

Titre / Title : Layers of non-ionic surfactants on fluid interfaces; adsorption and interactions in the frames of a statistical model

Auteurs / Authors

GURKOV theodor (main author), Faculty of Chemistry, University of Sofia, Bulgaria
IVANOV ivan, Laboratory of Chemical Physics Engineering, Bulgaria

Catégories / Categories

-2 Formulation. Conception. Préparation. / -2 Product design. Conception. Preparation.
2.7 Interfaces, nouvelles règles de formulation.
2.7 Interfacial phenomena; new formulation rules

Résumé / Abstract (1757 caractères / characters)

Titre / Title : Layers of non-ionic surfactants on fluid interfaces; adsorption and interactions in the frames of a statistical model

This is a theoretical work focused on the role of molecular interactions, and the configurational entropy, for the behavior of fluid layers of non-ionic surfactants. We discuss the surface equation of state, the concomitant adsorption thermodynamics and kinetics, and the interactions between two layers (i.e., in thin films). First, different two-dimensional equations of state are examined in view of the meaning of the minimum attainable area per molecule (the excluded area), and its dependence upon the surface coverage (effects of overlapping). Next, interactions between the molecules are considered. The case of one dimension is solved exactly, for interactions that are sufficiently short-ranged so as to act only between neighboring particles; equation of state valid for arbitrary density is derived. Phase transition is absent, as expected. The case of two dimensions is explored using approximate equations for the pair correlation function, together with a perturbation approach (Barker-Henderson). As a result, the known Helfand-Frisch-Lebowitz (HFL) equation of state is supplemented with terms that take into account the interactions. The level of approximation of other 2D equations (Volmer-van der Waals) is discussed. Adsorption isotherms consistent with the obtained relations are deduced, and the adsorption kinetics is described by formulating separately the rates of adsorption and desorption. The interaction force between two opposing surfactant layers in a film is found by calculation of the partition function which includes out-of-plane fluctuations of the molecules. The model incorporates the equation of state (for non-ionic surfactants); it yields a short-range repulsion that can be relevant to the stability of emulsions.

Mots clés / Keywords :

nonionic surfactants
surface equation of state
adsorption isotherms
adsorption kinetics
protrusion forces

1. Introduction

Surfactant adsorption is of primary concern when the stability of liquid dispersions is explored. The role of the surfactants, as manifested through the interfacial tension, elasticity, rheology, etc., is conveniently described in terms of the dependence of the surface pressure upon the adsorbed amount of amphiphilic substance. The latter dependence, called “surface equation of state”, basically encompasses two sources of contributions: the first comes from the finite size of the molecules in the 2D layer (affecting the thermal motion by volume exclusion), and the second one is due to the lateral interactions. The statistical mechanics (1, 2) offers theoretical description of the main effects and provides equations which can be utilized for interpretation of experimental data. These equations are often regarded as interpolation formulae whose suitability for each particular case has to be judged from the quality of the fit to the data (e.g., from the correlation coefficient). Then, there comes the question about the physical meaning and significance of the model parameters determined from such fits. Criteria for choice of a model should include analysis of the values of the adjustable parameters and their compliance with the assumptions of the corresponding theory. As an example, we can mention Ref. (3), where Frumkin and van der Waals isotherms were compared; it was shown that the van der Waals model gave more realistic values for the Gibbs elasticity.

In the present work, we first discuss the physical implications of the excluded area per molecule, α , in a plane interface containing adsorbed surfactant molecules. Several equations of state used in the literature (Langmuir, Volmer, Helfand-Frisch-Lebowitz (HFL)) are examined. It is demonstrated how α depends on the degree of surface coverage. Next, we consider the lateral molecular interactions; their contribution to the 1D isotherm is taken into account by statistical calculation via the partition function of one particle. Generalized Volmer equation, which is exact in the 1D case, is derived under the assumption that the interactions can be described in terms of a “sticky” potential. The same type of potential is also used for analysis of the 2D case (interacting circular disks in a plane). Explicit formulae are obtained for the second and third virial coefficients. The results are extended to the next coefficients using arguments from statistical theories available in the literature. Summation of the virial expansion yields an equation of state which is valid up to linear terms in energy. It is demonstrated that quite low levels of pair interaction energy ($\sim 0.1 kT$) are sufficient to induce phase transition in the layer, provided that the “sticky potential” model is adequate.

2. Excluded area per molecule

Let us consider the following three equations of state, used often for interpretation of surfactant adsorption data:

$$[1] \quad \Pi = \frac{kT \Gamma}{1 - \alpha_V \Gamma} \quad (\text{Volmer})$$

$$[2] \quad \Pi = -\frac{kT}{\alpha_L} \ln(1 - \alpha_L \Gamma) \quad (\text{Langmuir})$$

$$[3] \quad \Pi = \frac{kT \Gamma}{(1 - \omega \Gamma)^2} \quad (\text{Helfand - Frisch - Lebowitz, HFL})$$

Here Π denotes the surface pressure, Γ is the number of adsorbed molecules per unit area, α_V and α_L are model constants, and ω is the area physically occupied by one molecule (if the latter is regarded as a disk with diameter D , in thermal motion on the surface). Eqs. [1-3] account only

for the “hard core” interaction, in other words, for the fact that due to the finite size of the molecules (represented by ω), a fraction of the interface is not available for lateral motion, i.e., it is “excluded”. The Volmer equation has been derived by statistical-mechanical considerations (2) of the non-localized adsorption, when the layer is fully mobile and the molecules can freely migrate within the whole surface. The excluded area α_V is equal to 2ω for low surface densities (see Ref. (2) and the illustration in Fig. 1). For larger coverages, the parameter α_V becomes a complicated function of Γ due to partial overlapping of the areas inaccessible for the particle centers (note the dotted circles in Fig. 1). Analysis of the latter effect was carried out in Ref. (4). In the limit of close packing, $\alpha_V \rightarrow \omega$ can be anticipated.

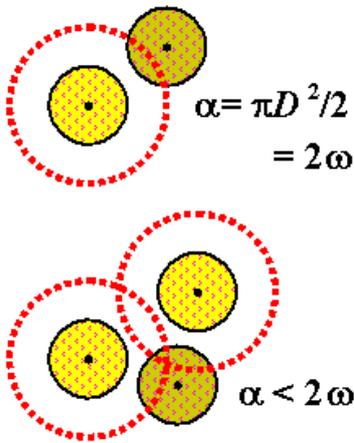


Fig. 1. Excluded area for mobile layers (Volmer).

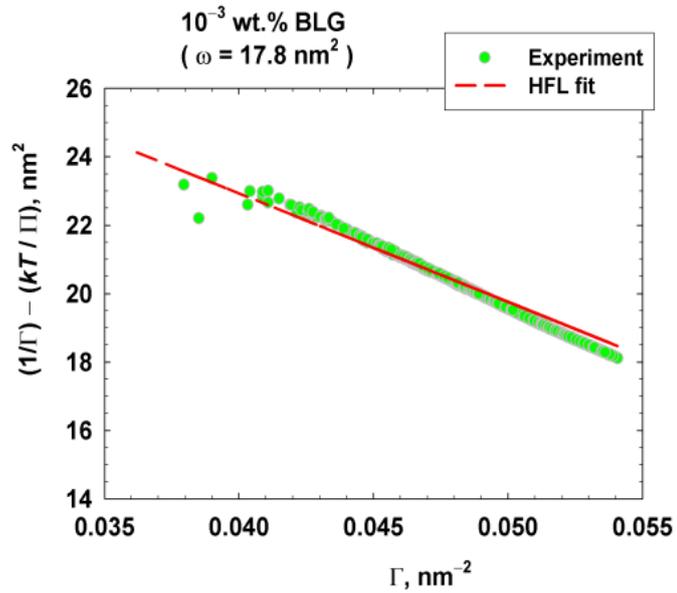


Fig. 2. Data for a globular protein; HFL is adequate.

The Langmuir equation [2] is rigorous for localized adsorption (2), when fixed sites exist; this is usually the case on solid surfaces. However, Eq. [2] is often applied to surfactant layers on fluid phase boundaries (5). Then, adsorption sites with area ω may be situated in such a way that the distance between them is smaller than one particle diameter, D . So, the space between these sites will be inaccessible for adsorption, and the “excluded area”, α_L in Eq. [2], will be larger than ω . For that reason, α_L should be regarded as an effective quantity, dependent on the degree of coverage. In the limit of close packing, $\alpha_L \rightarrow \omega$ is expected.

A third equation of state, Eq. [3], is available from the statistical mechanical theory of mobile 2D layers (6). The excluded volume effect is fully accounted for (by means of machine computations, cf. Ref. (6)), so ω in Eq. [3] is exactly the area occupied by one molecule. The applicability of Eq. [3] to real systems is illustrated by the fit in Fig. 2. Surface pressure and adsorption of beta-lactoglobulin are plotted in a scale which permits one to distinguish clearly between the Volmer and the HFL equations. Volmer would have given a horizontal straight line in Fig. 2. Evidently, the HFL isotherm is adequate, and from the slope we determine $\omega = 17.8 \text{ nm}^2$ for one adsorbed protein molecule.

Since Eq. [3] is the rigorous result for the equation of state of mobile surfactant layers, we can use it to reveal the dependence of α_V and α_L (effective quantities) upon Γ . The physical

state of the interface, in equilibrium, is characterized by a certain value of Π for each Γ ; this relation may be described by any one of the three equations [1-3], as a matter of choice. Hence, it will be instructive to equate the right-hand sides of [1] and [3], and of [2] and [3], for the same Γ , and this procedure will give us the particular values of α_V and α_L , if Volmer or Langmuir isotherms are preferred for description of the real layer. The results are displayed in Fig. 3.

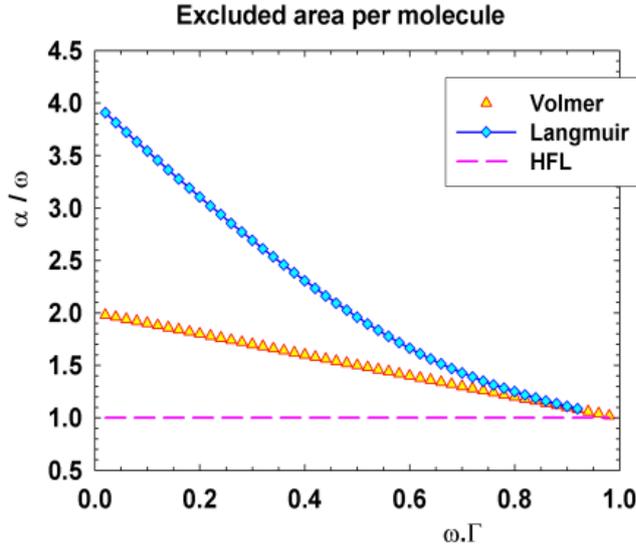


Fig. 3. Effective excluded area vs. surface coverage.

Fig. 3 demonstrates that (I) when the layer is almost fully saturated, $\omega\Gamma \rightarrow 1$, the excluded area per molecule coincides with ω ; (II) in diluted layers, α_V and α_L are substantially different from the actually occupied area ω . Hence, the concept of excluded area should be used with caution, bearing in mind the physical meaning of α_V , α_L , and the limitations of this approach.

3. The case of one dimension

We endeavour to consider the interactions between the molecules, and include their influence in Eqs. [1], [3]. Eq. [1] is exact in the case of one dimension (2), so we start with it. The relevant statistical-mechanical framework is given by the following relations (2):

$$[4] \quad V = \left(\frac{\partial G}{\partial p} \right)_{T,N}; \quad G = -kT \ln \Delta; \quad \Delta(N, p, T) = \sum_{i=\text{quantum states}} \sum_V e^{-E_i/kT} e^{-pV/kT}$$

where V is volume, p is pressure, G is the (Gibbs) free energy, Δ is the corresponding partition function, and E_i is the energy referring to the state i . At constant temperature, T , and number of particles, N , Eqs. [4] can be written for one particle, and in one dimension (a line); $v = V/N$ is the volume (i.e., length) per one particle. According to Ref. (7):

$$[5] \quad v = -kT \frac{\partial}{\partial p} \left[\ln \int_{r=0}^{\infty} e^{[-rp - \phi(r)]/kT} dr \right]_{N,T}$$

It is assumed that E_i contains the potential energy of pair interaction, ϕ , and ϕ is sufficiently short-ranged so that only the nearest neighbors interact with each other; V is replaced by r in one dimension. The integration in Eq. [5] can be taken if ϕ is identified with the square-well potential $u(r_{ij})$ in Fig. 4. The particle diameter is D ; $u = +\infty$ for $r < D$; $u = 0$ for $r > D+a$; in the interval from D to $D+a$ we set the absolute value of the energy to be equal to $-kT \ln(kT\lambda/E)$, where $\lambda = a/D$ and E is a constant. The latter statement is formulated in conformity with the potential proposed by Baxter (8). This specific form of u allows smooth transition to the so-called “sticky potential”: when λ goes down to zero, $a \rightarrow 0$, $|u| \rightarrow \infty$ at fixed E , and the interaction contributions to the thermodynamic quantities remain finite. Taking this limit in Eq. [5], we end up with the following equation of state:

$$[6] \quad \frac{p}{\rho kT} = \frac{1}{2} \frac{E\eta}{kT} \left[-1 + \sqrt{1 + 4 \frac{E}{kT} \frac{\eta}{1-\eta}} \right]$$

Here $\rho = 1/v$, $\eta = D/v$ (degree of saturation); $E > 0$ for attraction.

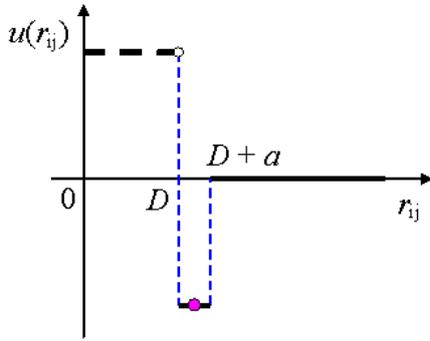


Fig. 4. Square well/ sticky potential.

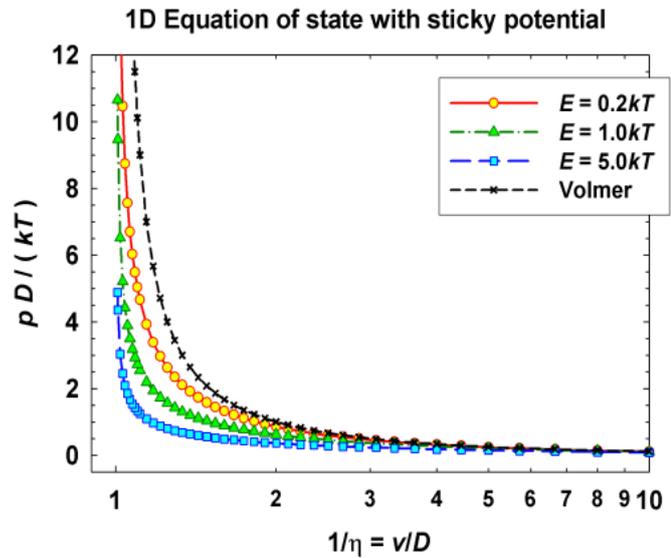


Fig. 5. Plot of Eq. [6].

The obtained equation of state is plotted in Fig. 5. There is no phase transition, as should be expected in a 1D system. Increasing attraction leads to diminishing pressure. Eq. [6] is an exact result for 1D; it represents a generalization of the Volmer equation when molecular interactions are taken into account. If we expand Eq. [6] for small $\eta E/(kT)$ (and small η), the van der Waals equation of state follows as a corollary (Eq. [7]). It is used as an interpolation formula to describe two-dimensional layers of adsorbed surfactant molecules (3).

$$[7] \quad \frac{p}{\rho kT} = \frac{1}{1-\eta} - \frac{E}{kT} \eta \quad (\text{van der Waals})$$

4. The case of two dimensions

We consider a flat layer of circular disks performing thermal motion in lateral direction. The disk diameter is D , and the occupied area is $\omega = \pi D^2/4$; the degree of surface coverage is $\eta = \rho\omega$, where ρ represents the number of particles per unit area (it is often denoted by Γ).

Our goal will be to derive a surface equation of state, taking into account the interactions between the particles; we will only be interested in the case of short-range interactions that can be modeled through the “sticky potential” (Fig. 4). We proceed in the following way: expressions for the second and third virial coefficients, B_2 , B_3 , are derived; next, they are compared with the statistical-mechanical results from Ref. (7), where relations between the virial coefficients were obtained for the case of sticky potential. Based on that, it is possible to write generalized formulae for all virial coefficients, and to sum up the virial expansion, Eq. [8], whereby the equation of state is found.

$$[8] \quad \frac{P}{\rho kT} = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + \dots = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1}$$

The virial coefficients B_2 , B_3 , can be calculated from the pair potential, $u(r_{ij})$, if a central particle “1” stays at a fixed position, and integration is carried out over the positions of other particles, \mathbf{r}_2 , \mathbf{r}_3 :

$$[9] \quad B_2 = -\frac{1}{2} \int_A \left[e^{-u(r_{12})/kT} - 1 \right] d\mathbf{r}_{12}$$

$$[10] \quad B_3 = -\frac{1}{3} \int \int_A \left[e^{-u(r_{12})/kT} - 1 \right] \left[e^{-u(r_{13})/kT} - 1 \right] \left[e^{-u(r_{23})/kT} - 1 \right] d\mathbf{r}_{12} d\mathbf{r}_{13}$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$; $r_{ij} = |\mathbf{r}_{ij}|$. The “sticky potential” is defined following Baxter (8), so that the exponents in Eqs. [9, 10] acquire the form:

$$[11] \quad e^{-u(r_{ij})/kT} - 1 = \begin{cases} -1 & \text{at } 0 \leq r_{ij} < D, \quad u(r_{ij}) = +\infty \\ \frac{E}{kT} D \delta(r_{ij} - D) & \text{at } D \leq r_{ij} \leq D + a, \quad a \rightarrow 0 \\ 0 & \text{at } D + a < r_{ij}, \quad u(r_{ij}) = 0 \end{cases}$$

We take the limit of $a \rightarrow 0$ with simultaneously increasing $|u|$ (Fig. 4), in such a way that the contribution in the integrals [9, 10] remains finite; the constant E has the dimension of energy, $E > 0$ for attraction. In B_3 , we restrict ourselves to linear terms in E/kT .

$$[12] \quad \int_{r < D} f(r) \delta(r - D) dr = f(D)$$

After some calculations, the following results are finally obtained:

$$[13] \quad B_2 = B_2^{HC} + B_2^{INT} = \frac{1}{2} \pi D^2 - \frac{E}{kT} \pi D^2 = 2\omega \left(1 - 2 \frac{E}{kT} \right)$$

$$[14] \quad B_3 = B_3^{HC} + B_3^{INT} = \frac{16}{3} \left(1 - \frac{3\sqrt{3}}{4\pi} \right) \omega^2 \left(1 - 4 \frac{E}{kT} \right)$$

The superscripts ‘‘HC’’ and ‘‘INT’’ designate the hard-core and the interaction parts of the quantities, respectively. The value of $B_3^{HC} = 3.12802\omega^2$ is in full agreement with the computer simulations (6). The equations [13, 14] comply with an explicit (and approximate) relation for the interaction contribution in the virial coefficients, which was derived in Ref. (7):

$$[15] \quad \frac{B_n^{INT}}{B_n^{HC}} = -2(n-1) \frac{E}{kT}; \quad n = 2, 3, 4, \dots$$

We utilize Eq. [15], taking B_n^{HC} from the 2D equation of state for hard disks, Ref. (6): Exact results for the first several virial coefficients, deduced from machine computations, were rounded to the closest integer numbers, and the obtained series was summed up to yield (6):

$$[16] \quad \frac{p}{\rho kT} = 1 + 2\eta + 3\eta^2 + 4\eta^3 + 5\eta^4 + \dots = \frac{1}{(1-\eta)^2}$$

Making use of the Eqs. [15, 16], and inserting B_n into [8], we end up with the equation of state sought for:

$$[17] \quad \frac{p}{\rho kT} = \frac{1}{(1-\eta)^2} - \frac{E}{kT} \frac{4\eta}{(1-\eta)^3}$$

The latter formula bears the following limitations: (I) Its derivation is justified only within the range of validity of the HFL equation [16]; the latter itself was proven to hold for η not greater than 0.674 (6), it is unknown whether Eq. [16] is applicable beyond that value of η . (II) There are terms of higher order in E/kT which should contribute to the RHS of Eq. [17]; the leading term of this kind is $\sim (E/kT)^2 \eta^2$ (coming from B_3). It is negligible if $E/kT \sim 0.1$ and η does not exceed 0.5-0.6 (see Fig. 6), but as the degree of coverage increases toward the close packing ($\eta = 0.907$), a strong repulsion will overwhelm the attraction in the pressure p , due to compensation of the interaction terms.

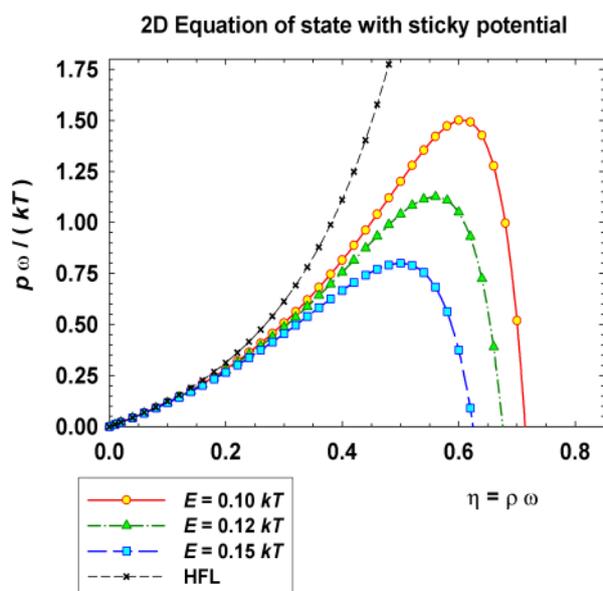


Fig. 6. Plot of Eq. [17] (multiplied by η).

From the graphical representation of Eq. [17] in Fig. 6 it is evident that quite low levels of energy (about $0.1 kT$) are sufficient to bring about phase transition. After the maximum in the curves (at larger η), the derivative $dp/d\rho$ becomes strongly negative, which means that instability will occur and the gaseous layer will collapse spontaneously into a 2D condensed phase. This result (in particular, the low energy required), is a consequence from the short-range nature of the considered interaction.

5. Conclusions

(I) It is shown that the Helfand-Frisch-Lebowitz equation is appropriate for description of the adsorption of a globular protein; (II) The hard-core contribution to the surface equation of state is examined in the cases of Volmer and Langmuir isotherms; the dependence of the excluded area per molecule upon the adsorption is discussed; (III) Lateral molecular interactions are incorporated into the equation of state. In one dimension, an exact equation (extended Volmer) is obtained by calculation of the free energy when the interaction potential is short-ranged (“sticky”). In two dimensions, the same type of potential is used to calculate virial coefficients and find an approximate equation of state. The latter suggests that rather low levels of energy ($\sim 0.1 kT$) may induce phase transition in 2D layers if the particles interact via sticky potential.

References

1. McQuarrie, D.A., *Statistical Mechanics*, Harper & Row, New York, 1976.
2. Hill, T.L., *An Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960.
3. Kolev, V.L., Danov, K.D., Kralchevsky, P.A., Broze, G., Mehreteab, A., *Langmuir*, **18** (2002) 9106-9109.
4. Corti, D.S., *J. Phys. Chem. B*, **105** (2001) 11772-11777.
5. Fainerman, V.B., Miller, R., *Langmuir*, **12** (1996) 6011-6014.
6. Helfand, E., Frisch, H.L., Lebowitz, J.L., *J. Chem. Phys.*, **34** (1961) 1037-1042.
7. Hemmer, P.C., Stell, G., *J. Chem. Phys.*, **93** (1990) 8220-8227.
8. Baxter, R.J., *J. Chem. Phys.*, **49** (1968) 2770-2774.