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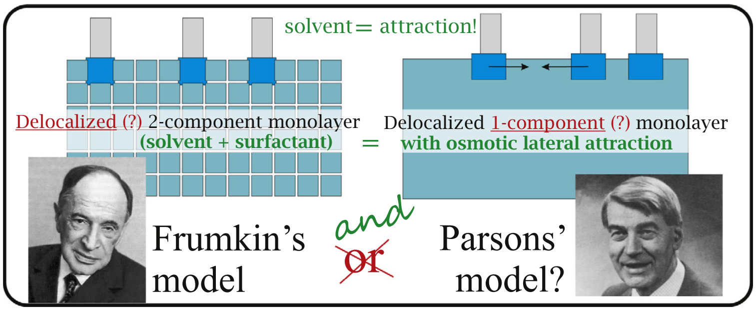
Effective osmotic cohesion due to the solvent molecules in a delocalized adsorbed monolayer

Radomir I. Slavchov [a],*, Ivan B. Ivanov [b]

[a] Department of Chemical Engineering, University of Cambridge, West Site, Philippa Fawcett Drive, Cambridge CB3 0AS, United Kingdom
[b] Laboratory of Chemical Physics and Engineering, Faculty of Chemistry and Pharmacy, Sofia University, 1 J. Bourchier, 1164 Sofia, Bulgaria

GRAPHICAL ABSTRACT



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ABSTRACT

A molecular thermodynamic model is derived for an uncharged delocalized surfactant monolayer adsorbed at a liquid interface, taking explicit account for the solvent molecules present in the monolayer. The model is based on the scaled particle theory of hard-disc mixtures, and is also extended to sticky discs (i.e. attraction between the adsorbed molecules). Upon compression of the adsorbed layer, the solvent is expelled from it. The respective osmotic effect on the equation of state is shown to be equivalent to an effective lateral depletion attraction between the surfactant molecules. This effective osmotic cohesion causes an increase of the value of the attraction parameter β of the monolayer. The smaller the size of the surfactant polar head group is, the larger the effective attraction the model predicts. This trend is verified with data for the adsorption at water|air surface of alcohols, undissociated acids, and hexaethyleneglycol monoalkyl ethers. The proposed theory allows the amount of solvent in the monolayer to be estimated, which is shown to be important for the neutron reflectivity of the surface.

1. Introduction[1]

Half a century has passed since the famous scientific "battle" between Frumkin and his collaborators, and Parsons, Buff and Stillinger. The battlefield was the theory of adsorption [1]. Parsons, Buff and Stillinger [2–4] argued that a site model such as Langmuir's cannot provide a satisfactory description for the strictly *delocalized* adsorption of ions at the water|mercury interface; they have championed instead the theory of two dimensional (2D) hard-disc liquids and a nearly exact equation of state (EoS) due to Helfand, Frisch, and Lebowitz [5] (HFL). In response, Frumkin [1,6] reminded that the Langmuir equation, when applied to adsorption of ions from aqueous solution, is not merely a surface

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* Corresponding author.
E-mail address: ris26@cam.ac.uk (R.I. Slavchov).

[1] Days before the completion of this work, Professor Ivan B. Ivanov (1935–2018) has sadly passed away. His relentless passion for knowledge, eloquence, and strength of character will always be an example to follow for me.

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site model – it is a direct consequence of the lattice (Flory-Huggins) theory for a *mixture* of water and ions. Frumkin further pointed out that a single component EoS such as HFL, with its complete neglect of the water molecules, is no sounder than the Langmuir model. The response of Parsons – then a young man having a great respect for his senior colleague [7] – to Frumkin's criticism was half-hearted [8].

The Langmuir model and its derivatives still dominate the adsorption literature [9–15]. Significantly, Parsons himself was not persistent in pursuing a delocalized description of the adsorbed layer and, in his later works, he developed localized models for liquid interfaces, e.g., [16]. This might seem as a victory for Frumkin, but Frumkin himself was not too convinced either, stating that his arguments "*cannot serve, of course, as a sufficient theoretical basis for the application of Langmuir's equation to real systems... but it seems to me that these arguments can help when choosing the direction for the further development of the theory of adsorption at the surface of solutions*" [6]. Occasionally, variants of the HFL EoS are used for surfactant monolayers [17–24], and indeed have clear advantages. In fact, the application of the Langmuir model (or its extensions to cohesive monolayers, such as Frumkin's model) to surfactant films adsorbed at liquid interfaces leads to several paradoxes which can be traced back to the delocalized nature of the monolayer [24]:

(i) the Langmuir model's area per molecule determined from adsorption data is as much as twice as large as the crystallographic one, while, in theory, the two quantities should have similar values.
(ii) The area parameter of Langmuir's model is not transferable from one type of interface to another – to fit the experimental data, one has to use one area of the surfactant for water|air (W|A) and another for water|oil interfaces.
(iii) Frumkin's model [25] (*localized* EoS with attraction) modifies Langmuir's to account for 1st neighbours' attraction via the lateral attraction parameter β. When applied to adsorption data for surfactants at water|oil interfaces, this model yields unphysical negative values of β, a paradox that disappears when Parsons' model (*delocalized* EoS with attraction) is used instead – the expected small positive β are obtained with it.

In any case, the advantage of this or the other model when compared to experimental data does not change the fact that both sides in the dispute were most definitely correct: the Langmuir model and the lattice theory of adsorption provide a description of the adsorption layer that is localized, which is not realistic for liquid interfaces; and, indeed, the HFL model is unconvincing for it neglects completely the solvent molecules at the surface (while the amount of solvent in the monolayer is essential for its properties, e.g., Ref. [26]).

The aim of this work is to resolve the dispute by providing a description that is both delocalized and accounts for the solvent. In other words, we propose a theory of the osmotic effect due to the solvent molecules present in a monolayer adsorbed at a liquid interface (*delocalized* adsorption) on the thermodynamic properties of this monolayer. In Section 2.2, we analyse the theory of a 2-component hard-disc mixture (direct attraction neglected) and we show that the presence of solvent in the monolayer results in effective osmotic cohesion of it (2D lateral depletion attraction between the surfactant head groups). In Section 2.3, we simplify the results for hard-disc mixture by making use of the concept for osmotic cohesion, and in Sections 2.3 and 3, we generalize it to strongly cohesive (attractive) surfactant molecules. The new model so-obtained is a natural theoretical approach to adsorption of non-ionic amphiphiles at liquid interfaces. We demonstrate the feasibility of the model by comparing it to data for the adsorption at water|air of 3 homologous series of surfactants of different hard-disc area of the polar head group: alcohols, non-dissociated acids and hexaethyleneglycol monoalkyl ethers (Section 3).

The terminology we use in this manuscript is standard for the field of statistical and chemical thermodynamics (localized, delocalized, osmotic effect, depletion force), but for the ease of readers of other backgrounds and to avoid confusion, we provide a description in the supplementary material S1; there, a list of symbols and abbreviations is also given.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.08.025.

2. Theory

2.1. Single-component hard-disc liquid

Before approaching the problem of two-component monolayers, we will briefly review the theory of delocalized single-component hard-disc 2D fluid. Helfand, Frisch and Lebowitz derived an almost exact surface EoS for delocalized adsorption layer of hard discs in the absence of attraction, by using the apparatus of the scaled particle theory [5]:

$$\frac{\alpha_s \pi^S}{k_B T} = \frac{\psi_s}{(1-\psi_s)^2}. \tag{1}$$

Here, π^S is the surface pressure of the monolayer, $\pi^S \equiv \sigma_0 - \sigma$; σ is surface tension; σ_0 is surface tension of the neat surface (at $\psi_s = 0$); $\psi_s \equiv \alpha_s \Gamma_s$ is the surface fraction covered by surfactant; Γ_s is adsorption of surfactant; α_s is the hard-disc area of the surfactant molecule. The HFL model has been found to agree excellently with data for monolayers of both ionic and non-ionic surfactants at water|oil interfaces [23,24], where other popular models lead to unreasonable adsorption parameters. The hard-disc (repulsion only) HFL model is not suitable for W|A, as at this interface there exists a significant lateral van der Waals attraction between the adsorbed molecules. Parsons [3] generalized the HFL EoS (1) to attractive molecules by adding to it a binary interaction term, $\beta\psi_s^2$, to obtain an EoS that has been reinvented many times [17,20]:

$$\frac{\alpha_s \pi^S}{k_B T} = \frac{\psi_s}{(1-\psi_s)^2} - \beta\psi_s^2; \tag{2}$$

here, β is the so-called lateral attraction parameter. The attraction term in Eq. (2) is semi-empirical; in result, the model is unsatisfactory at high ψ_s and large values of β [24]. A more reliable EoS for attractive molecules is offered by the sticky disc (SD) model of Ivanov et al. [21–24]:

$$\frac{\alpha_s \pi^S}{k_B T} = \frac{R_\beta - 1}{2\beta(1-\psi_s)}, \quad \text{where} \quad R_\beta = \sqrt{1 + 4\beta\frac{\psi_s}{1-\psi_s}}. \tag{3}$$

The corresponding SD surface activity coefficient γ_s follows from the Gibbs isotherm, $d(\alpha_s \pi^S/k_B T) = \psi_s d(\ln\gamma_s\psi_s)$, as:

$$\ln\gamma_s = -\ln(1-\psi_s) + \left(2 + \frac{1}{\beta}\right)\ln\frac{2}{1+R_\beta} + \frac{\psi_s(4-3\psi_s)}{(1-\psi_s)^2}\frac{2}{1+R_\beta}. \tag{4}$$

The respective adsorption isotherm (the chemical equilibrium condition for the surfactant at the surface and in the bulk) of the SD model reads

$$\alpha_s K_a C_s = \gamma_s \psi_s, \tag{5}$$

where K_a [m] is the adsorption constant ($RT\ln K_a$ is the standard adsorption free energy) and C_s [m^{-3}] is the concentration of the surfactant [24].