

Motomura's modified equation for surfactant penetration into spread monolayers

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Abstract

The extent of surfactant penetration into monolayers is often evaluated by thermodynamic approaches. The most formal treatment of the penetration phenomenon is due to Motomura et al. [K. Motomura, Y. Hayami, M. Aratono and R. Matuura, *J. Colloid Interface Sci.*, 87 (1982) 333–338]. However, this model seems to be inadequate to determine adsorption into films in the condensed state. It is also in contradiction with Hall's [O.G. Hall, *Langmuir*, 2 (1986) 809] work which demonstrated that it is impossible to calculate penetration quantities without extra thermodynamic assumptions. We present here a modified equation for determination of thermodynamic quantities of penetration and calculate the adsorption of poly(oxyethylene)–poly(oxypropylene) block copolymers into soya phospholipid films using our previously obtained experimental data. The proposed modified Motomura equation may yield penetration quantities more reasonable than those obtained with the use of the Alexander–Barnes or classical Motomura equations. It also indicates why the known penetration models give such different adsorption values. Moreover, these contributions allow one to clarify the relationship between different approaches aimed at quantifying surfactant penetration into insoluble films.

Keywords: Equilibrium penetration; Hall's thermodynamic treatment; Mixed monolayer; Phospholipids; Poly(oxyethylene)–poly(oxypropylene) copolymer; Surfactant adsorption; Thermodynamic treatment of penetration

1. Introduction

The extent of surfactant penetration into monolayers spread at the air/water interface has often been evaluated by different thermodynamic approaches. The most general and rigorous treatment of penetration phenomena is due to Motomura et al. [1]. The surface penetration phenomenon was also addressed by Ter-Minassian-

Saraga [2] who derived (by another method) a similar equilibrium penetration equation. In contrast with other methods [3,4], Motomura's equation can be used to evaluate surfactant adsorption into films in the expanded state. However, such a model seems to be unsatisfactory to determine adsorption into films in the condensed state. Referring to the negative adsorption values found for penetration of hexadecyltrimethylammonium bromide into cholesterol monolayers, Alexander et al. [5] stated that "... while this result is

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plausible in a quantitative sense, the depth from which surfactant would need to be excluded is unacceptably great" (sic). Similar results have also been observed by us for the penetration of soya phospholipid monolayers by poly(oxyethylene)–poly(oxypropylene) block copolymer injected into the underlying aqueous phase [6].

Hall's thermodynamic analysis [7] shows that it is impossible to solve the penetration problem (how to obtain Γ for the penetrating molecule from π – c – Γ_{film} data) without introducing non-thermodynamic assumptions. Since the approach of Motomura et al. does not require any extra hypothesis, there exists an incompatibility with Hall's result.

We shall focus here on the incompatibility of penetration quantities calculated from the Alexander–Barnes equations and the equation of Motomura et al. Although both approaches are intended to quantify surfactant adsorption, there is no clear relationship between them. We intend therefore to show that a certain modification of Motomura's equation is necessary in order to adapt it for films in the condensed state. We thus derive a new equation for adsorption calculations. The modified equation has been used to quantify the equilibrium penetration of poly(oxyethylene)–poly(oxypropylene) block copolymer into soya phospholipid monolayers from the data reported by Santos Magalhães et al. [6].

2. On surfactant adsorption into films

The Hansen thermodynamic approach [8,9] applied for a monolayer penetrated by a single surfactant gives the following equation describing the equilibrium surface tension γ_S of the systems:

$$d\gamma_S = -S^H dT + V^H dP - \Gamma_S^H d\mu_S - \Gamma_M d\mu_M \quad (1)$$

where the superscript H refers to Hansen quantities, subscripts M and S stand for monolayer and surfactant respectively, μ_i is the chemical potential of compound i , and S^H and V^H are the excess entropy and the volume at the interface respectively. Assuming temperature T and pressure P to be constant and applying Alexander–Barnes

notation [4] we obtain Eq. (1) in the form:

$$d\pi_S = RT\Gamma_M d \ln \lambda_M + RT\Gamma_S^H d \ln \lambda_S \quad (2)$$

Here, λ_i denotes the absolute activity of substance i , π_S is the surface pressure of the mixed film and $R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$ is the gas constant.

Combining Eq. (2) with that derived by Motomura et al. [1] we obtain:

$$d(\ln \lambda_M - \hat{A}_M \pi_S / RT) = -\frac{1}{RT} \pi_S d\hat{A}_M - \hat{A}_M \Gamma_S^H d \ln \lambda_S \quad (3)$$

where \hat{A}_M stands for the area per molecule of the film-forming substance.

Assuming that surfactant activities in the dilute solution are very low, we may consider that $\lambda_S = m_S$, where m_S is the surfactant concentration. The application of the Maxwell relationship to the above equation promptly yields:

$$\frac{1}{RT} \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} = \left(\frac{\partial \hat{A}_M \Gamma_S^H}{\partial \hat{A}_M} \right)_{T,P,m_S} \quad (4)$$

Independently, the surfactant adsorption on the monolayer-free interface can be calculated from the Gibbs equation according to the expression

$$\frac{1}{RT} \left(\frac{\partial \pi_S^0}{\partial \ln m_S} \right)_{T,P,\hat{A}_M \rightarrow +\infty} = \Gamma_S^0 \quad (5)$$

where Γ_S^0 denotes the surfactant adsorption at the air/water interface, the superscript 0 standing for a monolayer-free system.

We then define the following variation quantities:

$$\Delta \Pi_S \equiv \pi_S - \pi_S^0 \quad (6a)$$

and

$$\Delta \Gamma_S \equiv \Gamma_S^H - \Gamma_S^0 \quad (6b)$$

Subtracting Eq. (4) from Eq. (5), we have

$$\left(\frac{\partial \Delta \Pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} = RT \left(\frac{\partial \hat{A}_M \Delta \Gamma_S}{\partial \hat{A}_M} \right)_{T,P,m_S} \quad (7)$$

This expression corresponds to that which is known as the Motomura equation [Eq. (9) in the paper of Motomura et al. [1]]

However, the integration of the above equation should be carried out more precisely than was

done by Motomura et al. Let us remark first that Γ_S^H tends to Γ_S^0 as \hat{A}_M increases, so that

$$\lim_{\hat{A}_M \rightarrow +\infty} \Delta\Gamma_S = 0 \quad (8)$$

When the molar area \hat{A}_M increases indefinitely the limit $\hat{A}_M \Delta\Gamma_S$ yields an indetermination (0.∞):

$$\lim_{\hat{A}_M \rightarrow +\infty} \hat{A}_M \Delta\Gamma_S = K \quad (9)$$

We shall see that the crux of the matter is the evaluation of K which eventually could be zero, finite or infinite. The unknown constant K is easily shown to be

$$\lim_{\Gamma_M \rightarrow 0} \left(\frac{\partial \Gamma_S^H}{\partial \Gamma_M} \right)_{\ln m_S}$$

and, as indicated by Hall's Eq. (8), the above limit is expected to remain finite. The integration of Eq. (7) (in the way proposed by Riemann-Stieltjes [10]) within the interval from \hat{A}_M to infinity yields:

$$\int_{\hat{A}_M \Delta\Gamma_S}^K d(\hat{A}_M \Delta\Gamma_S) = \frac{1}{RT} \int_{\hat{A}_M}^{+\infty} \left(\frac{\partial \Delta\Pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} \cdot d\hat{A}_M \quad (10)$$

so that

$$-\hat{A}_M \Delta\Gamma_S = \frac{1}{RT} \int_{\hat{A}_M}^{+\infty} \left(\frac{\partial \Delta\Pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} \cdot d\hat{A}_M - K \quad (11)$$

and finally

$$\Gamma_S^H = \Gamma_S^0 - \frac{1}{\hat{A}_M} \left[\frac{1}{RT} \int_{\hat{A}_M}^{+\infty} \left(\frac{\partial \Delta\Pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} \cdot d\hat{A}_M - K \right] \quad (12)$$

From Eq. (12) it is immediately apparent that the surfactant adsorption Γ_S^H approaches Γ_S^0 as \hat{A}_M approaches infinity. Furthermore, it should be pointed out that under the assumption that K is zero Eq. (12) reduces to that proposed by Motomura et al. (i.e. Eq. (10) in Ref. [1]). However, the veracity of Eq. (12) has still to be verified using different experimental data. It should also be stressed that surfactant adsorption depends on the molar area of the film-forming substance, i.e. $\Gamma_S^H = \Gamma_S^H(\hat{A}_M)$.

It is worthwhile to mention that similar reasoning applies to Ter-Minassian-Saraga's approach since the integration Eq. (AIV') \Rightarrow (AV') (Ref. (2), p. 394) involves a

$$\lim_{a_1 \rightarrow +\infty} \Pi_1(\mu_2, a_1) \cdot a_1.$$

According to Eq. (12) and despite $K \neq 0$, for films in the expanded state (high \hat{A}_M values), the use of the Motomura equation leads to reasonable results for Γ_S^H .

One now has to find a way to determine the term K . For this purpose let us make an assumption based on the fact that adsorption is negligible near to the collapse of a monolayer. Therefore we put:

$$\Gamma_S^H(\hat{A}_M^*) \approx 0 \quad (13)$$

where \hat{A}_M^* stands for the area per molecule of a film-forming amphiphilic compound at collapse. Substituting Eq. (12) into Eq. (13), we first find the approximation:

$$\Gamma_S^H \approx \Gamma_S^0 \left[1 - \frac{\hat{A}_M^*}{\hat{A}_M} \right] + \frac{1}{RT \hat{A}_M} \int_{\hat{A}_M^*}^{\hat{A}_M} \left(\frac{\partial \Delta\Pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} \cdot d\hat{A}_M \quad (14)$$

It is worthwhile noting that the Alexander-Barnes equation was derived from that of Pethica [3,4] using the concept of the partial molar area. The Alexander-Barnes equation states:

$$\Gamma_S = \frac{1}{RT} \left(1 - \frac{\bar{A}'_M}{\bar{A}_M} \right) \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{A,n_M^0} \quad (15)$$

reducing to $\Gamma_S = 0$ when $\hat{A}_M = \bar{A}'_M$.

In terms of partial molar areas of constituents, the total area A at the interface is given by $A = n_M \bar{A}_M + n_S^H \bar{A}_S$, where n_M is the number of spread film-forming molecules at the surface and n_S^H is the number of adsorbed surfactant molecules at the interface. It follows that $\Gamma_M \bar{A}_M + \Gamma_S^H \bar{A}_S = 1$, or

$$\Gamma_S^H = \left[1 - \frac{\bar{A}_M}{\bar{A}_M} \right] \frac{1}{\bar{A}_S} \quad (16)$$

Eq. (16) implies that no surfactant adsorption

occurs at the molar area equal to the partial molar area at the surface. Therefore, it may be asserted that $\Gamma_S^H = 0$ for $\hat{A}_M = \bar{A}_M$, so that $\Gamma_S^H(\bar{A}_M) = 0$.

Under similar conditions, the proposed modified Motomura equation yields:

$$\Gamma_S^H = \left[1 - \frac{\bar{A}_M}{\hat{A}_M} \right] \frac{1}{RT} \left(\frac{\partial \pi_S^0}{\partial \ln m_S} \right)_{T,P,\hat{A}_M \rightarrow \infty} + \frac{1}{RT \hat{A}_M} \int_{\bar{A}_M}^{\hat{A}_M} \left(\frac{\partial \Delta H_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} \cdot d\hat{A}_M \quad (17)$$

The above equation resembles somewhat a modification of the Motomura equation proposed by Siegel and Vollhardt (Eq. (5) in Ref. [11]). However, in contrast to their equation, Eq. (17) naturally includes a “geometrical factor” and limiting cases such as $\hat{A}_M \rightarrow \bar{A}_M$ and $\hat{A}_M \rightarrow +\infty$.

Since Γ_S^0 is independent of \hat{A}_M , Eq. (17) reduces to

$$\Gamma_S^H = \frac{1}{RT \hat{A}_M} \int_{\bar{A}_M}^{\hat{A}_M} \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} \cdot d\hat{A}_M \quad (18)$$

As the partial molar area \bar{A}_M of a mixed film is unknown, we use the mean value theorem [10] to solve the integral in Eq. (18). This gives:

$$\Gamma_S^H = \frac{1}{RT} \left[1 - \frac{\bar{A}_M}{\hat{A}_M} \right] \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\bar{A}_M} \quad (19)$$

Usually, $\bar{A}_M < \hat{A}_M$ so that $\hat{A}_M^* < \bar{A}_M < \tilde{A}_M < \hat{A}_M < +\infty$. Hence, Eq. (19) is virtually the same as Eq. (15), especially for incompressible films for which $\bar{A}_M \approx \hat{A}_M$.

The area \tilde{A}_M may be considered as the partial molar area of a surfactant in a mixed monolayer expressed in units of “equivalent area” of the film-forming substance:

$$\frac{1}{\tilde{A}_S} = \frac{1}{RT} \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\bar{A}_M} \quad (20)$$

Eq. (19) can also be related to the “accessible area” theory describing the equilibrium penetration of a surfactant into a monolayer-covered surface [12,13]. According to this theory, the surfactant penetration quantity Γ_S is given by

$$\Gamma_S = \Gamma_w - a_M \Gamma_w (1/\hat{A}_M) \quad (21)$$

where Γ_w stands for adsorption into the accessible area, and a_M is the apparent cross-sectional area of a monolayer molecule. Comparison of Eqs. (19) and (21) gives:

$$\Gamma_w = \frac{1}{RT} \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{\tilde{A}_M} \quad \text{and} \quad a_M = \bar{A}_M \quad (22)$$

Moreover, as expected,

$$\lim_{\hat{A}_M \rightarrow +\infty} \Gamma_w = \Gamma_S^0$$

Thus, the area \tilde{A}_M may also be accounted for by the accessible area of the surface for adsorption. This alternative interpretation vindicates our arguments about surfactant adsorption evaluation.

3. Modified equation of the thermodynamic quantities of penetration

Combining Eqs. (16) and (17), it is possible to establish the relationship between partial molecular areas of film-forming constituents in a mixed monolayer:

$$\bar{A}_S = RT \frac{\hat{A}_M - \bar{A}_M}{\int_{\bar{A}_M}^{\hat{A}_M} \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} d\hat{A}_M} \quad (23)$$

The plot of \bar{A}_S vs. \bar{A}_M gives an “admissible partial areas curve”. Unfortunately, the modified Motomura approach presents the same drawback as other adsorption calculation equations, namely the fact that the molar area of the film-forming substance is unknown. Therefore, the surfactant adsorption quantity cannot be found from Eq. (23) and an additional equation is needed which is in perfect agreement with Hall’s work [7]. Usually, Pethica’s hypothesis has been used to circumvent this difficulty, but two conditions are required: firstly, the monolayer should be incompressible; and secondly, it holds true only for the monolayer in the condensed state. One of the possible ways to get out of this deadlock is to use the data from a “surface pressure vs. surface area” isotherm of a pure spread film, which is usually in a sigmoid form $\pi_M = \mathbf{S}(\hat{A}_M)$. We formulate then a “generalized Pethica hypothesis” as follows.

The surface pressure of a mixed film may be related to the surface pressure of the monolayer-free system and to that of a pure monolayer at the partial molar area of the film by

$$\frac{n_S^H}{n_S^H + n_M} \pi_S^0 + \frac{n_M}{n_S^H + n_M} \mathbf{S}(\bar{A}_M) = \pi_S \quad (24)$$

We promptly verify that under Pethica's assumptions the surfactant adsorption is low ($n_S^H \ll n_M$), so that our hypothesis simplifies to what is known as Pethica's hypothesis [3].

Eq. (24) can be rewritten as

$$\Gamma_S^H \pi_S^0 + \Gamma_M \mathbf{S}(\bar{A}_M) = \pi_S (\Gamma_S^H + \Gamma_M) \quad (25)$$

which leads to the relationship

$$(\hat{A}_M - \bar{A}_M) \pi_S^0 + \bar{A}_S \mathbf{S}(\bar{A}_M) = \pi_S [(\hat{A}_M - \bar{A}_M) + \bar{A}_S] \quad (26)$$

It is well known that the increase in the surfactant adsorption brings about the increase in the surface pressure of the film. Therefore, Eq. (24) appears to be sufficient to account for the pressure increase. In fact, as a result of the surfactant adsorption, the molar area of the film-forming substance is diminished ($\bar{A}_M < \hat{A}_M$). The surface pressure of the mixed film, $\pi_M \equiv \mathbf{S}(\bar{A}_M)$, may be higher than that of a monolayer or surfactant alone. Hence a two-equation, two-indeterminate, non-linear system is obtained from Eqs. (23) and (26):

$$\left\{ \begin{aligned} (\hat{A}_M - \bar{A}_M) \pi_S^0 + \bar{A}_S \mathbf{S}(\bar{A}_M) &= \pi_S [(\hat{A}_M - \bar{A}_M) + \bar{A}_S] \quad (27a) \\ \bar{A}_S &= RT \frac{\hat{A}_M - \bar{A}_M}{\int_{\hat{A}_M}^{\bar{A}_M} \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} d\hat{A}_M} \quad (27b) \end{aligned} \right.$$

Solving Eq. (27) for the partial molecular area \bar{A}_S of the surfactant, one can derive the adsorption Γ_S^H at the Hansen interface from Eq. (16).

The surfactant and the film-forming molecular ratios at the interface can easily be computed from the following two equations:

$$n_S^H \% = \frac{n_S^H}{n_M + n_S^H} = \frac{\Gamma_S^H}{\Gamma_S^H + \Gamma_M} = \frac{\hat{A}_M - \bar{A}_M}{\hat{A}_M - \bar{A}_M + \bar{A}_S} \quad (28)$$

and

$$n_M \% = \frac{n_M}{n_M + n_S^H} = \frac{\Gamma_M}{\Gamma_S^H + \Gamma_M} = \frac{\bar{A}_S}{\hat{A}_M - \bar{A}_M + \bar{A}_S} \quad (29)$$

with $n_M \% + n_S^H \% = 1$. With the known number of spread film-forming molecules n_M , the number of surfactant molecules adsorbed into a monolayer may be calculated provided that adsorption is not negative.

The system described by Eqs. (27) can be solved using a numerical method with a computer program. More specifically, numerical computations of \bar{A}_S can be done by increasing \bar{A}_M in small increments from the collapse pressure so that both Eqs. (27a) and (27b) yield identical solutions (within a tolerance level). We have then:

3.1. Algorithm for finding partial areas in a mixed monolayer

- S1. Initial conditions: $i = 0$; $\bar{A}_M^{(0)} \equiv \hat{A}_M^*$.
- S2. Updating: $i \leftarrow i + 1$; $\bar{A}_M^{(i)} \equiv \bar{A}_M^{(i-1)} + \Delta$.
- S3. Partial area computations: $\bar{A}_{S;1}^{(i)}, \bar{A}_{S;2}^{(i)}$

$$\bar{A}_{S;1}^{(i)} \equiv \frac{(\pi_S - \pi_S^0) [\hat{A}_M - \bar{A}_M^{(i)}]}{\mathbf{S}(\bar{A}_M^{(i)}) - \pi_S}$$

$$\bar{A}_{S;2}^{(i)} \equiv RT \frac{\hat{A}_M - \bar{A}_M^{(i)}}{\int_{\bar{A}_M^{(i)}}^{\hat{A}_M} \left(\frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\hat{A}_M} d\hat{A}_M}$$

- S4. If $|\bar{A}_{S;1}^{(i)} - \bar{A}_{S;2}^{(i)}| < \epsilon$ then stop; otherwise go to S2.

The solution of the algorithm yields the partial areas \bar{A}_M and \bar{A}_S from which the surfactant adsorption may be computed from:

$$\Gamma_S^H = \left[\frac{\hat{A}_M - \bar{A}_M}{\hat{A}_M} \right] \frac{10^{20}}{N_A \bar{A}_S} \mu\text{mol m}^{-2} \quad (30)$$

where N_A is Avogadro's number.

The data from the linear stepwise isotherm (\mathbf{S} curve $\pi_M \times \hat{A}_M$) were fitted by the linear interpolation and the numerical integration was carried out by a generalized Simpson formula with 10 equal parts, with a step $h = (\hat{A}_M - \bar{A}_M)/10$. Also, the values of $(\partial \pi_S / \partial \ln m_S)_{\bar{A}_M + ih}$, $i = 0, 1, 2, \dots, 10$, were obtained from linear interpolation. The

Table 1

Partial molecular areas for block copolymer/phospholipid mixed film ($\pi_s^0 = 9.65 \text{ mN m}^{-1}$ and $m_s = 5 \times 10^{-7} \text{ mol l}^{-1}$)

Pure phospholipid spread monolayer \hat{A}_M	Alexander–Barnes		Modified Motomura	
	\bar{A}_M	\bar{A}_S	\bar{A}_M	\bar{A}_S
102	95.7	353.0	87.8	47.2
108	102.3	244.0	102.2	774.3
122	110.1	218.0	109.1	299.5
146	112.8	136.0	111.3	248.0
182	100.0	271.0	84.7	129.7

algorithm was implemented on a 486 PC micro-computer using TURBO PASCAL language.

4. Application of the model to the adsorption of poly(oxyethylene)–poly(oxypropylene) block copolymer into soya phospholipid monolayers

In order to verify whether this new approach enables one to obtain more precise values we have recalculated the penetration data of poly(oxyethylene)–poly(oxypropylene) block copolymer into soya phospholipid monolayer at a molecular area of the pure spread film ranging from $\hat{A}_M = 108\text{--}182 \text{ \AA}^2 \text{ molecule}^{-1}$ with a surfactant concentration of $m_s = 5 \times 10^{-7} \text{ mol l}^{-1}$ at $T = 298 \text{ K}$. The molecular area of the copolymer at the monolayer-free surface is $40.77 \text{ \AA}^2 \text{ molecule}^{-1}$ [14]. A comparison of the penetration data obtained with the modified Motomura equation and those proposed by Alexander–Barnes gives the results summarized in Tables 1 and 2.

The admissible curve from our data furnishes a

Table 2

Copolymer adsorption into the phospholipid film ($\mu\text{mol m}^{-2}$)

Pure phospholipid spread monolayer \hat{A}_M ($\text{\AA}^2 \text{ molecule}^{-1}$)	Alexander–Barnes	Motomura	Modified Motomura
102	0.030	–1.33	0.49
108	0.036	–0.83	0.011
122	0.074	0.14	0.060
146	0.28	1.31	0.16
182	0.28	2.49	0.68

relatively robust estimate for \bar{A}_S , i.e. the partial molar area of the surfactant remains almost unchanged over a wide range of partial molar area values of the film-forming substance. Fig. 1 illustrates such a behavior and shows graphically the solution of the non-linear two-equation system Eq. (27) in a particular interfacial system for which $\hat{A}_M = 108 \text{ \AA}^2 \text{ molecule}^{-1}$ and $m_s = 5 \times 10^{-7} \text{ mol l}^{-1}$.

The surfactant is adsorbed into “gaps” in the monolayer. We consider the cross-sectional area \bar{A}_S of surfactant molecules adsorbed at the inter-

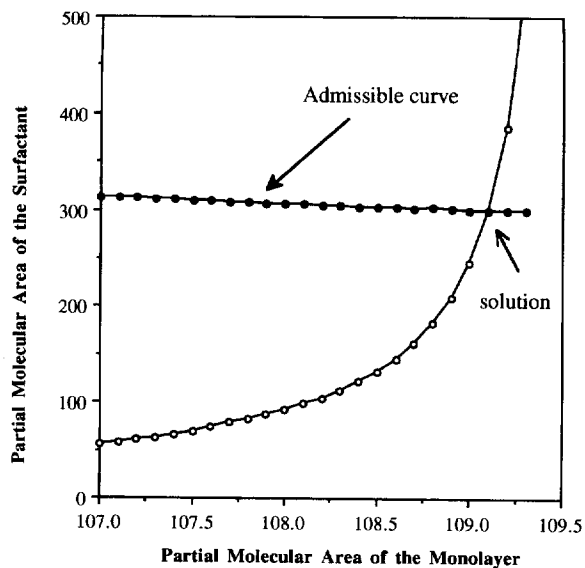


Fig. 1. Bidimensional partial area plot in a mixed phospholipid monolayer with one species adsorbed. $\hat{A}_M = 108 \text{ \AA}^2 \text{ molecule}^{-1}$ and $m_s = 5 \times 10^{-7} \text{ mol l}^{-1}$. Admissible curve (●) for surfactant partial molecular area is shown.

face. At very high film coverage, the pure spread monolayer presents quite small holes so that surfactant may be adsorbed with just one molecule per hole. As a consequence, the partial molecular area of the surfactant tends to the area of the surfactant polar head, $40 \text{ \AA}^2 \text{ molecule}^{-1}$. At low monolayer coverage, a large amount of surfactant per hole is adsorbed into the spread film and the partial molecular area of the surfactant also tends to the same value.

Fig. 2 shows the partial area of the monolayer-forming substance versus the molecular area of the pure spread film. The plot considers a surfactant concentration in the underlying phase of $m_s = 5 \times 10^{-7} \text{ mol l}^{-1}$. The values of \bar{A}_M are very close to those obtained by the Alexander–Barnes equation, especially for mixed films far from their condensed or expanded states. In the later case, we expect more plausible results using our approach. Copolymer adsorption into phospholipids is presently being evaluated over a wide range of surfactant concentrations.

Comparison of the equilibrium penetration values of phospholipid monolayer by a copolymer

estimated according to three models are shown in Fig. 3. The modified Motomura equation furnishes somewhat similar surface excess concentrations Γ_s to those from Alexander–Barnes. However, at low monolayer coverage and high surfactant concentration, adsorption values are halfway between Alexander–Barnes and Motomura levels. The penetration values obtained seem to be more reasonable than the Alexander–Barnes results since the surfactant adsorption at Hansen's interface tends to $4.07 \text{ \mu mol m}^{-2}$ for films in the expanded state [6]. Moreover, the composition of the surface — $n_s = 0.75\%$ for an area per molecule of $\hat{A}_M = 108 \text{ \AA}^2 \text{ molecule}^{-1}$ (near the condensed state), $n_s = 12.3\%$ for $\hat{A}_M = 1.46 \text{ \AA}^2 \text{ molecule}^{-1}$, and $n_s = 42.9\%$ for $\hat{A}_M = 182 \text{ \AA}^2 \text{ molecule}^{-1}$ (near the expanded state) — also seems to be realistic.

5. Conclusion

Penetration phenomena are not fully modeled or understood [5,11,15]. This work intended to present a new contribution to enable the evaluation

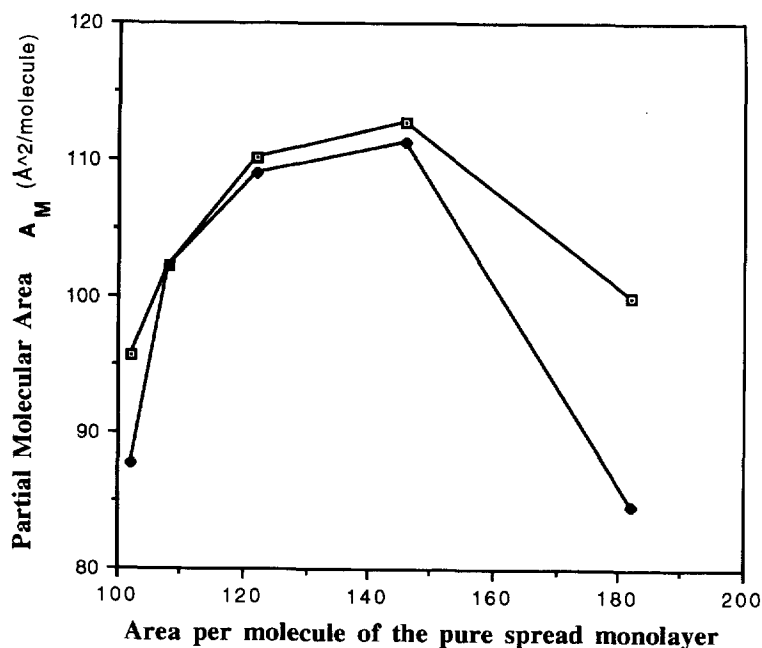


Fig. 2. Partial molecular area of the film-forming substance for different monolayer coverages: (□) Alexander–Barnes; (◆) modified Motomura.

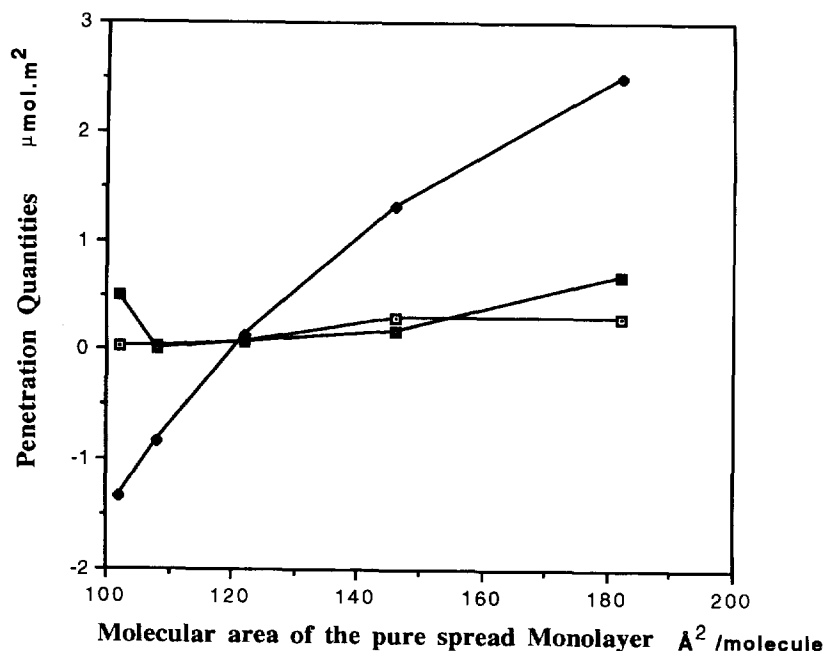


Fig. 3. Adsorption of poly(oxyethylene)–poly(oxypropylene) block copolymer into soya phospholipid monolayer according to three approaches: (□) Alexander–Barnes; (◆) Motomura; (■) modified Motomura.

of penetration into mixed films containing insoluble monolayers and one adsorbed species. Specifically, we have discussed the application of the approach of Motomura et al. to evaluate surfactant penetration into monolayers. Such an approach is often preferred because it is derived without extra-thermodynamic assumptions. However, in all data from the literature, the adsorption values calculated by this method differ appreciably from those calculated by the other procedures. Furthermore, they do not agree with Hall's conclusion which shows that such a problem is isomorphic with obtaining changes in the Galvani potential drops across a mercury/electrolyte solution interface as the solvent composition is varied [7]. A discrimination between these theories has long been sought. As a main contribution, our results reveal deficiencies in the classical model of Motomura et al. and suggest some refinements. New equations for adsorption phenomena have been derived which could explain the unrealistic (negative) results obtained by Motomura's equation for the films in their condensed state. They also elucidate the contradiction between the theories of Motomura and

Hall. The evaluation of the surfactant adsorption obtained with these new equations makes possible narrowing of the gap between adsorption values calculated with the Alexander–Barnes equation and with that of Motomura. They may also indicate why the models give different values for the composition of surfaces [5,6,11]. Another interesting point to be mentioned is a potential relationship between the Pethica and Motomura equations and even with the accessible area theory. Additionally, the new approach allows one to find out the partial molecular area of the surfactant in the mixed monolayer. Finally, we suggest the application of the reviewed model to other interfacial systems in order to provide a better understanding of its validity, possible deficiencies and/or limitations.

Acknowledgment

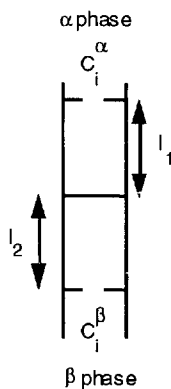
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Appendix A¹ (suggested by one of the reviewers): a Hansen interface model for surfactant equilibrium penetration of an insoluble monolayer at the air/water interface

We have presumed throughout this paper that $\Gamma_S^H = n_S^H/A$. In order to assess the composition of the surface we require a hypothesis for the character of the Hansen interface, leading to a model of the interface. Here α and β stand respectively for the gas phase (air) and the liquid phase (water). In the following calculations we assume that $T = 298.15$ K and $P = 760$ Torr and components i are w (water), N (nitrogen: for simplicity we neglect oxygen, argon, etc), M (monolayer) and S (surfactant).

The diagram illustrates a Hansen interface assuming a uniform composition both above the distance l_1 and below the distance l_2 , which are taken to be about 100 nm, corresponding to 10^{-4} l m⁻². As usual, we assume that C_M is negligible in both liquid and gas phases ($C_M^\alpha = C_M^\beta = 0$) and that C_S is negligible in the gas phase ($C_S^\alpha = 0$). We take the partial molar volume of the surfactant in the liquid phase to be 8.35 l mole⁻¹.



¹ The inclusion of this Appendix was suggested by one of the reviewers.

Considering a surfactant concentration C_S varying from 0 to 5×10^{-4} , the density and vapor pressure of water and the solubility of nitrogen in water are available from Ref. [16] yielding:

Water: $C_w^\alpha = 1.279 \times 10^{-3}$ and $C_w^\beta = 55.2$

Nitrogen: $C_N^\alpha = 3.959 \times 10^{-2}$ and $C_N^\beta = 6.33 \times 10^{-4}$

Note: rigorously, for $0 \leq C_S \leq 5 \times 10^{-4}$, one has C_w^β varying from 55.11 to 55.34 or 55.2 to a sufficient approximation. The equilibrium vapor pressure of water at 298.15 K is 23.77 Torr, unless the system is enclosed or the ambient humidity is 100% when there may be extensive water loss by evaporation — but we assume that this is not a problem.

We can ignore the regions above l_1 and below l_2 and consider just the subsystem between these regions (Ref. [8], p. 411):

$$\Gamma_i^H = n_i - \lambda_\alpha C_i^\alpha - \lambda_\beta C_i^\beta$$

Two degrees of freedom exist so we can define the interface setting $\Gamma_w^H = \Gamma_N^H = 0$ by choice of λ_α and λ_β . Therefore:

$$\begin{pmatrix} n_M \\ n_w \end{pmatrix} = \begin{pmatrix} C_N^\alpha & C_N^\beta \\ C_w^\alpha & C_w^\beta \end{pmatrix} \begin{pmatrix} \lambda_\alpha \\ \lambda_\beta \end{pmatrix}$$

The expression for λ_β and (and λ_α) can then be recast:

$$\lambda_\beta = \frac{\frac{n_w}{C_w^\beta} - \frac{C_w^\alpha}{C_w^\beta} \frac{n_M}{C_N^\alpha}}{1 - \frac{C_N^\beta}{C_N^\alpha} \frac{C_w^\alpha}{C_w^\beta}}$$

Remembering the concentrations we neglected, we can write $\Gamma_M^H = n_M$ and $\Gamma_S^H = n_S - \lambda_\beta C_S^\beta$. At this point it is convenient to assume that $n_i = n_i^1 + n_i^2 + n_i^M$, corresponding to amounts in the l_1 , l_2 and monolayer regions. To proceed further we need to assume a system model which is rather illustrative but still fairly reasonable. We assume that concentrations retain their distinct values right to the monolayer, i.e. $n_i^1 = l_1 C_i^\alpha$ and $n_i^2 = l_2 C_i^\beta$. In the examined case (air/water)

$$\frac{C_N^\beta}{C_N^\alpha} \cdot \frac{C_w^\alpha}{C_w^\beta} \ll 1 (\approx 3.71 \times 10^{-7})$$

so, after a bit of routine algebra, we obtain:

$$\Gamma_S^H \approx n_S^M - \frac{C_S^\beta}{C_w^\beta} n_w^M + \frac{C_w^\alpha}{C_w^\beta} \cdot \frac{C_S^\beta}{C_N^\alpha} \cdot n_N^M$$

Therefore the excess surfactant concentration at Hansen's interface for a given surface area can be roughly given by $\Gamma_S^H \approx n_S^M/A$, with negligible error for any reasonable values of n_w^M and n_N^M .

Appendix B: List of symbols

A	total area at the interface
\hat{A}_M	area per molecule of the film-forming substance
\bar{A}_M	partial molar area of the film-forming substance
\bar{A}_S	partial molar area of the surfactant
A_M^*	area per molecule of the film-forming amphiphilic compound at collapse
A'_M	Pethica's partial molar area of a monolayer
\tilde{A}_M	partial molar area of surfactant expressed in units of "equivalent area" of the film-forming substance
a_M	apparent cross-sectional area of a monolayer molecule
$A_{S,1}^{(i)}$	i th surfactant partial molar area estimation according to generalized Pethica hypothesis
$A_{S,2}^{(i)}$	i th surfactant partial molar area estimation according to the admissible curve
m_S	surfactant concentration (molality of surfactant)
n_S^H	number of adsorbed surfactant molecules at the interface
n_M	number of spread film-forming molecules at the surface
N_A	Avogadro's number
P	pressure
R	gas constant
S^H	excess entropy at the surface per unit area
T	temperature
V^H	excess volume at the surface per unit area

Greek letters

Δ	partial area increment in the numeric solution (step)
$\Delta\Gamma_S$	penetration variation quantity regarding the monolayer-free system
$\Delta\Pi_S$	surface pressure variation quantity regarding

ϵ	stop criterion for the numerical algorithm
γ_S	equilibrium surface tension of the mixed monolayer
Γ_S^H	surface excess number of moles of penetrating substance at the interface
Γ_M	surface excess number of moles of film-forming substance
Γ_S^0	surfactant adsorption at the air/water monolayer-free system
Γ_S	surfactant penetration quantity
Γ_w	adsorption into the accessible area
λ_i	absolute activity of the substance i , $i = S, M$
μ_i	chemical potential of species i , $i = S, M$
π_S	surface pressure of the mixed film
π_S^0	surface pressure of the monolayer-free system

Subscripts

M	monolayer molecules
S	surfactant molecules
i	compound i of the mixed film

Superscripts

0	monolayer-free system
H	Hansen quantities at the interface
(i)	i th numerical iteration

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