

ANOTHER LOOK AT THE SURFACTANT ADSORPTION PHENOMENON

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ABSTRACT

The surfactant penetration into an insoluble spread monolayer at the interface between two immiscible phases has long subject of several approaches. Evidence of the existence of such a phenomenon is an increase in the initial surface pressure of a monolayer owing to surfactant adsorption. This work overview the equations proposed to quantify the penetration of a surfactant into a mixed monolayer containing an insoluble monolayer and one adsorbed species. Particularly, it is brought up a novel interpretation of the classical Langmuir and Frumkin isotherms. The idea is to furnish a better understanding on the limitations of such models. It also derives an alternative vindication of the modified Motomura's equation recently introduced by the authors. Results are compared with those newly obtained by Sundaram-Stebe and by Santos-Magalhães et al. Surface plots of adsorption isotherms are also examined.

1. INTRODUCTION

A phenomenon of special interest in the Colloid Science with particular applications in the pharmaceuticals, herbicides, petroleum recovery, and detergency is that referred to as monolayer penetration. A soluble surface-active material in the substrate is injected just below the surface and enters into the spread surface monolayer. This study addresses models to quantify the adsorption of molecules at interface. It has mainly been motivated by quantifying model drug / proteins adsorption into biomembranes modeled as monolayers.

According to Hansen's thermodynamic approach, the equilibrium interface tension γ for a penetrated monolayer by a sole surfactant gives: $d\gamma = -S^H dT + V^H dP - \Gamma_2^H d\mu_2 - \Gamma_1^H d\mu_1$, where the superscript H refers to Hansen quantities, subscripts 1 and 2 stand for monolayer and surfactant, respectively, μ_i for the chemical potential of compound i , and S^H and V^H are the excess entropy and the volume at the interface. By assuming temperature T and pressure P to be constant, considering λ_i the absolute activity of the substance i , π the surface pressure of the mixed monolayer and $R=8.3143 \text{ J.mol}^{-1}.\text{K}^{-1}$ the gas constant, we obtain by assuming that surface-active material activities in the dilute solution are very low:

$$\frac{1}{RT} \left(\frac{\partial \pi}{\partial \ln C_2} \right)_{T,P,\Gamma_1} = \left(\frac{\partial \frac{\Gamma_2^H}{\Gamma_1}}{\partial \ln \Gamma_1} \right)_{T,P,C_2} \quad (1)$$

$\Delta\pi$ denotes the increase in the surface pressure of a film after surfactant injection below the surface, i.e. $\pi(C_2, \Gamma_1) - \pi(0, \Gamma_1)$. By integrating (3) regarding C_2 instead of \hat{A}_M , we derive a similar expression to Sundaren-Stebe's equation, excepted for the fact that Hansen's interface is used instead of Gibbs-Duhem's interface,

$$\Delta\pi = RT \int_0^{C_2} \left\{ \frac{\partial \left(\frac{\Gamma_2^H}{\Gamma_1} \right)}{\partial \left(\frac{1}{\Gamma_1} \right)} \right\}_{T, P, C_2} \frac{dC_2}{C_2} \Bigg|_{\Gamma_1} . \quad (2)$$

2. EXAMINING THE SURFACTANT PENETRATION

We rewrite the key equation in terms of normalized quantities $x_i = \Gamma_i / \Gamma_{i,\infty}$ $i=1,2$ and we denote the surfactant concentration by k . By a change of variables, it follows $\Delta\pi = RT \Gamma_{2,\infty} \int_0^k \left\{ x_2 - x_1 \left(\frac{\partial x_2}{\partial x_1} \right) \right\} \frac{dk}{k}$.

$$\frac{\partial \Delta\pi}{\partial k} = \frac{RT \Gamma_{2,\infty}}{k} \left\{ x_2 - x_1 \left(\frac{\partial x_2}{\partial x_1} \right) \right\}, \quad (3)$$

which may be rewritten as an Euler's homogeneous differential equation. The solution of such a differential equation is easily obtained by Mathematica[®] as DSolve[x y'[x] - y[x] == f(x), y[x], x] Consequently,

$$x_2 = x_1 \left(c_1 - \frac{k}{RT \Gamma_{2,\infty}} \int \left(\frac{\partial \Delta\pi}{\partial k} \right)_{x_1} \frac{dx_1}{x_1^2} \right). \quad (4)$$

Setting a constraint $x_2(1)=0$ (initial condition) and rewritten in terms of non-normalized variables,

$$\Gamma_2^H = C_2 \Gamma_1 \int_{\Gamma_1}^{\Gamma_{1,\infty}} \frac{1}{RT} \left(\frac{\partial \Delta\pi}{\partial C_2} \right)_{T, P, \Gamma_1} \frac{d\Gamma_1}{\Gamma_1^2}. \quad (5)$$

A relationship with the classical Alexander-Barnes model can be derived using the Mean Value Theorem (MVT):

$$\Gamma_2^H = \frac{1}{RT} \left(1 - \frac{\Gamma_1}{\Gamma_{1,\infty}} \right) \left(\frac{\partial \Delta\pi}{\partial \ln C_2} \right)_{T, P, \bar{\Gamma}_1}, \quad (6)$$

which has virtually the same form as the classical penetration equations.

3. BY WAY OF INTERPRETATION

Comparing eqn. (12) with the Pethica equation, we find out that the main problem is the establishment of boundary condition. The concept of the Partial molar area may be used and one can set $x_2(\bar{x}_1) = 0$, where \bar{x}_1 stands for the (normalized) partial area of the film-forming substance, defined as $\bar{x}_1 = (1 / \bar{A}_M) / \Gamma_{1,\infty} = \bar{A}_M^\infty / \bar{A}_M$.

Therefore,

$$\Gamma_2 = \frac{1}{RT \hat{A}_M} \int_{\hat{A}_M}^{\hat{A}_M^\infty} \left(\frac{\partial \Delta\pi}{\partial \ln C_2} \right)_{\hat{A}_M} d\hat{A}_M, \quad (7)$$

and therefore, the approach above described provides an alternative evidence of a correction that Motomura's equation requires.

No extra-thermodynamic hypotheses have been used until now, which agree with Hall's framework. Probably we cannot derive a precise closed formula because of the dependence of $\Delta\pi$ "variation

model" on k , fixed x_1 . For instance, we can assume that $\Delta\pi$ is proportional to $\ln(1+k)$ as Langmuir (model) or Frumkin's correction and so on.

By supposing a Langmuir relationship on the surface pressure changes due to surfactant penetration, i.e., $\Delta\pi = RT\Gamma_{2,\infty} \ln(1+k)$ as independent on x_1 , the adsorption isotherm eqn.(10) becomes the classical one $\frac{x_2}{(1-x_1)} = \frac{k}{k+1}$ ($x_1 \rightarrow 0$), as expected. The Frumkin model is the main model that accounts

for non-ideal interactions of both insoluble-soluble (1-2) and/or soluble-soluble (2-2) components.

One simplified model can be established remarking that asymptotic $\Delta\pi$ curves are like figure 1. We put $(RT\Gamma_{2,\infty})^{-1} \Delta\pi = \ln(1+k \cdot h(x_1))$. Indeed, we have asymptotically tends toward $\Delta\pi \rightarrow \ln k + \ln h(x_1)$. The term $\ln h(x_1)$ stands then for the intercept in a log-scale surface pressure changes vs. concentration plot. Such a function $h(\cdot)$ may be accounted for non ideal interactions of components in the mixed monolayer.

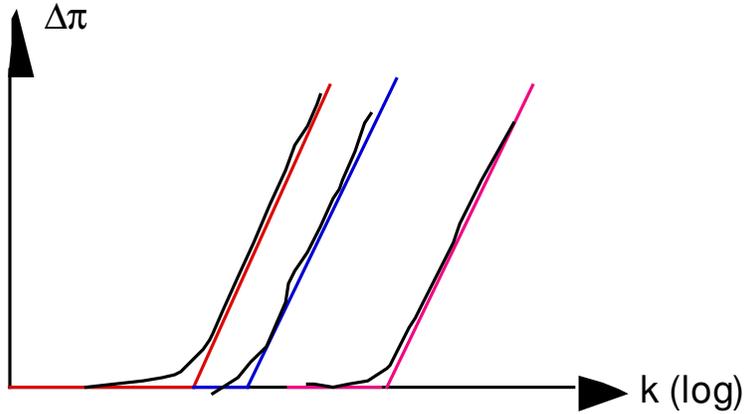


Figure 1. Asymptotic curves surface pressure changes vs. surfactant concentration.

Langmuir's model assumes $\Delta\pi = RT\Gamma_{2,\infty} \ln(1+k)$ so $(\partial\Delta\pi / \partial k)$ does not depends on x_1 . Therefore eqn.(14) reduces to the Langmuir isotherm when $h(A_M^*)=1$ and $\bar{x}_1 = 1$.

Frumkin's model for 1-2 interactions assumes $h(\cdot)=\exp(-K_1x_1)$ and also $\bar{x}_1 = 1$ so that $\frac{x_2}{(1-x_1)} = \frac{k'}{k'+1}$

($x_1 \rightarrow 0$). Thus, the intercept of the asymptotic straight line for high surfactant concentration in the log-scale surface pressure changes vs. concentration plot is proportional to the (normalized) surface concentration Γ_1 , i.e., $\lim_{k \rightarrow \infty} \ln h(x_1) = -K_1x_1$.

In order to take into account for *insoluble-soluble* component interactions (1-2 interactions), we define a "weighted" surfactant concentration $k'=k \cdot \exp(-K_1x_1)=k'(k,x_1)$.

$$\Delta\pi = RT\Gamma_{\infty 2} \ln(1+k') + RT\Gamma_{\infty 2} K_1x_1(1-x_1) \frac{k'}{k'+1}$$

In that case, Frumkin's isotherm is given by $\frac{x_2}{(1-x_1)} = \frac{k'}{k'+1}$ ($x_1 \rightarrow 0$).

In order to find out the behavior of $\Delta\pi$ when adsorption is driven by that isotherm, Eqn.(6) can be rewritten as

$$(RT\Gamma_{2,\infty})^{-1} \Delta\pi = \int_0^k x_2 \frac{dk}{k} - \int_0^k x_1 \frac{\partial x_2}{\partial x_1} \frac{dk}{k} = (1-x_1) \ln(1+k') - x_1 \frac{\partial}{\partial x_1} \{(1-x_1) \ln(1+k')\}.$$

After a few algebraic manipulations, we derive

$$\Delta\pi = (RT\Gamma_{2,\infty}) \left\{ -\ln\left(1 - \frac{x_2}{1-x_1}\right) - \frac{h_1'(x_1)}{h_1(x_1)} x_1 x_2 \right\}. \quad (8)$$

For classical Frumkin model $h_1(x_1) = \exp(-K_1 x_1)$ and the above equation reduces to the expected formula. A class of generalized non-ideal adsorption models is given by

$$\frac{x_2}{1-x_1/x_1} = \frac{k'}{1+k'}, \quad (9)$$

where $k' = kh_1(x_1)h_2(x_2)$ is an "apparent" concentration normally reduced due to component interactions.

The limiting cases are:

i) $k \rightarrow 0 \Rightarrow x_2 \rightarrow 0$; $\Delta\pi \rightarrow 0$ ii) $x_1 \rightarrow 0 \Rightarrow x_2 \rightarrow 1$; $\Delta\pi \rightarrow \pi(C_2)$ iii) $x_1 \rightarrow 1 \Rightarrow x_2 \rightarrow 0$; $\Delta\pi \rightarrow 0$.

The former condition always holds, but the following imply $h(0)=1$ and $h(1)=0$, respectively. Further models can be derived by assuming a different behavior to $h(\cdot)$, e.g., $h(x_1) = \exp\left[-K_1 \frac{x_1}{1-x_1}\right]$ referred to as a non-classical Frumkin model.

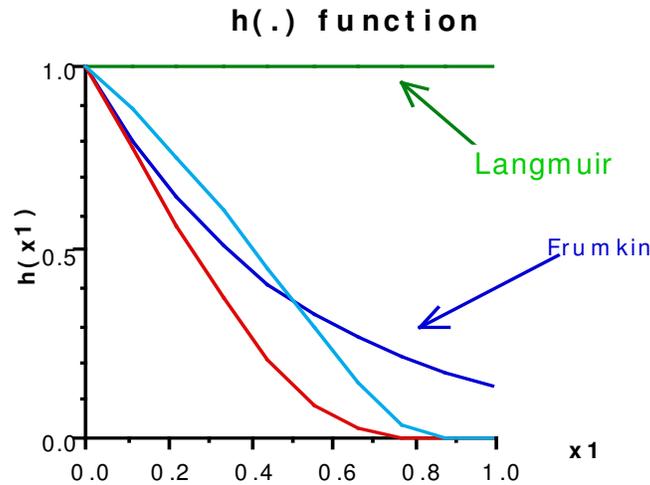


Figure 2. Different 1-2-interaction models. Classical $K_1=0, K_2=2$ (Langmuir, Frumkin); Non-classical Frumkin $K_1=1, K_2=2$.

The governing equation for $\Delta\pi$ define a surface plot $\Delta\pi = \Delta\pi(x_1, k)$ as sketched in the figure 3. Normalized values $(RT\Gamma_{2,\infty})^{-1} \Delta\pi$ are considered on the z-axis.

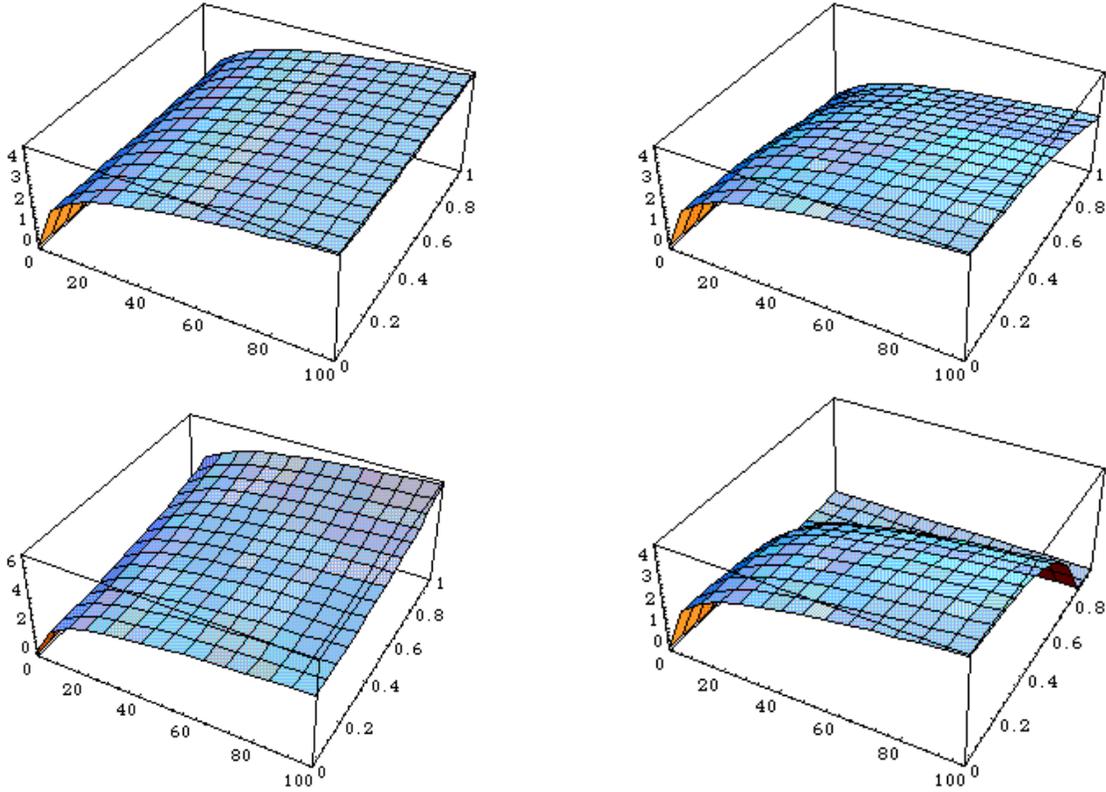


Figure 3. $\Delta\pi$ Surface plots: a) Langmuir $h(x_1)=1$, b) Frumkin repulsion $h(x_1)=\exp(-2x_1)$, c) Frumkin cohesion $h(x_1)=\exp(2x_1)$, d) Non-classical Frumkin $h(x_1)=\exp(-x_1/(1-x_1))$.

For a spread insoluble film near collapse, it is often expected a negligible increase in the surface pressure due to penetration of the bulk soluble surfactant, i.e., $\lim_{x_1 \rightarrow 1} \Delta\pi = 0$. Such a feature is not fulfilling by a $\Delta\pi$ corresponding to the classical Langmuir and Frumkin models.

4. CONSEQUENCES IN AN ISOMORPHIC PROBLEM: THE GALVANI POTENTIAL DROP

Hall showed that the estimation of surfactant penetration into an insoluble monolayer is an isomorphic problem with estimation of Galvani potential (ψ) changes across a mercury/electrolyte solution interface as the solvent composition is varied. Supposing that the inner potential of all neutral salts in solution remains constant, the phenomenon is described by $d\sigma = -q d\psi - \Gamma'_\alpha d\mu_\alpha$, where σ denotes the interfacial tension, q stands for the charge density of the mercury, μ_α is the chemical potential of the nonionic component α and Γ'_α is an excess quantity. Corresponding equations are (respect. Eqn.(3), (5) and (8)):

$$\left(\frac{\partial\Delta\sigma}{\partial\mu_\alpha}\right)_q = \left(\frac{\partial(\Gamma'_\alpha/q)}{\partial(1/q)}\right)_{\mu_\alpha}, \quad (10a)$$

$$\Delta\sigma = \int_0^{\mu_\alpha} \left(\frac{\partial(\Gamma'_\alpha/q)}{\partial(1/q)}\right)_{\mu_\alpha} d\mu_\alpha, \quad (10b)$$

$$\frac{\partial \Delta \sigma}{\partial \mu_{\alpha}} = \Gamma'_{\alpha} - q \frac{\partial \Gamma'_{\alpha}}{\partial q}. \quad (10c)$$

Equivalent equations to adsorption phenomena can be derived and the solution of the Differential equation yields:

$$\Gamma'_{\alpha} = q \left(c_1 + \int \left(\frac{\partial \Delta \pi}{\partial \mu_{\alpha}} \right)_q \frac{dq}{q^2} \right) \quad (11)$$

The gist of the matter is setting initial conditions. If we suppose $\Gamma'_{\alpha}(\bar{q}) = 0$ then

$$\Gamma'_{\alpha} = q \int_q^{\bar{q}} \left(\frac{\partial \Delta \pi}{\partial \mu_{\alpha}} \right)_q \frac{dq}{q^2} \quad (12)$$

Thus, the excess quantity Γ'_{α} can be determined from experimental measurements only knowing \bar{q} .

5. REVISITING SURFACTANT ADSORPTION ISOTHERMS

Since the surface excess Γ_2 (or x_2) depends upon both surfactant concentration C_2 (or k) and surface concentration of the film-forming substance Γ_1 (or x_1), Frumkin isotherms may be better described by a surface plot $x_2 = x_2(x_1, k)$.

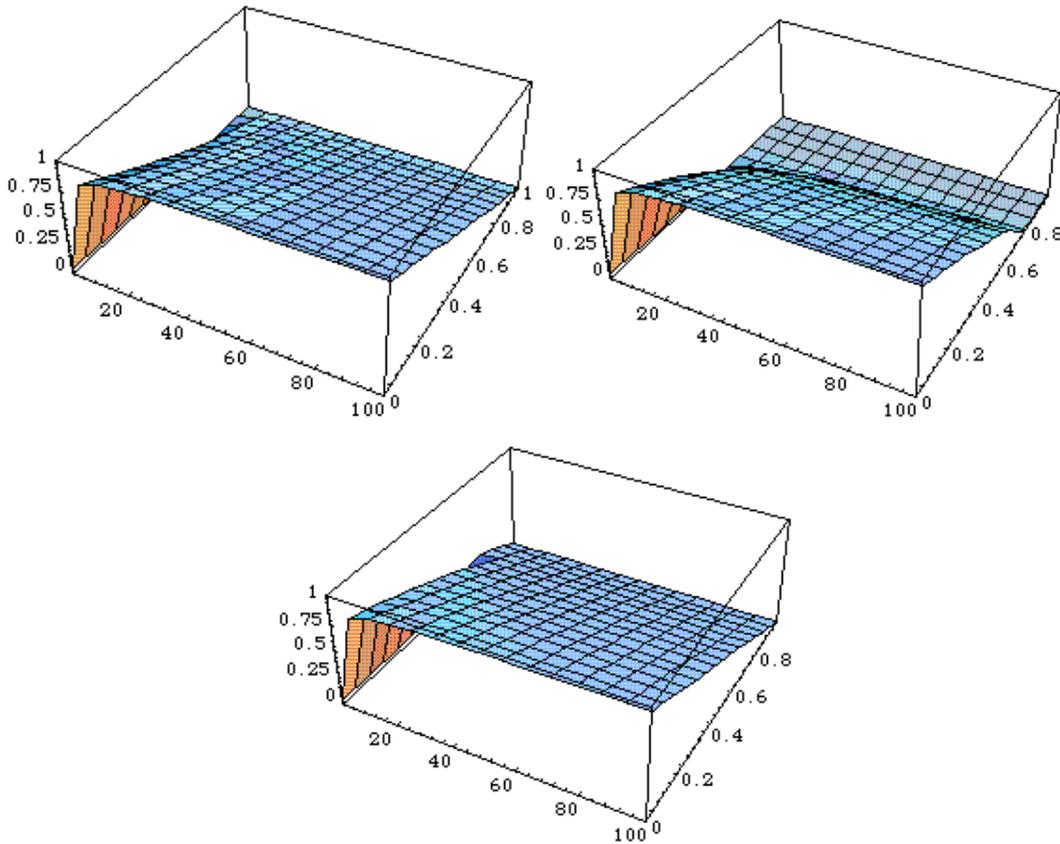


Figure 4. a) Frumkin's isotherm for 1-2 interactions ($K_I=2$). b) Non-classical Frumkin's isotherm for 1-2 interactions ($K_I=-2$). c) Non-classical Frumkin's isotherm for 1-2 interactions ($K_I=2$).

6. CONCLUSIONS

It is presented a new glance of Langmuir and Frumkin's models throughout the investigation of the asymptotic behavior of $\Delta\pi$ isotherms at high surfactant concentrations. Experimental data relating the increase in the surface pressure of a monolayer due to a surfactant adsorption enable to quantify the surfactant surface excess. The intercept of the straight line should be plotted in a scattergram versus x_I (or Γ_1) and some correlation indicates possible 1-2 type interactions. A family of non-ideal models for the equilibrium penetration of an insoluble spread monolayer at interface by a single bulk soluble surfactant is derived. Consequences on an isomorphic problem (namely Galvani potential drop) are also discussed. Surface isotherms are revisited in terms of surface plots. It clarifies the relationship between the Frumkin model and those previously known as well as allows gaining some insight into 1-2 compound interactions.

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