

The interfacial bending moment: thermodynamics and contributions of the electrostatic interactions

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Abstract

The problem concerning the magnitude and the sign of the interfacial bending moment of the droplets in fluid disperse systems is considered on the basis of a thermodynamic approach. It is demonstrated that the total bending moment can be expressed as a superposition of contributions connected with the different components in the system. Expressions for the contributions of the electric double layer, of the interactions between adsorbed dipoles and of the electrolyte excess osmotic pressure to the value of the bending moment are derived. The effect of a possible incomplete dissociation of the adsorbed ionic surfactant monolayer is also taken into account. The results show that the van der Waals and the electric double layer interactions provide significant contributions to the bending moment, both of them of the order of 10 pN. Even at high electrolyte concentrations, the electrostatic bending moment can be important owing to the contribution of the Stern layer. The results can be applied to study the curvature dependence of the interfacial tension in microemulsions and in liquid–gas dispersions.

1. INTRODUCTION

The effect of curvature on the interfacial tension was first studied by Gibbs in his theory of capillarity [1]. His approach was developed by Tolman [2], who established that a pronounced dependence of the interfacial tension on curvature can exist for very small drops or bubbles, whose radii are comparable with the so-called Tolman parameter δ_0 . (The latter represents the distance between the surface of tension and the equimolecular dividing surface (see Eqn (2.10) below).) Further development was achieved in the works by Koenig [3] and Buff [4–6]. Kondo [7] investigated the role of the choice of the dividing surface in the thermodynamics of curved interfaces (see also Refs [8–10]).

New interest in curvature effects was awakened by the studies on the thermodynamics of microemulsions [11–20]. In particular, Miller [16] pointed out

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that the Tolman parameter δ_0 can be large for microemulsions owing to their low interfacial tension. In this case, the role of the interfacial bending moment (stress) can be important for understanding the droplet size distribution. Moreover, Denkov et al. [20] have recently explained the anomalously low experimental values of the second virial coefficient for water-in-oil microemulsions by taking into account the deformations of the emulsion droplets during their collisions. Hence, a change in the droplet curvature can affect also the energy of the droplet–droplet interactions.

An essential contribution to understanding microemulsions was provided in the work of Overbeek et al. [19]. These authors considered the interfacial bending moment amidst the other important features of the microemulsions and achieved good agreement with the experimental data on the influence of salt and cosurfactant on droplet size and interfacial tension.

The contributions of the diffuse electric double layer inside the droplets and of the steric interactions between the surfactant tails were accounted for in Ref. [19]. However, the van der Waals component of the bending moment as well as the effect of the Stern layer were entirely disregarded there.

The formation of a microemulsion is a rather complicated phenomenon in a multicomponent system. Therefore in the present study we will focus our attention only on the interfacial bending moment effect for an “isolated” microemulsion droplet, without studying the whole complicated situation. We believe that in this way one can understand better a detail of the picture. A combination of such details can lead to a more reliable description of microemulsions.

First, a brief review is given about the role of the bending moment in the thermodynamics of spherical interfaces. Afterwards, we derive a general thermodynamic expression for the interfacial bending moment and then estimate the magnitude of its different components. In this paper we describe in more detail four bending effects, all of them having electrostatic origin: (i) the contribution due to the dipole moments of the adsorbed molecules, (ii) the bending effect of the Stern electric double layer, (iii) the contribution of the diffuse electric double layer and (iv) the additional bending effect connected with the electrolyte excess osmotic pressure. The van der Waals component of the bending moment, which turns out to be one of the most important components, is studied in separate works [21, 22].

2. THE INTERFACIAL BENDING MOMENT

2.1 Basic equations

The three basic equations in the thermodynamics of spherical interfaces are [8–10]

$$dU^s = TdS^s + \sum_{i=1}^k \mu_i dN_i^s + \gamma dA + A \left(\frac{\partial \gamma}{\partial a} \right) da \quad (2.1)$$

$$U^s = TS^s + \sum_{i=1}^k \mu_i N_i^s + \gamma A \quad (2.2)$$

$$\frac{2\gamma}{a} + \left(\frac{\partial \gamma}{\partial a} \right) = P_\alpha - P_\beta \quad (2.3)$$

Here a is the radius of an arbitrarily chosen spherical dividing surface, representing the interface in the Gibbs' approach [1]; U^s , S^s and N_i^s ($i=1,2,\dots,k$) are respectively the surface excesses of the internal energy, entropy and number of molecules of the i th component, which correspond to this choice of the dividing surface; T is the temperature; μ_i ($i=1,2,\dots,k$) are chemical potentials; P_α (P_β) is the pressure inside (outside) the spherical drop; A is the interfacial area; γ is the thermodynamic interfacial tension and $(\partial\gamma/\partial a)$ is its formal derivative with respect to a . (Here and hereafter the derivatives in parentheses symbolize formal derivatives corresponding to a variation in the choice of a at fixed physical conditions.)

Equation (2.2) is a result of an integration of the Gibbs fundamental equation, Eqn (2.1), over the whole interfacial area at constant intensive parameters. Generally speaking, such an integration is possible only for interfaces of uniform curvature (plane, cylinder, sphere), because γ depends on curvature, which is not uniform throughout an arbitrarily curved interface. Equation (2.3) represents a generalized form of the known Laplace equation for a spherical interface.

As demonstrated in Refs [23–25], the quantity

$$B = a^2 \left(\frac{\partial \gamma}{\partial a} \right) \quad (2.4)$$

has the meaning of an interfacial bending moment (see also Ref. [14]). In particular, as shown in Ref. [25] B leads to a difference between the thermodynamical and the mechanical interfacial tensions, γ and σ :

$$\sigma = \gamma + \frac{B}{2a} \quad (2.5)$$

(γ can also be called “the dilational surface energy” [25])

One can define the position of the dividing surface in such a way that γ is always equal to σ :

$$B|_{a=\alpha_s} = a_s^2 \left(\frac{\partial \gamma}{\partial a} \right)_{a=\alpha_s} = 0 \quad (2.6)$$

This special dividing surface is usually called “the surface of tension” [8–10] and its radius is denoted a_s . γ and γ_s (with $\gamma_s = \gamma|_{a=a_s}$) are connected by the relation [8,9,25]

$$\gamma = \gamma_s \frac{a}{a_s} \left(\frac{2}{3} + \frac{1}{3} \frac{a_s^3}{a^3} \right) \quad (2.7)$$

Equation (2.7) represents explicitly the formal dependence of γ on the choice of a at a given physical state. By substituting from Eqn (2.7) into Eqn (2.4) one derives the respective dependence for the interfacial bending moment [23,25]:

$$B = 2\gamma a \frac{a^3 - a_s^3}{2a^3 + a_s^3} \quad (2.8)$$

2.2 Equimolecular dividing surface

To have the radius of the dividing surface, a , uniquely defined, one has to introduce an additional equation. Let this equation be

$$\frac{\partial \gamma_V}{\partial a_V} = \left(\frac{\partial \gamma}{\partial a} \right)_{a=a_V} \quad (2.9)$$

where a_V is the radius of this special dividing surface, called “the equimolecular dividing surface” [2,3,6,8], and $\gamma_V = \gamma|_{a=a_V}$. The partial derivative $\partial \gamma_V / \partial a_V$ represents the physical dependence of γ_V on a_V with the remaining parameters of state fixed. Different choices of these parameters correspond to different definitions of a_V . The distance $\delta = a_V - a_s$ between the equimolecular surface and the surface of tension tends to a limiting value δ_0 at $1/a_V \rightarrow 0$. Tolman [2] has derived the following equation

$$\gamma_V = \gamma_0 \left(1 - \frac{2\delta_0}{a_V} + \dots \right) \quad (2.10)$$

representing approximately the curvature dependence of γ_V (see also Refs [8,10]). Here $\gamma_0 = \gamma_{1/a \rightarrow 0}$. By setting $a = a_V$ in Eqn (2.8) and by expanding in series for $\delta_0/a_V \ll 1$ one obtains [5]

$$B_V = 2\gamma_0 \delta_0 + \dots \quad (2.11)$$

where $B_V = B|_{a=a_V}$. The next terms in the expansions (2.10) and (2.11) can be derived only when the dependence $\delta = \delta(a_V)$ is known. By means of Eqn (2.11) one can transform Eqn (2.10) to read

$$\gamma_V = \gamma_0 - \frac{B_{V0}}{a_V} + \dots \quad (2.12)$$

where

$$B_{v0} = B_{V|1/\alpha_v \rightarrow 0} = 2\gamma_0 \delta_0 \quad (2.13)$$

Equation (2.13) reveals the close relation between the bending moment and the Tolman parameter δ_0 , whereas Eqn (2.12) demonstrates that the bending moment determines the curvature dependence of the interfacial tension. The thermodynamic approach for the calculation of B_V considered in the next section is based on some local thermodynamic relations discussed briefly below.

2.3 Local form of the surface fundamental equations

Let us introduce the surface densities

$$u^s = U^s/A, \quad s^s = S^s/A \quad \Gamma_i = N_i^s/A \quad (2.14)$$

and the relative interfacial dilation

$$d\alpha = \frac{dA}{A} \quad (2.15)$$

then $dU^s = A (du^s + u^s d\alpha)$ etc., and Eqn (2.1) can be transformed to read [23, 25]

$$du^s = T ds^s + \sum_{i=1}^k \mu_i d\Gamma_i + (\gamma - \omega^s) d\alpha + B dH \quad (2.16)$$

where

$$\omega^s = u^s - T s^s - \sum_{i=1}^k \mu_i \Gamma_i \quad (2.17)$$

is the interfacial density of the grand thermodynamic potential. H in Eqn (2.16) is the mean curvature of the surface. The sign of H is a matter of convention. Here and hereafter in this study we will use the convention

$$H = \begin{cases} -1/a & \text{for a drop} \\ 1/a & \text{for a bubble} \end{cases} \quad (2.18)$$

For emulsion systems, instead of Eqn (2.18) we will use the convention

$$H = \begin{cases} -1/a & \text{for a water drop in oil} \\ 1/a & \text{for an oil drop in water} \end{cases} \quad (2.19)$$

Hence, H is negative for convex liquid/gas or water/oil interfaces, and H is positive for concave liquid/gas or water/oil interfaces. It will be demonstrated below, that this convention makes the sign of B dependent only on the kind of interactions (electrostatic, van der Waals etc.) prevailing in the interfacial zone, rather than on the sign of the curvature.

According to Eqn (2.16) the work for bending of the interface is

$$dw_B = B dH$$

When $B < 0$ a spontaneous process of bending ($dw_B < 0$) will lead to $dH > 0$. Hence a negative B tends to bend the interface around the gas (oil) phase. In the opposite case, a positive B tends to bend the interface around the liquid phase (for liquid-gas dispersions) or around the aqueous phase (for emulsion-type dispersions).

From Eqns (2.2) and (2.14) one obtains

$$u^s = Ts^s + \sum_{i=1}^k \mu_i \Gamma_i + \gamma \quad (2.20)$$

The comparison between Eqns (2.17) and (2.20) yields

$$\gamma = \omega^s \quad (2.21)$$

It should be noted that Eqn (2.21), as well as Eqns (2.2) and (2.20), hold only for uniform interfaces. A combination of Eqns (2.21), (2.16) and (2.17) gives

$$d\gamma = -s^s dT - \sum_{i=1}^k \Gamma_i d\mu_i + B dH \quad (2.22)$$

representing a form of the Gibbs adsorption equation. It should be noted that Eqn (2.22) holds both for soluble and for insoluble adsorbed components. It provides a basis for our considerations below.

3. BENDING MOMENT OF MICROEMULSION DROPS

The bending moment effect is important for microemulsion droplets because of their high curvature and low interfacial tension [16,19]. To specify the system we will consider microemulsions below. However, the approach can be easily adapted to small bubbles as well as to liquid droplets in a gas phase.

3.1 Thermodynamic expression for B

A typical microemulsion system contains the following components: water (w), oil (o), surfactant (s), cosurfactant (c) and neutral electrolyte (e) [26-28]. We choose the dividing surface to be the equimolecular surface with respect to water, i.e. $\Gamma_w = 0$. Then at constant temperature T and chemical potential of the oil phase, μ_o , Eqn (2.22) can be transformed to read

$$d(\gamma + \Gamma_s \mu_s) = \mu_s d\Gamma_s - \Gamma_c d\mu_c - \Gamma_e d\mu_e + B dH \quad (3.1)$$

All differentials in the right-hand side of Eqn (3.1) are independent. Indeed, the number of the independent intensive parameters in the system under con-

sideration is equal to the number of the components plus one [3,8]. Then from Eqn (3.1) one derives

$$\left(\frac{\partial B}{\partial \Gamma_s}\right)_{H, \mu_c, \mu_e} = \left(\frac{\partial \mu_s}{\partial H}\right)_{\Gamma_s, \mu_c, \mu_e} \quad (3.2)$$

The integration of Eqn (3.2) yields

$$B(H, \Gamma_s, \mu_c, \mu_e) = B_1(H, \mu_c, \mu_e) + B_s \quad (3.3)$$

where

$$B_s = \int_0^{\Gamma_s} \left(\frac{\partial \mu_s}{\partial H}\right)_{\Gamma_s, \mu_c, \mu_e} d\Gamma_s \quad (3.4)$$

is the contribution of the surfactant to the bending moment.

The term $B_1(H, \mu_c, \mu_e)$ on the right-hand side of Eqn (3.3) represents the bending moment of an imaginary emulsion drop in a system containing only cosurfactant and neutral electrolyte as solutes. For such a drop a counterpart of Eqn (3.1) holds:

$$d(\gamma + \Gamma_c \mu_c) = \mu_c d\Gamma_c - \Gamma_e d\mu_e + B_1 dH \quad (3.5)$$

From Eqn (3.5) one derives

$$\left(\frac{\partial B_1}{\partial \Gamma_c}\right)_{H, \mu_e} = \left(\frac{\partial \mu_c}{\partial H}\right)_{\Gamma_c, \mu_e} \quad (3.6)$$

By integrating Eqn (3.6) one obtains

$$B_1(H, \mu_c, \mu_e) = B_2(H, \mu_e) + B_c \quad (3.7)$$

Here

$$B_c = \int_0^{\Gamma_c(\mu_c)} \left(\frac{\partial \mu_c}{\partial H}\right)_{\Gamma_c, \mu_e} d\Gamma_c \quad (3.8)$$

represents the contribution of the cosurfactant to the interfacial bending moment. $B_2(H, \mu_e)$ is the bending moment of an imaginary emulsion drop in a system containing neutral electrolyte of chemical potential μ_e in the aqueous phase. For such a system, instead of Eqn (3.5) one can write

$$d(\gamma + \Gamma_e \mu_e) = \mu_e d\Gamma_e + B_2 dH \quad (3.9)$$

Then by analogy with Eqn (3.7) one derives

$$B_2(H, \mu_e) = B_p(H) + B_e \quad (3.10)$$

where

$$B_e = \int_0^{\Gamma_e(\mu_e)} \left(\frac{\partial \mu_e}{\partial H} \right)_{\Gamma_e} d\Gamma_e \quad (3.11)$$

accounts for the contribution of the neutral electrolyte to the bending moment and $B_p(H)$ is the bending moment of an imaginary emulsion drop of surface curvature H in a system containing only pure aqueous and oil phases. A combination of Eqns (3.3), (3.7) and (3.10) leads to

$$B = B_s + B_c + B_e + B_p \quad (3.12)$$

In other words, the total interfacial bending moment of a typical microemulsion droplet can be represented as a superposition of four components. Their physical nature and importance are discussed below.

3.2 Discussion

Since B_p is the bending moment at the boundary between pure water and oil, its value is determined by the van der Waals interactions between the two phases. The calculation of B_p is the subject of Ref. [22], where values of B_p are estimated for different liquid/gas and oil/water interfaces. The order and the sign of B_p can be easily estimated by using Eqn (2.13). For a pure argon drop at 84.3K Croxton and Ferrier [29] calculated $\delta_0 = 3.84 \text{ \AA}$ (δ_0 of the same magnitude and sign were calculated by Hill [30], Kirkwood and Buff [31], Plesner and Platz [32]). Then by using $\gamma_0 = 13.45 \text{ mN m}^{-1}$ [33] one obtains $B_{p0} = 10 \text{ pN}$. The positive sign of B_{p0} means that it tends to bend the interface around the liquid argon phase. For the interface between water and decane one has $\delta_0 = -5.07 \text{ \AA}$, $\gamma_0 = 51.2 \text{ mN m}^{-1}$ [22] and thus $B_{p0} = -51.9 \text{ pN}$. The negative sign means that B_{p0} tends to bend around the oil phase (cf. Eqn (2.19)).

The contribution of the van der Waals interactions in B_e (see Eqn (3.11)) is negligible because of the relatively small concentrations of the electrolyte ions compared with the water concentration. That is why B_e is due mainly to the pronounced negative adsorption of the electrolyte ions leading to changes in the osmotic pressure in a close vicinity of the interface [8, 34–36]. An estimate of B_e on the basis of the theory of Buff and Stillinger [36] is presented in Section 7 below.

The B_c is due predominantly to the steric and dipole–dipole interactions between the adsorbed cosurfactant molecules. Theoretical models accounting for the steric interactions are presented in Refs. [37 and 38] and an empirical expression is used in Ref. [19]. The contribution of the dipole–dipole interactions is estimated in Section 4 below. For a liquid/gas interface the van der Waals energy of the cosurfactant tails should also be taken into account.

In the case of a non-ionic surfactant, the calculation of B_s is similar to that

of B_c . However, in the case of ionic surfactant the calculation of B_s deserves special attention.

The chemical potential of an adsorbed molecule of an ionic surfactant can be presented in the form

$$\mu_s = \mu_{si} + \mu_{ci} = \mu_{si} - Ze\Psi_s + \eta_{ci} \quad (3.13)$$

where the subscripts si and ci indicate surfactant ion and counterion, respectively; $\eta_{ci} = \mu_{ci} + Ze\Psi_s$ is the electrochemical potential of a counterion with Ze being its electrical charge and Ψ_s the surface potential. As usual, we choose the zero of the electric potential Ψ to be the potential in an imaginary reference solution of a neutral electrolyte, resting in chemical equilibrium with the aqueous microemulsion phase. We suppose that the dissociation of the surfactant and of the neutral electrolyte provide the same counterions (just like the sodium dodecyl sulfate and the sodium chloride both provide Na^+ counterions). Then η_{ci} is constant throughout the aqueous phase and equal to the electrochemical potential in the reference solution. Hence

$$\left(\frac{\partial \eta_{ci}}{\partial H}\right)_{\Gamma_s, \mu_c, \mu_e} = 0 \quad (3.14)$$

The substitution of Eqn (3.13) into Eqn (3.4) along with Eqn (3.14) leads to

$$B_s = \int_0^{\Gamma_s} \left(\frac{\partial \mu_{si}}{\partial H}\right)_{\Gamma_s, \mu_c, \mu_e} d\Gamma_s + B_{dl} \quad (3.15)$$

where

$$B_{dl} = -Ze \int_0^{\Gamma_s} \left(\frac{\partial \Psi_s}{\partial H}\right)_{\Gamma_s, \mu_c, \mu_e} d\Gamma_s \quad (3.16)$$

is the contribution of the electric double layer to the interfacial bending moment. The first term in the right-hand side of Eqn (3.15) accounts for the energy of steric and van der Waals interactions of the adsorbed surfactant molecules.

When the adsorbed surfactant is completely dissociated, the density of the surface charge, $\tilde{\sigma}$, is equal to $-Ze \Gamma_s$. In this case Eqn (3.16) reduces to

$$B_{dl} = \int_0^{\tilde{\sigma}} \left(\frac{\partial \Psi_s}{\partial H}\right)_{\tilde{\sigma}, \mu_c, \mu_e} d\tilde{\sigma} = \left(\frac{\partial}{\partial H} \int_0^{\tilde{\sigma}} \Psi_s d\tilde{\sigma}\right)_{\tilde{\sigma}, \mu_c, \mu_e} \quad (3.17)$$

Similar expressions were used by Mitchell and Ninham [39] and by Overbeek et al. [19] in their studies on the curvature dependence of the interfacial tension due to the diffuse electric double layer.

When the surfactant is a strong electrolyte and Γ_s is comparatively low, one can expect that $\alpha = 1$. However, for high values of Γ_s the degree of dissociation α can be smaller than unity even for strong electrolytes. An estimate (see Appendix A) based on the Poisson–Boltzmann equation provides an upper limit for α in the case of high surface potentials:

$$\alpha \leq \frac{\epsilon k T}{8 \pi e^2 Z^2 r_i \Gamma_s} \quad (3.18)$$

where r_i is the radius of the counterion and ϵ is the dielectric permittivity of the medium (water). For a sodium dodecyl sulfate (NaDS) micelle of radius 24 Å and aggregation number 67 at 25°C [40] one has $\Gamma_s^{-1} = 108 \text{ Å}^2$, $Z = 1$, $r_i \approx 2 \text{ Å}$, $\epsilon = 78.3$ and Eqn (3.18) yields $\alpha \leq 0.30$. The experimental value of α varies between 0.24 and 0.30 (see Refs [41–44]). For a flat NaDS adsorption layer at c.m.c. the experiment [45] yields $\Gamma_s^{-1} = 52 \text{ Å}^2$ and from Eqn (3.18) one calculates $\alpha \leq 0.14$. This value is in agreement with the low degree of dissociation of the thin liquid film surfaces determined in Ref. [45].

Contributions to the interfacial bending moment having an electrostatic origin are considered in more detail below.

4. BENDING MOMENT DUE TO REPULSION BETWEEN ADSORBED DIPOLES

The adsorbed cosurfactant molecules, as well as the non-dissociated surfactant molecules have non-zero dipole moments oriented along the normal to the drop surface. The interaction energy of one dipole of moment $\mathbf{p}^{(1)}$ situated at \mathbf{r}_1 with another dipole of moment $\mathbf{p}^{(2)}$ situated at \mathbf{r}_2 (Fig. 1) is [46]

$$u_d = -\frac{3}{\epsilon r^5} (\mathbf{p}^{(1)} \cdot \mathbf{r}_{12}) (\mathbf{p}^{(2)} \cdot \mathbf{r}_{12}) + \frac{\mathbf{p}^{(1)} \cdot \mathbf{p}^{(2)}}{\epsilon r^3} \quad (4.1)$$

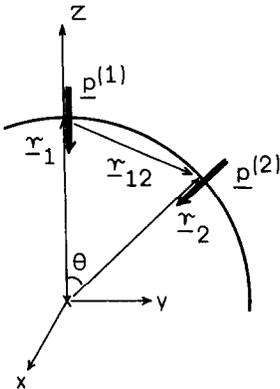


Fig. 1. Permanent dipoles $\mathbf{p}^{(1)}$ and $\mathbf{p}^{(2)}$ adsorbed on a spherical interface.

where

$$\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1 \quad r = |\mathbf{r}_{12}| \quad (4.2)$$

Let $|\mathbf{p}^{(1)}| = |\mathbf{p}^{(2)}| = p$. Then from Fig. 1 one obtains $\mathbf{p}^{(1)} \cdot \mathbf{r}_{12} = -\mathbf{p}^{(2)} \cdot \mathbf{r}_{12} = pr \sin(\theta/2)$; $\mathbf{p}^{(1)} \cdot \mathbf{p}^{(2)} = p^2 \cos \theta$; and Eqn (4.1) reduces to

$$u_d = \frac{p^2}{2\epsilon r^3} (3 - \cos \theta) \quad (4.3)$$

If the dipoles are situated on a sphere of radius R , then

$$r = R\sqrt{2(1 - \cos \theta)} \quad (4.4)$$

The interaction energy of one dipole with all other adsorbed dipoles is

$$U_d = \int_{\theta_0}^{\pi} \Gamma u_d 2\pi a^2 \sin \theta d\theta \quad (4.5)$$

where Γ is the number of dipoles per unit area of the equimolecular dividing surface (with respect to the water) of radius a , and

$$\sin(\theta_0/2) = \delta_l / (2a) \quad (4.6)$$

$\delta_l \approx 1/\sqrt{\Gamma}$ is the distance between two neighboring dipoles. Equations (4.3)–(4.6) yield

$$U_d = \frac{\pi \Gamma p^2 a^2}{\epsilon R^3} \left(\frac{2a}{\delta_l} - \frac{\delta_l}{2a} \right) \quad (4.7)$$

The total number of dipoles is

$$N = 4\pi a^2 \Gamma \quad (4.8)$$

and the total dipole–dipole interaction energy reads

$$W_d = \frac{1}{2} N U_d = \frac{N^2 p^2}{8\epsilon R^3} \left(\frac{2a}{\delta_l} - \frac{\delta_l}{2a} \right) \quad (4.9)$$

The contribution of the dipoles to the chemical potential of the adsorbed molecules is

$$\mu_d(H) = \left(\frac{\partial W_d}{\partial N} \right)_H \quad (4.10)$$

where

$$H = -1/a \quad (4.11)$$

is the curvature of the equimolecular dividing surface. In accordance with Eqns

(3.13) and (4.8)–(4.11) the bending moment due to the dipole–dipole interaction is

$$B_{\text{dp}} = \int_0^r \left(\frac{\partial \mu_d}{\partial H} \right)_r d\Gamma = \frac{\partial}{\partial H} \int_0^r \left(\frac{\partial W_d}{\partial N} \right)_H d\Gamma \quad (4.12)$$

$$= \frac{\partial}{\partial H} \left(\frac{W_d}{4\pi a^2} \right)$$

The substitution from Eqns (4.8) and (4.9) into Eqn (4.12) after some transformations gives

$$B_{\text{dp}}(H) \approx - \frac{3\pi\Gamma^{5/2}p^2l}{\epsilon(1+lH)^4} \quad (4.13)$$

where $l = a - R$ is the distance between the equimolecular dividing surface with respect to the water and the surface where the dipoles are situated.

For an $-\text{OH}$ group $p = 1.5 \cdot 10^{-18}$ CGSE units. With $\Gamma = 3 \cdot 10^{14} \text{ cm}^{-2}$, $l = 3 \text{ \AA}$ and $\epsilon = 78.3$ one calculates from Eqn (4.13) $B_{\text{dp}}(0) = 1.3 \cdot 10^{-8} \text{ dyn} = 0.13 \text{ pN}$. This value is about 100 times smaller than the contribution B_p due to the van der Waals forces (see above).

5. BENDING MOMENT DUE TO A STERN LAYER

According to the classical concept of Helmholtz, an electric double layer can be considered as a molecular condenser. A spherical molecular condenser is sketched in Fig. 2: the adsorbed surfactant ions and their counterions are situated at spheres of radii R_2 and R_1 respectively. As usual, a is the radius of the

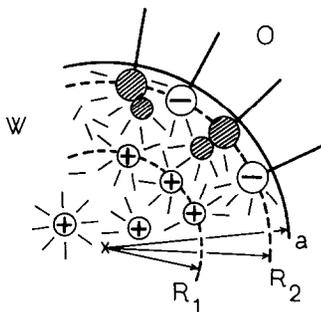


Fig. 2. Stern and diffuse electric double layers inside a water drop in oil: a is the radius of the equimolecular surface; R_2 is the radius of the surface where the polar heads of the surfactant molecules are situated; R_1 is the radius of the surface on which counterions of closest approach are situated.

equimolecular dividing surface with respect to water. With $\eta_{ci} = \mu_{ci}(R_1) + Ze\Psi(R_1)$, Eqn (3.13) yields

$$\mu_s = \mu_{si}(R_2) + \mu_{ci}(R_1) - Ze\Delta\Psi_{st} \quad (5.1)$$

where

$$\Delta\Psi_{st} = \Psi_s - \Psi(R_1) = \Psi(R_2) - \Psi(R_1) \quad (5.2)$$

Then by analogy with Eqn (3.16) one can write

$$B_{st} = -Ze \int_0^{\Gamma_s} \left(\frac{\partial \Delta\Psi_{st}}{\partial H} \right) d\Gamma_s \quad (5.3)$$

Let q denote the total charge of the condenser:

$$q = 4\pi a^2 Ze \alpha \Gamma_s \quad (5.4)$$

where as earlier α is the degree of dissociation of the adsorbed surfactant molecules. Then in view of Eqns (5.2) and (5.4)

$$\Delta\Psi_{st} = \frac{q}{\epsilon} \left(\frac{1}{R_2} - \frac{1}{R_1} \right) = \frac{-4\pi Ze \alpha \Gamma_s (l_1 - l_2)}{\epsilon(1 + Hl_1)(1 + Hl_2)} \quad (5.5)$$

where

$$l_1 = a - R_1 \quad l_2 = a - R_2 \quad (5.6)$$

and $H = -1/a$. For a Stern layer, l_1 and l_2 do not depend on H and by substitution from Eqn (5.5) into (5.3) one derives

$$B_{st} = -4\pi Z^2 e^2 (l_1 - l_2) \frac{l_1 + l_2 + 2Hl_1 l_2}{\epsilon(1 + Hl_1)^2(1 + Hl_2)^2} \int_0^{\Gamma_s} \Gamma_s \alpha(\Gamma_s) d\Gamma_s \quad (5.7)$$

where the subscript st indicates the Stern layer. The integral in the right hand side of Eqn (5.7) can be estimated by means of Eqn (A.13) in Appendix A:

$$\int_0^{\Gamma_s} \Gamma_s \alpha(\Gamma_s) d\Gamma_s \leq \Gamma_s^2 \alpha_m (1 - \alpha_m/2) \quad (5.8)$$

where α_m is connected with Γ_s through Eqn (A.13). When the adsorbed surfactant monolayer is completely dissociated, $\alpha_m = 1$ and the integral in Eqns (5.7) and (5.8) simply equals $\Gamma_s^2/2$.

From Eqns (5.7) and (5.8) one can estimate the bending moment B_{st}^0 of a flat Stern layer ($H \rightarrow 0$):

$$-B_{st}^0 \leq \frac{4}{\epsilon} \pi Z^2 e^2 \Gamma_s^2 (l_1^2 - l_2^2) \alpha_m (1 - \alpha_m/2) \quad (5.9)$$

With $l_1 = 9 \text{ \AA}$, $l_2^2 \ll l_1^2$, $\alpha_m = 0.14$ and the other data for a NaDS adsorption layer given after Eqn (3.18) one calculates from Eqn (5.9)

$$-B_{st}^0 \leq 15.6 \text{ pN}$$

It is seen that the magnitude of B_{st} can be comparable with the van der Waals contribution to the bending moment (see above). The negative sign of B_{st} means that it tends to bend the interface around the oil phase.

In the special case, where the equimolecular surface with respect to water is situated just in the middle between the spheres of radii R_1 and R_2 one has $l_2 = -l_1$ and Eqn (5.9) yields $B_{st}^0 = 0$. In the case where $l_2 \ll l_1$, $l_2 H \ll 1$ and $\alpha = 1$, Eqn (5.7) reduces to

$$B_{st} \approx -\frac{2\pi Z^2 e^2 l_1^2 \Gamma_s^2}{\epsilon(1+l_1 H)^2} \quad (5.10)$$

Let H change at constant μ_s and the other chemical potentials in Eqn (3.1). Then one obtains

$$\gamma(\mu_s, H) - \gamma(\mu_s, 0) = \int_0^H B(H, \Gamma_s(H)) dH \quad (5.11)$$

and

$$\gamma_{st}(\mu_s, H) - \gamma_{st}(\mu_s, 0) = \int_0^H B_{st}(H, \Gamma_s(H)) dH \quad (5.12)$$

where the subscript st indicates contributions of the Stern layer, and $\Gamma_s = \Gamma_s(H)$ due to the constancy of μ_s . If under the integral sign of Eqn (5.12) the dependence of Γ_s on H can be neglected, then by substitution from Eqn (5.10) into Eqn (5.12) one obtains

$$\gamma_{st}(\mu_s, H) - \gamma_{st}(\mu_s, 0) = -\frac{2\pi Z^2 e^2 l_1^2 \Gamma_s^2}{\epsilon(1+Hl_1)} H \quad (5.13)$$

Hence, γ_{st} decreases when increasing H (cf. Eqn (2.19)). In particular, γ_{st} is larger for a water-in-oil emulsion drop ($H = -1/a$) than for an oil-in-water emulsion drop of the same radius ($H = 1/a$).

6. BENDING MOMENT DUE TO A DIFFUSE ELECTRIC DOUBLE LAYER

The effect of a diffuse electric double layer on the curvature dependence of the interfacial tension has been studied by Mitchell and Ninham [39] for oil-in-water microemulsions, by Levine and Robinson [47] and by Overbeek et al. [19] for water-in-oil microemulsions. Below we briefly reconsider this problem

by taking into account the contribution of the Stern layer and the role of the precise definition of the dividing surface.

According to Eqn (5.2)

$$\Psi_s = \Delta\Psi_{st} + \Psi_1 \quad \Psi_1 = \Psi(R_1) \quad (6.1)$$

(see Fig. 2). Then in view of Eqns (3.16) and (5.3) the bending moment due to the electric double layer can be expressed as

$$B_{dl} = B_{st} + B_{df} \quad (6.2)$$

where

$$B_{df} = -Ze \int_0^{\Gamma_s} \left(\frac{\partial \Psi_1}{\partial H} \right)_{\Gamma_s, \mu_c, \mu_e} d\Gamma_s \quad (6.3)$$

is the contribution of the diffuse part of the double electric layer. We accept that the electrostatic potential, $\Psi(r)$, of the diffuse layer satisfies the Poisson equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Psi}{dr} \right) = -\frac{4\pi}{\epsilon} \rho(r) \quad (6.4)$$

with $\rho(r)$ being the charge density. The electroneutrality condition applied to an inner double layer (an aqueous drop in oil) yields

$$\int_0^{R_1} \rho(r) 4\pi r^2 dr = 4\pi a^2 Ze \alpha \Gamma_s \quad (6.5)$$

It should be noted that according to its definition, Γ_s is the number of surfactant molecules per unit area of the equimolecular dividing surface (of radius a) with respect to the water. For an outer double layer (an oil drop in water) instead of Eqn (6.5) one has

$$\int_{R_1}^{\infty} \rho(r) 4\pi r^2 dr = 4\pi a^2 Ze \alpha \Gamma_s \quad (6.6)$$

From Eqns (6.4)–(6.6) along with Eqn (A.11) one obtains

$$\left. \frac{d\Psi}{dr} \right|_{r=R_1} = \pm \frac{4\pi \delta a^2}{\epsilon R_1^2} \quad (6.7)$$

Here and hereafter the upper and the lower signs refer to inner and outer electric double layers, respectively.

6.1 Low surface potential Ψ_1

In the case when $Ze\Psi_1/(kT) \ll 1$ the Boltzmann equation

$$\rho(r) = Zec_0 \left(\exp\left(-\frac{Ze\Psi}{kT}\right) - \exp\left(\frac{Ze\Psi}{kT}\right) \right) \quad (6.8)$$

can be linearized (see for example Ref. [48]):

$$\rho(r) \approx \frac{2Z^2e^2c_0}{kT} \Psi(r) \quad (6.9)$$

c_0 is the electrolyte concentration in the reference solution where $\Psi=0$. From Eqns (6.4), (6.7) and (6.9) one derives

$$\Psi_1 = \frac{4\pi\tilde{\sigma}a^2}{\epsilon\kappa R_1^2} \left(1 + \frac{1}{\kappa R_1}\right)^{-1} \quad (\text{outer double layer}) \quad (6.10)$$

or

$$\Psi_1 = \frac{4\pi\tilde{\sigma}a^2}{\epsilon\kappa R_1^2} \left(\coth(\kappa R_1) - \frac{1}{\kappa R_1}\right)^{-1} \quad (\text{inner double layer}) \quad (6.11)$$

with

$$\kappa^2 = \frac{8\pi Z^2e^2c_0}{\epsilon kT} \quad (6.12)$$

Besides, we have

$$R_1 = a \mp l_1 \quad H = \mp 1/a \quad (6.13)$$

(see the sign convention after Eqn (6.7)). Thus $\coth(\kappa R_1) \approx 1$ for $\kappa R_1 \geq 2$. Then in view of Eqn (6.13) one can represent both Eqn (6.10) and Eqn (6.11) in the form

$$\Psi_1 = \frac{4\pi\tilde{\sigma}}{\epsilon\kappa(1+Hl_1)[1+(l_1+\kappa^{-1})H]} \quad (6.14)$$

The substitution from Eqns (6.14) and (A.8) into Eqn (6.3) yields

$$B_{df} = -4\pi Z^2e^2 \frac{2l_1 + \kappa^{-1} + 2Hl_1(l_1 + \kappa^{-1})}{\epsilon\kappa(1+Hl_1)^2[1+(l_1 + \kappa^{-1})H]^2} \int_0^{\Gamma_s} \Gamma_s \alpha(\Gamma_s) d\Gamma_s \quad (6.15)$$

the last equation being a counterpart of Eqn (5.7). By analogy with Eqn (5.9) one derives

$$-B_{df}^0 \leq \frac{4}{\epsilon} \pi Z^2e^2 \Gamma_s^2 (2l_1\kappa^{-1} + \kappa^{-2}) \alpha_m (1 - \alpha_m/2) \quad (6.16)$$

The combination of Eqns (5.9) and (6.16) in accordance with Eqn (6.2) leads to

$$-B_{\text{dl}}^0 \leq -\frac{4}{\epsilon} \pi Z^2 e^2 \Gamma_s^2 [(l_1 + \kappa^{-1})^2 - l_2^2] \alpha_m (1 - \alpha_m / 2) \quad (6.17)$$

The comparison between Eqns (5.9) and (6.17) implies that the combination of a Stern and a diffuse layer gives the same bending moment as a molecular condenser (Helmholtz double layer), in which the counterions are situated at a distance $l_1 + \kappa^{-1}$ from the interface. This result is in consonance with the Gouy–Chapman theory (see for example Ref. [48]).

As in the case of Eqn (5.12) one can write

$$\gamma_{\text{df}}(\mu_s, H) - \gamma_{\text{df}}(\mu_s, 0) = \int_0^H B_{\text{df}}(H, \Gamma_s(H)) dH \quad (6.18)$$

where the subscript df indicates contributions of the diffuse double layer. If the dependence of Γ_s on H can be neglected in Eqns (6.18) and (6.3) one obtains

$$\gamma_{\text{df}}(\mu_s, H) - \gamma_{\text{df}}(\mu_s, 0) = -Ze \int_0^{\Gamma_s} [\Psi_1(H) - \Psi_1(0)] d\Gamma_s \quad (6.19)$$

then from Eqns (6.14), (6.19) and (A.8) with $\alpha = 1$ one derives

$$\gamma_{\text{df}}(\mu_s, H) - \gamma_{\text{df}}(\mu_s, 0) = -\frac{2\pi Z^2 e^2 \Gamma_s^2 [(2l_1 + \kappa^{-1})H + l_1(l_1 + \kappa^{-1})H^2]}{\epsilon \kappa (1 + Hl_1) [1 + H(l_1 + \kappa^{-1})]} \quad (6.20)$$

Equation (6.20) can be also presented in the form

$$\gamma_{\text{df}}(\mu_s, H) = \gamma_{\text{df}}(\mu_s, 0) + B_{\text{df}}^0 H + O(H^2) \quad (6.21)$$

with

$$B_{\text{df}}^0 = -\frac{2}{\epsilon} \pi Z^2 e^2 \Gamma_s^2 (2l_1 \kappa^{-1} + \kappa^{-2}) \quad (6.22)$$

Equation (6.21) is to be compared with Eqn (2.12). For $l_1 \ll \kappa^{-1}$, Eqn (6.22) reduces to

$$B_{\text{df}}^0 = -\frac{2}{\epsilon} \pi Z^2 e^2 \Gamma_s^2 \kappa^{-2} \quad (6.23a)$$

Levine and Robinson [47] derived an expression for $\gamma_{\text{df}}(H)$ (see Eqn (3.9) in [47]), which can be presented in the form

$$\gamma_{\text{df}}(H) = \gamma_{\text{df}}(0) - \frac{3}{\epsilon} \pi Z^2 e^2 \Gamma_s^2 \kappa^{-2} H + O(H^2) \quad (6.23b)$$

The comparison of Eqn (6.23b) with Eqns (6.21) and (6.23a) shows a difference in the numerical multiplier: two in Eqn (6.23a) and three in Eqn (6.23b). This difference is probably due to the circumstance that the mechanical approach used by Levine and Robinson [47] to derive their Eqn (2.18) is not equivalent to the thermodynamic approach based on Eqn (5.11) used by us.

6.2 High surface potential Ψ_1

As suggested by Overbeek et al. [19], in the case when $Ze\Psi/(kT) \geq 1$, the bending moment of the diffuse layer can be calculated by using the Stokes [49] asymptotic solution of the Poisson–Boltzmann equation. From Eqn (3.1) in Ref. [49] one obtains

$$\Psi_1 = \pm \frac{kT}{Ze} \left[b_0 \pm \frac{b_1}{\kappa R_1} + \frac{b_2}{(\kappa R_1)^2} + \dots \right] \quad (6.24)$$

where the same sign convention as in Eqn (6.7) is used and

$$x = \frac{Ze}{2\kappa kT} \frac{d\Psi}{dr} \Big|_{r=R_1} \quad y = (1+x^2)^{1/2} \quad (6.25)$$

$$b_0 = 2\ln(x+y) \quad b_1 = 4(y-1)/(xy) \quad (6.26)$$

$$b_2 = 4 \left[b_1^2(1+2y)/16 - \ln\left(\frac{1+y}{2}\right) \right] / (xy) \quad (6.27)$$

The accuracy of the asymptotic expansion (6.24) was studied by Stokes [49] in the case of the outer diffuse double layer. The form of Eqn (6.24) for an inner diffuse double layer was first derived in Ref. [19]. (In contrast to what is stated in Ref. [19], it is not necessary to neglect the potential in the droplet center in order to derive Eqn (6.24) (see Appendix B).)

In accordance with Eqns (6.7), (6.13), (A.8) and (6.25), x depends both on H and on Γ_s . Then the substitution of Ψ_1 from Eqn (6.24) into Eqn (6.3) leads to an expression for the bending moment, B_{df} , due to the diffuse electric double layer. For the case of complete dissociation of the adsorbed surfactant molecules ($\alpha=1$) this expression reads

$$B_{df}^{(1)}(H, \Gamma_s) = -\frac{16c_0 kT}{\kappa^2} \left\{ \ln\left(\frac{1+y}{2}\right) + \kappa l_1 (y-1) \mp \frac{H}{\kappa} \left[\int_{\frac{1}{2}}^1 \frac{\ln z dz}{1-z} \right. \right. \\ \left. \left. + \frac{(y+2)(y-1)}{y(y+1)} + 2\kappa l_1 \left(\frac{2x^2}{y(y+1)} - \ln\left(\frac{1+y}{2}\right) \right) + \kappa^2 l_1^2 \left(\frac{2x^2}{y} - y + 1 \right) \right] \right\} \quad (6.28)$$

where c_0 , κ , H and l_1 are the same as in Eqns (6.12) and (6.13).

When the dissociation of the adsorbed surfactant monolayer is not complete ($\alpha < 1$) one can estimate B_{df} by using Eqn (A.13). The combination of Eqns (6.3), (A.13) and (A.14) yields

$$B_{df}^{(\alpha)}(H, \Gamma_s) = B_{df}^{(1)}(H, \bar{\Gamma}_s) - Ze(\Gamma_s - \bar{\Gamma}_s) \left(\frac{\partial \Psi_1}{\partial H} \right)_{\Gamma_s} \quad (6.29)$$

where $B^{(1)}$ is to be calculated from Eqn (6.28). By differentiation of Eqn (6.24) one derives

$$\left(\frac{\partial \Psi_1}{\partial H} \right)_{\Gamma_s} = -\frac{2}{\kappa} \left\{ \frac{2(y-1)}{xy} + 2\kappa l_1 \frac{x}{y} + \frac{H}{\kappa} \left[\frac{4}{xy} \left(\frac{(y-1)^2(2y+1)}{x^2 y^2} - \ln \left(\frac{1+y}{2} \right) \right) + 8\kappa l_1 \left(\frac{x^2+y^2-y^3}{xy^3} + \frac{y-1}{2xy} \right) + \kappa^2 l_1^2 \left(\frac{6x}{y} - 4 \frac{x^3}{y^3} \right) \right] \right\} \quad (6.30)$$

It should be recalled that the sign convention introduced after Eqn (6.7) holds everywhere in this section.

The curves in Fig. 3 represent the dependence of B_{df} on Γ_s at $1/H=60 \text{ \AA}$, $l_1=3 \text{ \AA}$, $c_0=0.3 \text{ mol l}^{-1}$ and $Z=1$. Curve 1 is calculated from Eqn (6.29) with $r_1=2 \text{ \AA}$ (cf. Eqn (A.14)), whereas curve 2 is calculated from Eqn (6.28), i.e. $\alpha=1$ is suggested to hold identically for curve 2. It is seen that the incomplete

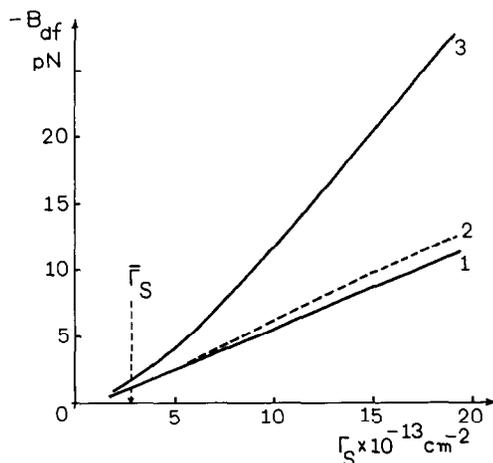


Fig. 3. Interfacial bending moment due to the diffuse part of the electric double layer as a function of the adsorption at the equimolecular surface ($1/H=60 \text{ \AA}$, $l_1=3 \text{ \AA}$, $c_0=0.3 \text{ mol l}^{-1}$, $Z=1$: curve 1, according to Eqn (6.29) with $\alpha=\alpha_m$ (Eqn (A.13)) and $r_1=2 \text{ \AA}$; curve 2, according to Eqn (6.28) ($\alpha=1$); curve 3, according to Eqn (72) in Ref. [19].

dissociation of the adsorbed surfactant monolayer leads to a decrease in $|B_{df}|$ for $\Gamma_s > \bar{\Gamma}_s$.

It should be noted that Eqn (6.28) is somewhat different from the respective expression Eqn (72), derived in Ref. [19], which also corresponds to complete dissociation ($\alpha = 1$). To elucidate the source of this difference we will suppose below that the parameter ζ in Ref. [19] coincides with our l_1 (see Fig. 2). Curve 3 in Fig. 3 is calculated by using Eqn (72) in Ref. [19] with the same values of the parameters H , l_1 , c_0 and Z as for the other two curves. (It should be noted that the bending moment c_{el} in Ref. [19] is simply connected with $B_{df} : c_{el} = -B_{df}/2$.)

The basic equation used by Overbeek et al. [19] for calculation of the bending moment (in our notation) reads

$$B_{df}^{(ov)} = Ze \frac{\partial}{\partial (1/R_1)} \int_0^{\Gamma_{s1}} \Psi_1(\Gamma_s, H) d\Gamma_{s1} \quad (6.31)$$

where

$$\Gamma_{s1} = \frac{a^2}{R_1^2} \Gamma_s \quad (6.32)$$

By means of Eqns (6.13) and (6.32) one can represent Eqn (6.31) in the form

$$B_{df}^{(ov)} = -Ze(1+l_1H)^2 \frac{\partial}{\partial H} \int_0^{\Gamma_s} \Psi_1(\Gamma_s, H) \frac{d\Gamma_s}{(1+l_1H)^2} \quad (6.33)$$

The last equation is to be compared with the relation

$$B_{df} = -Ze \frac{\partial}{\partial H} \int_0^{\Gamma_s} \Psi_1(\Gamma_s, H) d\Gamma_s \quad (6.34)$$

which follows easily from the thermodynamic definition of B_{df} , Eqn (6.3), used by us. The comparison between Eqns (6.33) and (6.34) reveals not only the source of the difference between B_{df} and $B_{df}^{(ov)}$ at the same $\Psi_1(\Gamma_s, H)$, but also the reason why $B_{df}^{(ov)} = B_{df}$ for $l_1 = 0$. Actually, l_1 should be of the order of 6 Å. Even $l_1 = 3$ Å (as assumed in Ref. [19]) turns out to be large enough to account for the difference between curves 2 and 3 shown in Fig. 3.

7. CONTRIBUTION OF THE NEUTRAL ELECTROLYTE TO THE BENDING MOMENT

As mentioned above, the electrolyte contribution to the bending moment, given by Eqn (3.11), is due to the negative adsorption of the electrolyte ions, creating an excess osmotic pressure in the vicinity of the interface. This effect

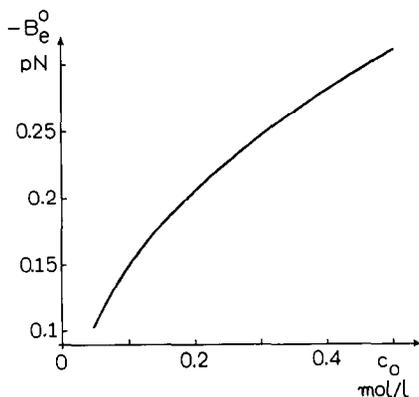


Fig. 4. Bending moment at a flat interface, B_e^0 , due to the excess osmotic pressure of the electrolyte, as a function of the electrolyte concentration; $\epsilon = 78.3$.

leads also to an increase $\Delta\gamma_e$ in the interfacial tension. The $\Delta\gamma_e$ has been calculated by Buff and Stillinger [36] for flat interfaces on the ground of the statistical theory of electrolyte solutions (a comprehensive review of this theory is available in Ref. [8]). In particular, Eqn (39.38) in Ref. [8] can be presented in the form

$$\Delta\gamma_e = \int_0^{\infty} \Delta\Pi(z) dz \quad (7.1)$$

where $-z$ is the distance from a point in the solution to the flat interface, and

$$\Delta\Pi(z) = \frac{2}{\epsilon} \kappa Z^2 e^2 c_0 \left[\frac{3}{u^3} - \left(\frac{1}{u} + \frac{3}{u^2} + \frac{3}{u^3} \right) \exp(-u) \right] \exp(-v) \quad (7.2)$$

is an excess osmotic pressure. Here

$$u = 2\kappa z \quad v = \frac{Z^2 e^2 \kappa}{2\epsilon k T u} \exp(-u) \quad (7.3)$$

cf. also Eqns (39.28), (39.31) and (40.4)–(40.6) in Ref. [8]. The symbols κ and c_0 are the same as those in Eqn (6.12) above.

As far as we know, for the time being, no generalization of the Buff–Stillinger theory [36] is available for curved interfaces. Nevertheless, the bending moment B_e^0 of a flat interface can be estimated by using Eqns (7.1)–(7.3). Indeed, the bending moment of the osmotic pressure distribution $\Delta\Pi(z)$ reads

$$B_e^0 = - \int_0^{\infty} \Delta\Pi(z) z dz \quad (7.4)$$

The minus sign reflects the fact that B_e^0 tends to bend the interface around the oil (gas) phase (cf. Eqn (7.2)).

The theoretical values of B_e^0 , calculated from Eqn (7.4) along with Eqns (7.2) and (7.3), are plotted in Fig. 4 as a function of the electrolyte concentration c_0 . It is seen that $-B_e^0$ increases with the electrolyte concentration and equals 0.3 pN at $c_0 = 0.5 \text{ mol l}^{-1}$. Hence in this concentration region, B_e^0 is much smaller than B_p and B_{dl} . It seems that the electrolyte contribution to the bending moment can be neglected, at least when $B_e \approx B_e^0$ (for not extremely curved interfaces).

CONCLUDING REMARKS

The interfacial bending moment B determines the curvature dependence of the interfacial tension (see Eqn (2.22) or (5.11)). The limiting value of B for a flat interface is simply connected with the Tolman parameter δ_0 [Eqn (2.13)]. As in the case of the disjoining pressure [50], B can be represented as a sum of different components accounting for the contributions of different kinds of interactions: electrostatic, van der Waals, steric etc.

Alternatively, the interfacial bending moment can be expressed as a superposition of contributions due to the different components in the system. In the case of a typical microemulsion considered in this paper, these are the water, the oil, the surfactant, the cosurfactant and the electrolyte (see Eqn (3.12)). The last equation is easily derived by means of consecutive integrations of thermodynamic relations of the same type as Eqn (3.2) or (3.6).

The B_p in Eqn (3.12) represents the bending moment contribution due to the interactions between contacting pure aqueous and oil phases. Hence the value of B_p is determined by the van der Waals forces. Some estimates show that for a liquid-gas dispersion, B_p is positive and tends to bend the interface around the liquid phase. For a dispersion of microemulsion type, B_p as a rule is negative and tends to bend around the oil phase. In both cases the magnitude of B_p can be of the order of 10 pN. Values of B_p for different liquid-gas and oil-water dispersions are calculated in Ref. [22].

When an ionizable surfactant is present at the interface, the electric double layer in the aqueous phase can provide a significant contribution, B_{dl} , to the interfacial bending moment (see Eqn (3.16)). B_{dl} can be of the order of B_p ($\approx 10 \text{ pN}$) and has a negative sign, i.e. it tends to bend the interface around the oil (gas) phase. In general B_{dl} is a sum of two bending moments, B_{st} and B_{df} , generated respectively by the Stern layer and by the diffuse part of the electric double layer (cf. Eqn (6.2)). It turns out that B_{st} and B_{df} are quantities of the same order of magnitude for not too low electrolyte concentrations. In particular, B_{st} can be calculated by means of Eqn (5.7) or (5.10), B_{df} by means of Eqn (6.15) or (6.17) in the case of low surface potentials and by means of Eqns (6.28) and (6.29) for high surface potentials.

The degree of dissociation α of the adsorbed surfactant molecules strongly affects the magnitude of B_{dl} . This problem is discussed in Appendix A, where an estimate of α for strong electrolytes, Eqn (3.18), and a model expression for α , Eqn (A.13), are obtained.

The bending moment B_{dp} due to the interactions between the dipole moments of non-dissociated adsorbed molecules, and the bending moment B_e due to the effective negative adsorption of the electrolyte in the aqueous phase are studied in Sections 4 and 7 of the present paper. Both B_{dp} and B_e turn out to be of the order of 0.1 pN, i.e. under normal conditions they are negligible compared with B_p and B_{dl} .

It is worthwhile noting that all expressions for the different components of the interfacial bending moment B are derived in this paper for the equimolecular dividing surface with respect to water. The sign of B and its components is related to the conventions [Eqns (2.18) and (2.19)] for the sign of the mean curvature H .

The results in this paper demonstrate that the total bending moment of an interface is a result of interplay of various effects. All of them should be taken into consideration and estimated for each specified fluid disperse system. We hope the equations for the different components of the interfacial bending moment derived in this paper will be useful for a realistic description of the size distribution and interactions in microemulsions.

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APPENDIX A: DEGREE OF DISSOCIATION OF IONIC SURFACTANT MONOLAYERS

It has been established experimentally [42–44] that the degree of dissociation α of ionic surfactant molecules incorporated in a micelle is about 0.2–0.3, whereas $\alpha = 1$ for isolated monomers in the solution. (In the case of surfactant monolayers or aggregates, we accept that α represents the portion of the adsorbed surfactant molecules, whose counterions belong to the diffuse part of the electric double layer.) This fact implies that the close distances between the ionizable surfactant groups in a micelle make the complete dissociation energetically unfavorable. The shorter the intermolecular distances, the lower the degree of dissociation. If this is true, one can expect that α for a dense flat surfactant monolayer should be even lower than α for a micelle. An estimate of this effect is proposed below.

Let us consider a flat surfactant monolayer situated at the plane $x = -d$ (Fig. A1), where d is the distance of closer approach to the surface of a counterion belonging to the diffuse electric double layer. We are interested in the counterion distribution in a close vicinity of the plane $x = 0$. That is why it is convenient to choose

$$\phi = 0 \quad \text{at } x = 0 \quad (\text{A.1})$$

($\phi(x)$ is the electrostatic potential). Then the linearized Poisson–Boltzmann equation reads

$$\frac{d^2 \phi}{dx^2} = \kappa_D^2 \left(\phi - \frac{kT}{Ze} \zeta \right) \quad (\text{A.2})$$

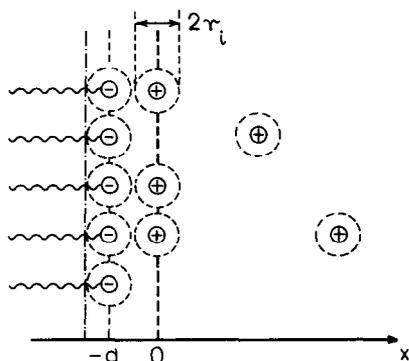


Fig. A1. Surfactant monolayer adsorbed on a flat interface. $z = -d$ is the plane where the polar heads of the surfactant molecules are situated; $z = 0$ is the plane on which counterions of closest approach are situated; $2r_i$ is the diameter of a counterion.

where

$$\kappa_0^2 = \frac{4\pi Z^2 e^2 (c_1^0 + c_2^0)}{\epsilon kT} \quad (\text{A.3})$$

$$\zeta = \frac{c_1^0 - c_2^0}{c_1^0 + c_2^0} \quad (\text{A.4})$$

where c_1^0 and c_2^0 are the concentrations of the counterions and of the co-ions at the plane $x=0$, respectively; it is assumed that we deal with a symmetrical $Z-Z$ electrolyte, where Ze is the charge of a counterion ($Z \pm 1, \pm 2, \dots$). The solution of Eqn (A.2) along with the boundary conditions (A.1) and $\phi < \infty$ at $x \rightarrow \infty$ reads

$$\phi(x) = \frac{kT}{Ze} \zeta (1 - \exp(-\kappa_0 x)) \quad (\text{A.5})$$

By substitution from Eqn (A.5) into the electroneutrality condition

$$\left. \frac{d\phi}{dx} \right|_{x=0} = -\frac{4\pi\tilde{\sigma}}{\epsilon} \quad (\text{A.6})$$

one obtains

$$\frac{kT}{Ze} \zeta \kappa_0 = -\frac{4\pi\tilde{\sigma}}{\epsilon} \quad (\text{A.7})$$

where

$$\tilde{\sigma} = -\alpha Ze \Gamma_s \quad (\text{A.8})$$

is the surface charge density. The elimination of κ_0 and $\tilde{\sigma}$ in Eqn (A.7) by means of Eqns (A.3) and (A.8) yields

$$c_1^0 + c_2^0 = \frac{4\pi (Ze\alpha\Gamma_s)^2}{\epsilon kT \zeta^2} \quad (\text{A.9})$$

Since c_1^0 and c_2^0 are the ion concentrations close to the charged monolayer, one has $c_1^0 \gg c_2^0$ at sufficiently large $\tilde{\sigma}$. Then Eqn (A.4) gives $\zeta \approx 1$, whence Eqn (A.9) reduces to

$$c_1^0 \approx \frac{4\pi (Ze\alpha\Gamma_s)^2}{\epsilon kT} \quad (\text{A.10})$$

However, from Fig. A1 it can be seen that

$$c_1^0 \leq \frac{\alpha\Gamma_s}{2r_i} \quad (\text{A.11})$$

where r_i is the radius of a counterion. The combination of Eqns (A.10) and (A.11) yields Eqn (3.18).

Equation (3.18) provides an upper limit for the magnitude of the interfacial charge density. Indeed, from Eqns (3.18) and (A.8) one easily obtains

$$\left| \frac{\bar{\sigma}}{e} \right| \leq \frac{\epsilon k T}{8\pi e^2 |Z| r_i} \quad (\text{A.12})$$

With $r_i = 2 \text{ \AA}$, $\epsilon = 78.3$, $T = 298\text{K}$ and $Z = 1$, Eqn (A.12) yields $|\bar{\sigma}/e| \leq 2.7 \cdot 10^{13} \text{ cm}^{-2}$. It should be noted that the right-hand side of Eqn (A.12) does not depend on Γ_s . In accordance with Eqn (3.18) the dependence of the upper limit of the degree of dissociation, α_m , on Γ_s can be represented in the form

$$\alpha_m(\Gamma_s) = \begin{cases} \Gamma_s/\bar{\Gamma}_s & \text{for } \Gamma_s \geq \bar{\Gamma}_s \\ 1 & \text{for } \Gamma_s \leq \bar{\Gamma}_s \end{cases} \quad (\text{A.13})$$

where

$$\bar{\Gamma}_s = \frac{\epsilon k T}{8\pi Z^2 e^2 r_i} \quad (\text{A.14})$$

Equation (A.13) is used for estimating some integrals in the text.

APPENDIX B: ON THE ELECTROSTATIC FIELD OF AN INNER SPHERICAL DIFFUSE DOUBLE LAYER

The Poisson-Boltzmann equation for spherical symmetry and Z - Z symmetrical electrolyte can be written as

$$\frac{d^2\psi}{d(\kappa r)^2} + \frac{2}{\kappa r} \frac{d\psi}{d(\kappa r)} = \sinh \psi \quad (\text{B.1})$$

where

$$\psi = \frac{Ze\Psi}{kT} \quad (\text{B.2})$$

and κ is given by Eqn (6.12). In general

$$\psi = \psi(\kappa r, R_1) \quad (\text{B.3})$$

where R_1 is the radius of the sphere enveloping the diffuse electric double layer inside the drop (cf. Fig. 2). ψ is supposed to satisfy the boundary condition [Eqn (6.7)] and this is the source of the dependence on R_1 in Eqn (B.3). Following the approach developed in Refs. [19,49] one can introduce the function

$$H[\psi(\kappa r, R_1), \kappa r] = \frac{d\psi}{d(\kappa r)} \quad (\text{B.4})$$

By substituting from Eqn (B.4) in Eqn (B.1) one derives [19,49]

$$H\left(\frac{\partial H}{\partial \psi}\right)_{\kappa r} + \left(\frac{\partial H}{\partial \kappa r}\right)_{\psi} + \frac{2H}{\kappa r} = \sinh \psi \quad (\text{B.5})$$

For large κr one can seek H in the form of an asymptotic expansion [19,49]

$$H(\psi, \kappa r) = \sum_{n=0}^{\infty} \frac{C_n(\psi)}{(\kappa r)^n} \quad (\text{B.6})$$

Then a standard procedure of substituting H from Eqn (B.6) in Eqn (B.5) yields equations for the coefficient functions [19]

$$C_0 \frac{dC_0}{d\psi} = \sinh \psi \quad (\text{B.7})$$

etc. Overbeek et al. [19] integrated Eqn (B.7) along with the boundary condition

$$C_0(\psi_m) = 0 \quad (\text{B.8})$$

where ψ_m is the dimensionless potential in the middle of the spherical drop. We deem Eqn (B.8) not to be the right boundary condition. Indeed, the series (B.6) represents an outer asymptotic expansion satisfying the outer boundary condition [Eqn (6.7)] (see Ref. [51] for the theory of the asymptotic expansions). Hence the series (B.6) cannot satisfy the inner boundary condition in the middle of the sphere where $\kappa r = 0$. (The inner boundary condition is to be satisfied by an inner asymptotic expansion for small κr and then ψ_m can be determined by matching of these two expansions.)

To overcome this difficulty, let us look again at the left-hand side of Eqn (B.4). At fixed κr , ψ can vary only because of its dependence on R_1 . Then the variation in ψ in Eqn (B.7) is connected with some variation in R_1 . For $1/R_1 \rightarrow 0$ the electrolyte solution inside the drop (at a fixed finite κr) becomes identical with the reference solution. Since the latter has potential $\psi = 0$, one can write

$$C_0(\psi = 0) = 0 \quad (\text{B.9})$$

Equation (B.9) is to be used as a boundary condition instead of Eqn (B.8) when solving Eqn (B.7).

In their calculations, Overbeek et al. [19] have supposed that $\psi_m \ll 1$ and have neglected ψ_m . This procedure is equivalent to the use of the boundary condition (B.9). Hence Eqn (6.24), derived in Ref. [19], turns out to be a correct asymptotic expansion. It was utilized by us in Section 6 when considering the interfacial bending moment due to an electric double layer inside an aqueous drop.