet. In this paper we have analysed theoretically data for oil/water micro-emulsions in the presence of the surfactant $C_{12}E_5$. We have determined the spontaneous area per polar head in the surfactant monolayer, a_s, and its dependence on the temperature, $a_s(T)$, which is satisfactorily described by the same straight line for both types of microemulsion droplet containing heptane or tetradecane as oil. The results obtained allow us to conclude qualitatively that the spontaneous area per surfactant polar head is deter-mined by the interaction between the polar heads. At the same time the spontaneous curvature of the monolayer is strongly affected by the penetration of oil molecules between the alkyl chains of the surfactant molecules.

We have proposed a mechanism for the aggregation of two microemulsion droplets during heating of the system. This mechanism is based on the relaxation of the elastic energy of area extension due to the breakdown of the surfactant monolayer during the aggregation process. The numerical evaluation of the corresponding change of the elastic energy supports the considered mechanism.

The properties of microemulsions are strongly dependent upon the structural and elastic characteristics of the sur-factant monolayers covering the microemulsion droplets.[1,2] The effective structure of the monolayer is described by the spontaneous geometrical characteristics: the spontaneous curvature J_s and the spontaneous area per surfactant mol-ecule a_s, corresponding to the mechanically unstressed state of the system.[3] The elastic properties of the monolayer are described in terms of the elastic moduli.[3] The processes occurring in microemulsions (interaction of the droplets, inversion of microemulsions, phase separation *etc.*) are related to the appearance of elastic stresses in the surfactant monolayers.[4,5] Hence values of the spontaneous geometrical characteristics of surfactant monolayers and the kind of elastic tensions appearing in the system are important in understanding the properties of microemulsions.

It is almost impossible to measure directly the spontaneous geometrical characteristics and the elastic stresses of the monolayers covering microemulsion droplets. Therefore the only way is to determine the characteristics of the system from an analysis of experimental data in the framework of a certain model. Modern experimental investigations have allowed us to collect an extensive set of data concerning the simplest kind of microemulsion comprising only three com-ponents: water, oil and non-ionic surfactant, dodecyl pen-taoxyethylene alcohol, $C_{12}E_5$.[6-9] The properties of such microemulsions probably reflect the main features of more complex systems, containing surfactant and cosurfactant mol-ecules with electric charge. Some data on the structure of molecules of $C_{12}E_5$ have been given in a series of experiments on micellar solutions of this substance in water.[10] This paper reports a theoretical analysis of the structural and elastic properties of $C_{12}E_5$ monolayers covering oil-in-water micro-emulsion droplets. The analysis is based on the experimental data of ref. 6–8.

Statement of the Problem

The single-phase domain of the phase diagram of a water-in-oil microemulsion corresponds to a narrow temperature interval bounded at low temperature by the solubilization phase boundary and at high temperature by the cloud-point boundary. At the solubilization phase boundary the excess oil phase separates and at the cloud-point boundary a surfactant-rich phase appears in the system.[6] The results of experiments quoted give information about the spontaneous state of $C_{12}E_5$ monolayers and the behaviour of the micro-emulsion droplets with the stressed covering monolayers.

The spontaneous states of the monolayer correspond to the solubilization phase boundary.[6] The measured parameters are the molar ratio of dispersed oil to the surfactant covering the droplets, R, the hydrodynamic radius of a droplet, r_h, and the temperature of the system, T. The experiments were per-formed with heptane or tetradecane as oil. The solubilization boundaries for heptane- and tetradecane-containing micro-emulsions are given in ref. 6. The values of the hydrodynamic radii of the droplets at the solubilization boundary are rep-resented by the following phenomenological expressions:[6]

$$r_h/nm = 1.89 R_{hept} + 3.3 \qquad (1)$$

$$r_h/nm = 4.51 R_{tetr} + 3.0 \qquad (2)$$

corresponding to the microemulsions containing heptane and tetradecane as oil, respectively.

The results concerning the microemulsion droplets in a stressed state were obtained by means of turbidity measure-ments.[6-8] It was shown that at temperatures close to the solubilization boundary the system consists of spherical, non-interacting droplets. As the system moves from the solu-bilization phase boundary towards the cloud-point boundary, the droplet size remains constant but an effective attraction between the droplets appears. The droplets cluster together.[6-8]

The first aim of this work is to determine the spontaneous geometrical characteristics of the $C_{12}E_5$ monolayer from the experimental results given in ref. 6–8. The second goal is to develop a possible mechanism of aggregation of micro-emulsion droplets at temperatures close to the cloud-point boundary.

Description of the System

Consider a spherical droplet of oil in water covered by a monolayer of surfactant $C_{12}E_5$. To describe the geometry of

---

† Permanent address: A. N. Frumkin Institute of Electrochemistry, USSR Academy of Science, Leninsky Prospect 31, Moscow 117071, USSR.

the surfactant monolayer we choose a dividing surface[11] situated in the region of the polar heads of the surfactant molecules. The radius r of the dividing surface under consideration coincides with the hydrodynamic radius of the droplet r_h. It is reasonable to assume that the Gibbs excess of water is zero with respect to this dividing surface.

The mean curvature $J = 2/r$ and the area per surfactant molecule a at the dividing surface characterise the geometry of the monolayer. In the spontaneous state the mechanical stresses in the monolayer vanish and the elastic energy takes a minimal value.[3] The geometrical characteristics of the monolayer in the spontaneous state are: r_s, the spontaneous radius, and a_s, the spontaneous area per surfactant molecule.

Now we introduce a deformation of the monolayer with respect to the spontaneous state. Then the elastic energy is given by the following expression:

$$F = Na_s\left[\frac{1}{2} E_{AA}\left(\frac{a - a_s}{a_s}\right)^2 + \frac{1}{2} E_{JJ}\left(\frac{2}{r} - \frac{2}{r_s}\right)^2 \right.$$
$$\left. + E_{AJ}\left(\frac{a - a_s}{a_s}\right)\left(\frac{2}{r} - \frac{2}{r_s}\right)\right] \quad (3)$$

where E_{AA}, E_{JJ} and E_{AJ} are the elastic moduli corresponding to the deformation of area extension, bending and to the mixed deformation, respectively.[3] N is the number of surfactant molecules in the monolayer.

Spontaneous Geometrical Characteristics of the $C_{12}E_5$ Monolayer

Let us assume that the molecular volumes of all components of the system do not depend on the temperature. A simple geometrical consideration gives the following expression, which relates a_s to the directly measurable values of r_s and R:

$$a_s = 3\frac{v^a}{r_s}\left(R + \frac{v^s}{v^a}\right) \quad (4)$$

where v^s and v^a are the molecular volumes of surfactant and alkane, respectively. The molecular volumes of surfactant $C_{12}E_5$, heptane and tetradecane are:[6–8] $v^s = 0.73$ nm^3, $v^{hept} = 0.25$ nm^3 and $v^{tetr} = 0.43$ nm^3. By substituting these values in eqn. (4), (1) and (2) one obtains the following final expressions for a_s as a function of R in the cases of heptane- and tetradecane-containing droplets:

$$a_s = 0.4 \frac{2.92 + R^{hept}}{1.75 + R^{hept}} \quad (5)$$

$$a_s = 0.29 \frac{1.55 + R^{tetr}}{0.67 + R^{tetr}} \quad (6)$$

The dependence of a_s on the temperature can be determined by inserting the values of R at the solubilization phase boundary[6] in eqn. (5) and (6). The results are presented in Fig. 1. The series of points in the temperature interval 21–28 °C corresponds to heptane droplets. The points in the interval 35–45 °C are for tetradecane droplets.

We are describing the system in terms of the dividing surface situated between the surfactant monolayer and the surrounding water. Hence the values of a_s obtained (Fig. 1) refer to the polar head of the surfactant molecule. Inspection of Fig. 1 shows that the same straight line can reasonably describe both series of points. One can conclude that the spontaneous area per surfactant polar head depends on the temperature but does not depend on the kind of alkane forming the droplet core.

The spontaneous area of the $C_{12}E_5$ polar head (Fig. 1) is a decreasing function of temperature. At room temperature
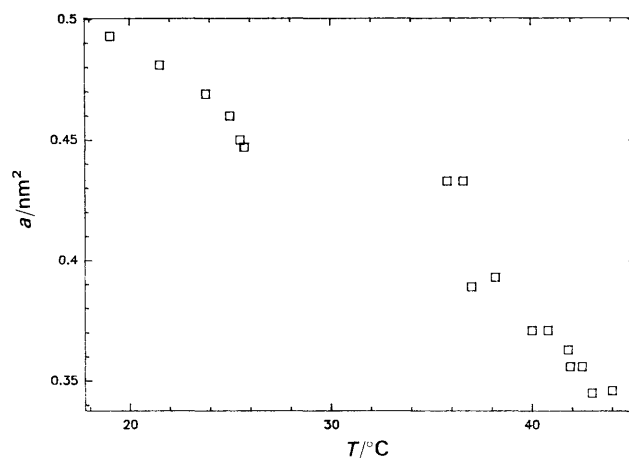

Fig. 1 Spontaneous area per $C_{12}E_5$ head group *vs.* temperature. The two series of points correspond to heptane-containing (left) and tetradecane-containing (right) droplets

$a_s = 0.47$ nm^2. Both results are in agreement with the qualitative conclusions of ref. 10, which reports the structure of aqueous $C_{12}E_5$ micelles in the absence of oil. Such accordance allows us to assume that the presence of alkane does not change the spontaneous area of the $C_{12}E_5$ polar head.

We can estimate the minimal thickness of the surfactant monolayer δ by means of the calculated function $a_s(T)$ and the value v_s, $\delta = v_s/a_s$. The values of δ vary from 1.5 to 2.1 nm as a function of temperature. These are reasonable values for a pure surfactant monolayer with the alkyl chains in an unstretched conformation. The true thickness must be larger owing to penetration of oil molecules between the alkyl chains of the surfactant.[6–8]

Let us consider the dependence of the monolayer spontaneous radius r_s on the temperature. The results given in ref. 6–8 are summarized in Fig. 2. The dependence $r_s(T)$ is presented by two different curves. The first (21–28 °C) refers to heptane droplets and the second (35–45 °C) describes tetradecane droplets. It follows from the results of Fig. 2 that the spontaneous curvature of the $C_{12}E_5$ monolayer is strongly dependent on the choice of alkane.

A comparison of the dependences of spontaneous geometrical characteristics on the temperature, $a_s(T)$ and $r_s(T)$, illustrated in Fig. 1 and 2 leads to the following assumptions about the interactions inside the surfactant monolayer.
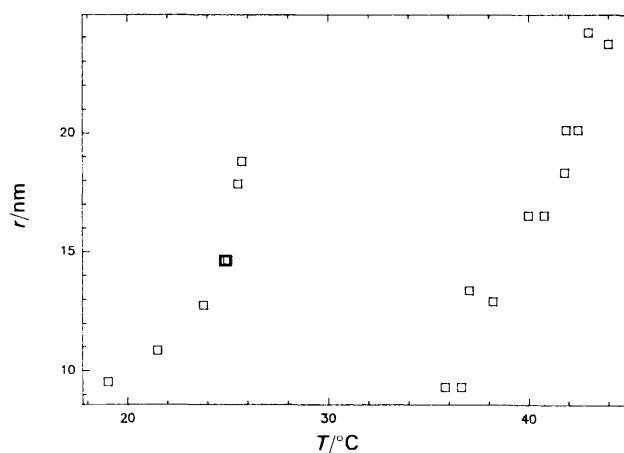

Fig. 2 The spontaneous radius of $C_{12}E_5$ monolayers *vs.* temperature.[6] The two series of points correspond to heptane-containing (left) and tetradecane-containing (right) droplets

The spontaneous area a_s of the surfactant polar head is determined by a mutual interaction between polar heads and does not depend on the interaction in the region of the alkyl chains.

The spontaneous radius r_s is strongly determined by the interaction between the alkyl chains of the surfactant molecules and the oil molecules. Probably, the increase of the spontaneous radius of the monolayer is due to the penetration of oil molecules in the region of the surfactant alkyl chains. The possibility of such a penetration in the case of flat monolayers was investigated in ref. 12. The analysis in Fig. 2 shows that heptane molecules penetrate at temperatures lower than those typical for tetradecane molecules. This conclusion agrees qualitatively with the results of ref. 12.

Mechanism of Droplet Aggregation

An increase of temperature at a constant value of R leads to the effective mutual attraction of the microemulsion droplets and to the formation of droplet aggregates.[6,8] According to the assumptions of ref. 6 and 8 the first stage of the aggregation process consists of the formation of a droplet encounter pair.

In the present work we suggest the mechanism of formation of droplet dimers. This mechanism is based on a decrease of monolayer elastic energy due to the breakdown of the monolayer as a result of droplet contact. Let us consider this mechanism in detail.

The monolayer covering the microemulsion droplet at a temperature higher than the solubilization phase boundary is stressed, and its elastic energy is given by eqn. (3). In this case the elastic stresses are due to the difference between the actual and spontaneous values of the geometrical characteristics. In the heating process the actual droplet radius r remains constant.[6,7] According to the experimental data we assume that the number of surfactant molecules in the droplet monolayer does not change. This means that the actual area per surfactant molecule a also remains constant with increasing temperature. At the same time the heating leads to a change in the spontaneous geometrical characteristics, r_s and a_s (Fig. 1 and 2).

The spontaneous area a_s decreases as the temperature increases (Fig. 1). As a result the actual area per molecule a becomes larger than a_s. The difference between these values $a - a_s$ increases with temperature. The monolayer becomes extended with respect to the spontaneous state.

Owing to the increase of the spontaneous radius r_s (Fig. 2) a difference appears between the real curvature and the spontaneous one. The monolayer becomes curved with respect to the spontaneous state. The last effect was pointed out in ref. 7.

Let us assume that the formation of a droplet pair is accompanied by the breakdown of the surfactant monolayers. This event (Fig. 3) gives rise to a relaxation of the elastic stresses due to a decrease of the actual monolayer area and increase of its actual radius. As a result, the elastic energy in eqn. (3) decreases.

To estimate the change of elastic energy we will assume that the area of the rupture is much smaller than the area of the monolayer. Therefore one can neglect the change of monolayer radius accompanying the breakdown. The main effect is the relaxation of the monolayer area to the spontaneous value. This leads to the following change in the elastic energy:

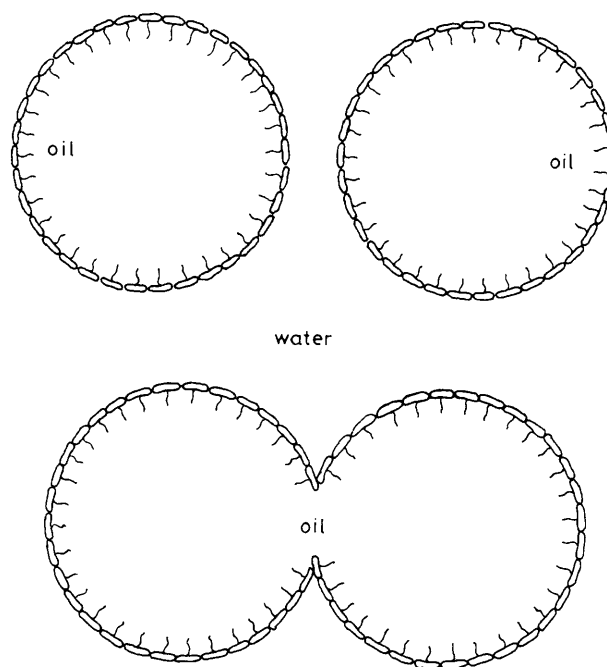$$\Delta F = -\frac{1}{2} E_{AA} 4\pi r^2 \left(\frac{a - a_s}{a_s}\right)^2 \tag{7}$$

Fig. 3 The first step of droplet aggregation, including the breakdown of the surfactant monolayer and relaxation of the monolayer area

The variation of the energy in eqn. (7) depends on temperature through the dependence $a_s(T)$. In Fig. 4 the dependence $\Delta F(T)$ is illustrated for the case of a droplet with a radius of 12 nm. The curve in Fig. 4 is obtained by substitution in eqn. (7) of the values $a_s(T)$ from Fig. 1. The elastic modulus of area extension is assumed to be equal to the appropriate value of a lipid bilayer $E_{AA} = 0.1$ N m^{-1}.[13] The temperature range in Fig. 4 corresponds to the interval between the solubilization phase boundary and the cloud-point boundary. At the solubilization phase boundary $a = a_s$ and the change of the energy in eqn. (7) is zero, $\Delta F = 0$. The increase of temperature leads to negative values of ΔF. The higher the temperature the more energetically favourable is the aggregation of droplets.

The maximal absolute value of the energy change ΔF_{max} corresponds to the cloud-point boundary (Fig. 4). Fig. 5 shows the dependence of ΔF_{max} on the droplet radius. One can compare these values with the values of the energy
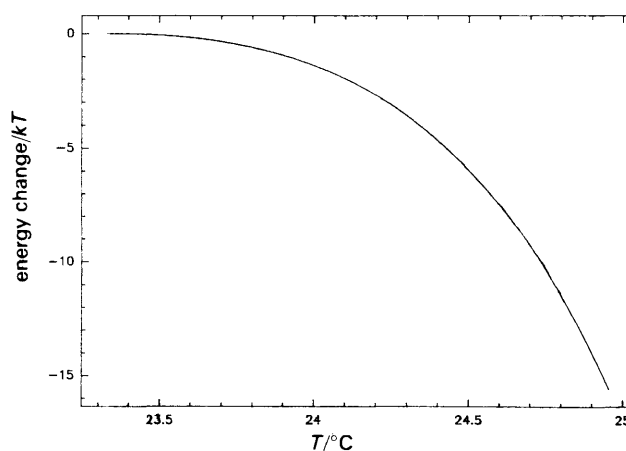

Fig. 4 The change of the energy of area extension resulting from monolayer breakdown vs. temperature. The droplet radius is equal to 12 nm
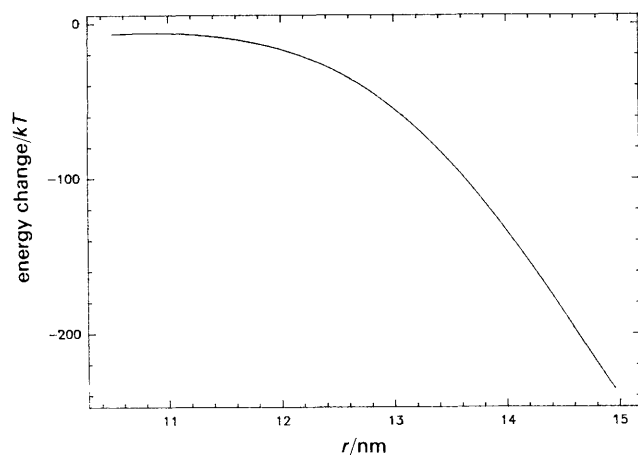
Fig. 5 The maximal change of energy of area extension resulting from monolayer breakdown *vs.* radius of microemulsion droplet

barrier of aggregation ΔF^* estimated in ref. 8. ΔF^* corresponds to the aggregation of droplets at the solubilization phase boundary and probably includes all factors preventing this process. The energy barriers for the droplets with radii 12 and 21 nm are equal to $6.3kT$ and $4.7kT$, respectively.[8] Fig. 5 shows that the absolute value of the maximal energy change ΔF_{max} is larger than the energy barrier ΔF^* and increases drastically as the droplet radius increases.

The evaluation performed supports the possibility of the suggested mechanism of aggregation of microemulsion droplets.

Discussion

In the present work we have considered the questions discussed previously in ref. 6–8. Let us point out the difference between the approach developed here and previous considerations of the problem.[6–8]

For a description of the monolayer geometry, the internal dividing surface situated between the surfactant monolayer and the oil volume inside the droplet has been used in ref. 6–8. The geometry of the system has been characterised by the hydrodynamic radius r_h, the area per molecule at the internal dividing surface A_s and the thickness of the monolayer δ. Two assumptions were made to explain the experimental results, namely that A_s and δ have the same values for all states at the solubilization phase boundary. In other words A_s and δ in the spontaneous state were assumed to be independent of the temperature. In the framework of this model the change of the area per polar head along the solubilization phase boundary has been calculated in ref. 12. The values obtained corresponding to room temperature are approximately twice the values of polar heads determined for the micellar systems in ref. 10.

Our present approach uses only one assumption: the molecular volumes of surfactant and oil have to remain constant as a function of temperature. The results obtained are in

accordance with the qualitative estimations of ref. 10 and allowed us to analyse the role of different interactions in the system under consideration. The real behaviour of the geometrical parameters of the monolayer is probably intermediate between two extreme cases considered in ref. 6 and in the present work.

The hypothesis concerning the mechanism of droplet aggregation presented in ref. 7 is based on the change of spontaneous curvature of surfactant monolayer as a function of temperature. It was assumed that this change makes more favourable the formation of a 'neck' connecting the monolayers of two droplets.[7] In our previous studies we calculated the bending energy of such a 'neck' participating in the fusion of bilayer lipid membranes.[14,15] It was shown that the formation of the 'neck' is energetically favourable only for the monolayer with negative spontaneous curvature. At the same time, the spontaneous curvature of the $C_{12}E_5$ monolayer covering the oil microemulsion droplet is positive for all temperatures experimentally investigated in ref. 6–8. The bending energy of the 'neck' in this system has to be positive.

In the present work we have shown that the relaxation of the area of the monolayer to the spontaneous value due to the monolayer breakdown gives a negative change of the elastic energy making the aggregation process favourable.

References

1 P. G. De Gennes and C. Taupin, *J. Phys. Chem.*, 1982, **86**, 2294.
2 S. A. Safran, L. A. Turkevich and P. A. Pinkus, *J. Phys. (Paris) Lett.*, 1984, **45**, L69.
3 M. M. Kozlov, S. L. Leikin and V. S. Markin, *J. Chem. Soc., Faraday Trans. 2*, 1989, **85**, 277.
4 J. Th. G. Overbeek, G. J. Verhoeckx, P. L. De Bruyn and H. N. W. Lekkerkerker, *J. Coloid Interface Sci.*, 1987, **119**, 422.
5 E. Ruckenstein, in *Surfactants in Solutions*, ed. K. L. Mittal and B. Lindman, Plenum, New York, 1984, vol. 3, p. 1551.
6 R. Aveyard, B. P. Binks and P. D. I. Fletcher, *Langmuir*, 1989, **5**, 1210.
7 S. Clark, P. D. I. Fletcher and X. Ye, *Langmuir*, 1990, **6**, 1301.
8 P. D. I. Fletcher and J. F. Holzwarth, *J. Phys. Chem.*, 1991, **95**, 2550.
9 P. K. Vinson, J. G. Sheehan, W. G. Miller, L. E. Scriven and H. T. Davis, *J. Phys. Chem.*, 1991, **95**, 2546.
10 D. J. Mitchell, G. J. T. Tiddy, L. Waring, T. Bostock and M. P. McDonald, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 975.
11 J. W. Gibbs, *Trans. Connect. Acad.*, 1876, **3**, 108; 1878, **3**, 343.
12 R. Aveyard, B. P. Binks, S. Clark and P. D. I. Fletcher, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3111.
13 D. Needham and R. S. Nunn, *Biophys. J.*, 1990, **58**, 997.
14 M. M. Kozlov and V. S. Markin, *Biofizika*, 1983, **28**, 242.
15 L. V. Chernomordik, M. M. Kozlov, G. B. Melikyan, I. G. Abidor, V. S. Markin and Yu. A. Chizmadzhev, *Biochim. Biophys. Acta*, 1985, **812**, 643.