NOTE

Electric Component of the Interfacial Bending Moment and the Curvature Elastic Moduli

The interfacial bending moment and curvature elastic moduli are related theoretically to the surface potential, ΔV, which is liable to direct measurement. The dependence of the interfacial bending properties on the position of the Gibbs dividing surface is investigated. As an application, experimental data for the surface potential of micellar surfactant solutions containing Al^{3+} ions are analyzed. The changes in the bending moment, as determined from ΔV potential, correlate with the transition from spherical to cylindrical micelles induced by the Al^{3+} ions. The results can be important for interpretation of data for formation of microemulsions, flocculation in emulsions, fluctuation capillary waves at interfaces and biomembranes, interactions between inclusions in lipid bilayers, etc.   © 1996 Academic Press, Inc.

Key Words: interfacial bending moment; curvature elastic moduli; surface potential; micellar shape.

1. INTRODUCTION

The flexural properties of an interface, viz. the bending moment and the curvature elastic moduli, have been recognized as being important for micellar and microemulsion systems (1, 2), where they play a major role in determining size distribution. Other phenomena governed by curvature effects are the fluctuation capillary waves on liquid surfaces of low tension (3) and the undulation repulsive forces between surfactant lamellae and biomembranes (4).

From the viewpoint of molecular theory one has to account for the contributions of the electrostatic, van der Waals, and steric interactions to the interfacial bending properties. This article is focused on electrostatics. The latter has been given much attention in the literature. The considerations are based predominantly on theories of the electric double layer formed in the vicinity of a charged surface. Thus, in Refs. (5–7) the curvature effects in the diffuse part of the double layer were studied. The presence of a Stern layer was accounted for in Ref. (8), and its contribution to the bending moment was shown to be comparable with that which is due to the diffuse ionic atmosphere.

The aim of the present work is to relate the electrostatic component of the interfacial bending moment and the curvature elastic moduli to the surface potential, ΔV. As the latter is a directly measurable quantity, this provides a new approach to the determination of the interfacial flexural properties. The treatment proposed here is relevant (i) when there is an adsorption layer of zwitterions or dipoles, such as lipids, at the interface—see Fig. 1; (ii) when the electrolyte concentration is high and the counterions are located in a close vicinity of the charged interface to form a ''molecular capacitor''; (iii) when the surface potential is low, then the Poisson–Boltzmann equation can be linearized and the diffuse layer behaves as a molecular capacitor of thickness equal to the inverse Debye screening length (8).

The Helmholtz model and the derived expressions are not adequate when the surface potential is high and, simultaneously, the ionic concentration is low; then a voluminous electric double layer is formed. In the latter case the double layer theories (5–8) should be applied to calculate the electrostatic contributions to the interfacial flexural properties.

2. BASIC THERMODYNAMIC EQUATIONS

The elementary work of flexural deformation per unit area can be represented in the form (see Ref. (9) for a detailed review)

$$dw_f = B dH + \Theta dD, \qquad [2.1]$$

where

$$H = \tfrac{1}{2}(c_1 + c_2), \quad D = \tfrac{1}{2}(c_1 - c_2) \qquad [2.2]$$

are the mean and the deviatoric curvatures (with c_1 and c_2 being the two principal curvatures of the surface), B and Θ are the bending and torsion moments.

In general, B and Θ are curvature dependent. To determine the latter dependence one must specify the flexural rheology of the interface. The frequently employed model of Helfrich (10) implies that the work of flexural deformation can be written in the form

$$w_f = 2k_c(H - H_0)^2 + \bar{k}_c K. \qquad [2.3]$$

Here $K = H^2 - D^2$ is the Gaussian curvature, H_0 is called the spontaneous curvature, k_c and $\bar{k}_c$ are coefficients (moduli) of bending and torsion elasticity (supposedly constants). From Eqs. [2.1] and [2.3] one derives

$$B = B_0 + 2(2k_c + \bar{k}_c)H, \quad \Theta = -2\bar{k}_c D, \qquad [2.4]$$

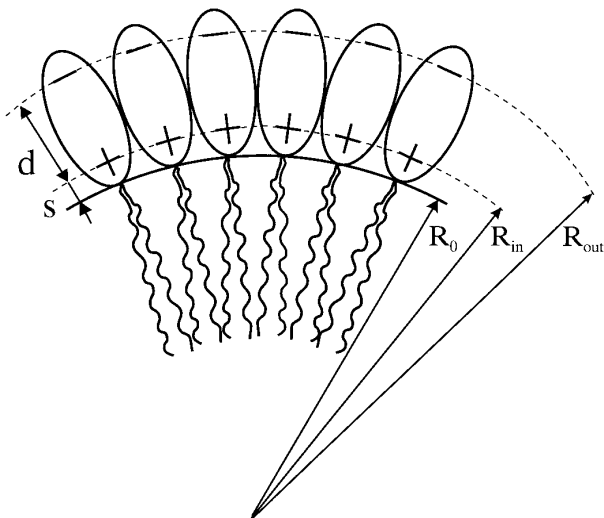where

$$B_0 \equiv B|_{H=0} = -4k_c H_0 \qquad [2.5]$$

is the bending moment of a planar interface. Note that Eqs. [2.4] can be considered as truncated series expansions of B and Θ for small curvatures (small deviations from planarity). Note also that B_0 is connected with the Gibbs–Tolman parameter, δ_0 (which represents the distance between the equimolecular dividing surface and the surface of tension in spherical geometry), as $B_0 = 2\gamma_0 \delta_0$ (8), where γ_0 is the surface tension of a flat interface.

We mention here that the sign of the curvature H and the bending moment B is a matter of convention. It is specified by the definition of the direction of the running unit surface normal, **n**. The general rule is that *positive B* tends to bend the interface around the *inner* phase (the phase for which **n** is an *outer* normal). From Eqs. [2.1] and [2.4] one can realize that the signs of k_c and $\bar{k}_c$ do not depend on the convention for the sign of H and D.

Our aim below is to check whether a surfactant monolayer can be treated as a Helfrich interface and to determine B_0, k_c, and $\bar{k}_c$. With this end in view from Eqs. [2.3] and [2.5] we derive the auxiliary expressions

$$\left(\frac{\partial w_f}{\partial H}\right)_K = B_0 + 4k_c H \qquad [2.6]$$

$$\left(\frac{\partial w_f}{\partial H}\right)_D = B_0 + 2(2k_c + \bar{k}_c)H, \qquad [2.7]$$

FIG. 1. Sketch of a lipid monolayer at water/oil interface. The electric charges can be due to zwitterions, dipoles, or electric double layer.

where the differentiation is to be carried out at constant temperature, T, and surface concentration, Γ_i, of the species i, see, e.g., Eq. [3.6] in Ref. (9). We will use Eq. [2.6] for $K = 0$ (cylindrical interface) and Eq. [2.7] for $D = 0$ (spherical interface).

As far as the van der Waals, electrostatic, and steric interactions can be treated as being independent, they give additive contributions in B and Θ (8):

$$B = B^{\text{vw}} + B^{\text{el}} + B^{\text{st}}, \quad \Theta = \Theta^{\text{vw}} + \Theta^{\text{el}} + \Theta^{\text{st}}. \qquad [2.8]$$

Then, in accordance with Eq. [2.4] one can seek B_0, k_c, and $\overline{k}_c$ in the form

$$B_0 = B_0^{\text{vw}} + B_0^{\text{el}} + B_0^{\text{st}}, \quad k_c = k_c^{\text{vw}} + k_c^{\text{el}} + k_c^{\text{st}},$$
$$\overline{k}_c = \overline{k}_c^{\text{vw}} + \overline{k}_c^{\text{el}} + \overline{k}_c^{\text{st}}. \qquad [2.9]$$

In Ref. (11), B_0^{vw} is estimated to be about 5×10^{-11} N for the boundary between water and liquid hydrocarbons.

Expressions for k_c^{el} and $\overline{k}_c^{\text{el}}$ in terms of the nonlinear double layer theory can be found in Ref. (7). Contributions of ''point dipoles'' and diffuse and Stern parts of the electric double layer in B_0 are evaluated in Ref. (8). In the next section we propose an alternative approach, which is applicable to the calculation of B_0^{el}, k_c^{el}, and $\overline{k}_c^{\text{el}}$ in the cases of both adsorbed dipoles (including zwitterions) and electric double layer.

3. ELECTROSTATIC CONTRIBUTION TO THE BENDING PROPERTIES

We assume that the positive and negative electric charges are situated on two parallel surfaces separated at a distance d from each other—Fig. 1. For adsorbed zwitterions d is the distance between the positive and the negative ionizable groups resolved along the normal to the interface. In the case of electric double layer d is of the order of Debye length, κ^{-1}.

In general, the energy of a condenser of total charge Q is (12)

$$W_{\text{el}} = \frac{Q^2}{2C}, \qquad [3.1]$$

where C is capacitance. Let us introduce a dividing surface of radius R_0. For example, it can be the equimolecular surface with respect to oil, as sketched in Fig. 1. The charges lie on surfaces of radii R_{in} and R_{out} ($R_{\text{in}} < R_{\text{out}}$). For the sake of simplicity we assume that the distances between the three surfaces of question do not depend on the curvature

$$s = R_{\text{in}} - R_0 = \text{const}, \quad d = R_{\text{out}} - R_{\text{in}} = \text{const}. \qquad [3.2]$$

This represents a plausible supposition since s and d are determined by the molecular structure. The mean curvature of the *dividing surface* will be denoted by H.

a. Cylindrical Molecular Condenser

The capacitance per unit length of a cylindrical condenser is (12)

$$C = \frac{\epsilon}{2 \ln(R_{\text{out}}/R_{\text{in}})}, \qquad [3.3]$$

where ϵ is dielectric permittivity; R_{in} and R_{out} are the radii of the inner and the outer cylinders. In accordance with Eq. [2.2] (with $c_1 = -1/R_0$ and $c_2 = 0$) one can write

$$R_{\text{in}} = -(2H)^{-1} + s, \quad R_{\text{out}} = -(2H)^{-1} + s + d. \qquad [3.4]$$

The surface charge density is

$$\sigma_s = \frac{Q}{A_1}, \quad A_1 = 2\pi R_0 = -\pi H^{-1}, \qquad [3.5]$$

where Q and A_1 are electric charge and area per unit length of the cylinder. We emphasize that σ_s refers to the Gibbs dividing surface, R_0. From Eqs. [3.1], [3.3]–[3.5] one determines the electrostatic energy per unit area:

$$w_{\text{el}} = \frac{W_{\text{el}}}{A_1} = -\frac{\pi \sigma_s^2}{\epsilon H} \ln \frac{1 - 2H(s + d)}{1 - 2Hs}$$
$$= \frac{\pi \sigma_s^2 d}{\epsilon} \left[2 + 2H(d + 2s) + \frac{8}{3} H^2(d^2 + 3sd + 3s^2) + \cdots \right].$$
$$[3.6]$$

The differentiation of Eq. [3.6] at constant σ_s finally yields

$$\left(\frac{\partial w_{\text{el}}}{\partial H} \right)_{K=0}$$
$$= \frac{\pi}{\epsilon} \sigma_s^2 \left[2(d^2 + 2sd) + \frac{16}{3} (d^2 + 3sd + 3s^2)Hd + \cdots \right]. \qquad [3.7]$$

The constancy of σ_s stems from the fact that in order to calculate the bending moment one must formally differentiate the energy at fixed adsorption (9), the latter being proportional to σ_s. The condition $K = 0$ denotes that we deal with a cylindrical interface.

b. Spherical Molecular Condenser

As the derivations for spherical and cylindrical condensers are similar, we give only an outline of the main steps. The capacitance of a spherical condenser is (12)

$$C = \frac{\epsilon R_{\text{in}} R_{\text{out}}}{R_{\text{out}} - R_{\text{in}}}, \qquad [3.8]$$

where R_{in} and R_{out} are the radii of the inner and outer spheres. In accordance with Eq. [2.2] (with $c_1 = c_2 = -1/R_0$) one can write

$$R_{in} = -H^{-1} + s, \quad R_{out} = -H^{-1} + s + d. \qquad [3.9]$$

The surface charge density is

$$\sigma_s = \frac{Q}{A}, \quad A = 4\pi H^{-2}. \qquad [3.10]$$

Then by using Eqs. [3.1] and [3.8]–[3.10] one determines the electrostatic energy per unit area:

$$w_{el} = \frac{W_{el}}{A} = \frac{2\pi\sigma_s^2 d}{\epsilon(1 - sH)[1 - (d + s)H]}$$

$$= \frac{\pi\sigma_s^2 d}{\epsilon}[2 + 2H(d + 2s) + 2H^2(d^2 + 3sd + 3s^2) + \cdots]. \quad [3.11]$$

The differentiation of Eq. [3.11] at constant σ_s leads to

$$\left(\frac{\partial w_{el}}{\partial H}\right)_{D=0}$$

$$= \frac{\pi}{\epsilon}\sigma_s^2[2(d^2 + 2sd) + 4(d^2 + 3sd + 3s^2)Hd + \cdots]. \quad [3.12]$$

The condition $D = 0$ denotes that we deal with a spherical interface, cf. Eq. [2.2].

c. Bending Moment and Curvature Elastic Moduli

The comparison between Eqs. [2.6] and [3.7], along with Eq. [2.9], yields

$$B_0^{el} = \frac{2\pi}{\epsilon}\sigma_s^2(d^2 + 2sd); \quad k_c^{el} = \frac{4\pi}{3\epsilon}\sigma_s^2 d(d^2 + 3sd + 3s^2). \quad [3.13]$$

In addition, the comparison between Eqs. [2.7] and [3.12] leads to the same expression for B_0^{el} (as it should be) and to

$$2k_c^{el} + \overline{k}_c^{el} = \frac{2\pi}{\epsilon}\sigma_s^2 d(d^2 + 3sd + 3s^2). \qquad [3.14]$$

From Eqs. [3.13] and [3.14] we obtain

$$\overline{k}_c^{el} = -\frac{2\pi}{3\epsilon}\sigma_s^2 d(d^2 + 3sd + 3s^2). \qquad [3.15]$$

Since the coefficients in the series expansions [3.7] and [3.12] refer to a planar interface ($H = 0$), one can utilize the expression for the charge of a plane-parallel condenser (12):

$$\sigma_s = \frac{Q}{A} = \frac{\epsilon\Delta V}{4\pi d}. \qquad [3.16]$$

Here ΔV can be identified with the change of the Volta potential across the interface due to the surfactant adsorption. The substitution of Eq. [3.16] into Eqs. [3.13] and [3.15] yields

$$B_0^{el} = \frac{\epsilon}{8\pi}(\Delta V)^2\left(1 + \frac{2s}{d}\right) \qquad [3.17]$$

$$k_c^{el} = \frac{\epsilon d}{12\pi}(\Delta V)^2\left(1 + 3\frac{s}{d} + 3\frac{s^2}{d^2}\right) \qquad [3.18]$$

$$\overline{k}_c^{el} = -\frac{\epsilon d}{24\pi}(\Delta V)^2\left(1 + 3\frac{s}{d} + 3\frac{s^2}{d^2}\right). \qquad [3.19]$$

Obviously, the flexural properties, B_0^{el}, k_c^{el}, and $\overline{k}_c^{el}$, depend on the *choice* of the dividing surface (that is, on s in the frames of our model, Fig. 1). In general, such a dependence exists for all quantities assigned to a curved fluid interface (13). Physical choices for the dividing surface are those which are located within the real transition region between the two phases. For example, we may choose to identify the dividing surface as that surface of the molecular condenser which is closer to the inner phase. In other words, $R_0 = R_{in}$ and $s = 0$, so that Eqs. [3.17]–[3.19] reduce to

$$B_0^{el} = \frac{\epsilon}{8\pi}(\Delta V)^2 \qquad [3.20]$$

$$k_c^{el} = \frac{\epsilon d}{12\pi}(\Delta V)^2 \qquad [3.21]$$

$$\overline{k}_c^{el} = -\frac{\epsilon d}{24\pi}(\Delta V)^2. \qquad [3.22]$$

One can check that k_c^{el} is positive for every value of s, whereas $\overline{k}_c^{el}$ is negative and equal to $-k_c^{el}/2$. It is interesting to note that the same relation, $\overline{k}_c = -k_c/2$, has been obtained in Ref. (14) by means of a quite different model.

In Eqs. [3.16]–[3.22], ΔV must be substituted in CGSE units; i.e., the value of ΔV in volts must be divided by 300. As B_0^{el}, k_c^{el}, and $\overline{k}_c^{el}$ are proportional to $(\Delta V)^2$, they are independent of the sign of the surface potential. The experiment (15, 16) yields $a \cdot \Delta V = 2.34 \times 10^{-15}$ V·cm² for lipid monolayers (a is area per molecule). Then with $a = 67$ Å² and $\epsilon = 78.2$ from Eq. [3.20] one calculates $B_0^{el} = 4.2 \times 10^{-11}$ N. It is worthwhile to note that B_0^{el}, as given by Eq. [3.20], does not depend on the model parameter d and can be calculated from the directly measurable ΔV potential.

Unlike B_0^{el}, the bending and torsion moduli, k_c^{el} and $\overline{k}_c^{el}$, depend on d even when $s = 0$. Assuming $d = 5$ Å from Eqs. [3.21] and [3.22] we calculate (with the same values of ϵ and ΔV) $k_c^{el} = 1.4 \times 10^{-20}$ J and $\overline{k}_c^{el} = -7 \times 10^{-21}$ J.

4. DISCUSSION

First we note that the interfacial bending moment, B_0, and curvature elastic moduli, k_c and $\overline{k}_c$, are defined as coefficients in the series expansions of B and Θ for small curvatures ($H \to 0$, $D \to 0$), cf. Eq. [2.4]. On the other hand, the popular constitutive relation due to Helfrich (10), Eq. [2.3], introduces the concept of spontaneous curvature, H_0, which turns out to be in a simple formal relation with B_0, see Eq. [2.5]. In fact, the Helfrich formula, Eq. [2.3], is an emanation of the classical theory of elastic plates and shells in the sense that the energy of deformation is a quadratic function of the strain, see, e.g., Ref. (17). However, if H_0 is formally calculated from the value of B_0 through Eq. [2.5], there is no guarantee that H_0 thus determined corresponds to a minimum of w_f, i.e., that H_0 has a real physical meaning of spontaneous curvature. In particular, from Eq. [2.7] it follows that for spherical surfaces $(\partial w_f/\partial H)_D$ is nonzero at $H = H_0$. Therefore, we conclude that the analogy between the theoretical description of shells and fluid interfaces is limited and that the concept of spontaneous curvature is not very fruitful when applied to fluid interfaces.

Second, we discuss the importance of the relations between the interfacial
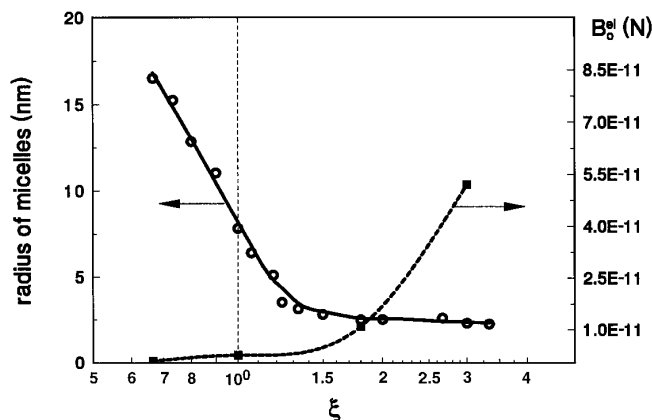
FIG. 2. Plot of experimental data for the micelle radius, R_h, and the bending moment, B_0^{el}, vs the parameter $\xi \equiv (C_T - CMC)/(3C_{Al})$; $C_T = 0.008\ M$ is the total surfactant concentration, CMC $= 1.33 \times 10^{-4}\ M$ is the critical micellization concentration; C_{Al} is the concentration of Al^{3+} ions, which is different for the different experimental points.

flexural parameters and the ΔV potential, Eqs. [3.20]–[3.22] and [3.17]–[3.19], in view of the fact that double layer theories of B_0^{el}, k_c^{el}, and $\bar{k}_c^{el}$ are present (5–8). In fact, these are two alternative and complementary approaches. The double layer theories predict the values of B_0^{el}, k_c^{el}, and $\bar{k}_c^{el}$ in terms of surface charge (or potential) and electrolyte concentration. Complications arise sometimes in the conventional double layer theory because the finite size of the ions is usually neglected, and the decrease of the dielectric permittivity, ϵ, in a vicinity of the charged surface is disregarded (18).

In the present study we do not consider the detailed structure of the double electric layer around a charged surface. Instead, we propose a different approach by relating B_0^{el}, k_c^{el}, and $\bar{k}_c^{el}$ with the directly measurable ΔV potential (of course, we are to assume some value of ϵ in Eqs. [3.20]–[3.22]). As an illustration in Fig. 2 we present data for B_0^{el} calculated by means of Eq. [3.20] from the experimentally measured ΔV in Ref. (19); $\epsilon = 78.2$ was used. The values of ΔV were measured for aqueous solutions of sodium dodecyl dioxyethylene sulfate in the presence of $AlCl_3$ and NaCl; the total ionic strength, $I = 0.024\ M$, is fixed but the ratio of Al^{3+} to Na^+ concentrations is varied. The effective hydrodynamic radius of the surfactant micelles, R_h, measured by dynamic laser light scattering, is also plotted in Fig. 2. The sharp transition in both B_0^{el} and R_h takes place close to the concentration for which one Al^{3+} ion corresponds to three surfactant molecules incorporated in a micelle. For the smaller Al^{3+} concentrations the micelles are spherical and B_0^{el} is larger; for larger Al^{3+} concentrations the micelles are larger and cylindrical (rod-shaped), and B_0^{el} is smaller. A detailed experimental study of the effect of divalent and trivalent counterions on the shape and solubilization ability of ionic surfactant micelles can be found elsewhere (20). Here we will only point out that the transition from sphere to cylinder in the micellar shape is most probably due to the fact that one Al^{3+} ion can bind three surfactant headgroups at the surface of a micelle, thus changing both the optimal surface area per molecule and the interfacial bending energy, which in turn determine the shape of the micelles.

Another case in which the interfacial bending energy gives a considerable contribution is the interaction between deformable droplets in emulsions and microemulsions. The surfaces of two colliding droplets of such kind are flattened in the zone of contact. This is accompanied with a change in the interfacial bending energy. In Ref. (21) it was estimated that this energy change can be of the order of dozens of kT. It is curious to note that such an effect was experimentally established in a recent independent study (22), where interdroplet attraction of the same order of magnitude was found out for water-in-oil microemulsions.

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