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Short communication

The surface chemical potential from a surface equation of state versus Butler's equation

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ABSTRACT

In the last years, our research group has been committed to the development of bulk–surface equilibrium models that relate surface tension, bulk composition, and bulk activity coefficients; in this paper, we focus on two of them. The starting premise is the equality of bulk and surface chemical potentials. Instead of the common practice of expressing the surface chemical potential analogously to the bulk, in the first model, surface chemical potential is obtained from the integration of Gibbs adsorption equation coupled to Volmer's equation of state, and written as a function of surface pressure shown to be a measure of surface activity. In the second model, Gibbs adsorption equation was evaluated in the surface saturated region and then coupled to the bulk chemical potential avoiding the use of an explicit expression for the surface. Both models are equivalent in meaning and structure to the widely accepted Sprow and Prausnitz equation (Trans. Faraday Soc. 62 (1966) 1105), originally derived by Butler (Proc. R. Soc. A 138 (1932) 348), where it is necessary to introduce non-thermodynamic approximations for the calculation of partial molar areas, surface activity coefficients and surface composition. On the contrary, the parameters of the two proposed models are attained from the fitting to the experimental data. Obeying a monolayer model, Butler arrived to the conclusion that bulk and surface chemical potentials are not equal, but it is demonstrated that in Gibbs adsorption equation, the equality of chemical potentials is valid and that the models are thermodynamically consistent.

1. Introduction

The thermodynamic description of a bulk liquid phase in equilibrium with its surface has been the purpose of several models relating bulk and interfacial properties, namely phase composition and surface tension, aiming to elucidate the structure of the surface. There have been two main streams for the development of such models. One is the proposal of expressions for the chemical potential at the surface, like in Belton and Evans [1] and Fowler and Guggenheim [2,3] works, where the starting point is the Helmholtz energy change of the system upon the formation of a surface and its consequent minimization, as Shereshefsky [4] also did posteriorly, and on the other hand, there is the integration of Gibbs adsorption equation under determined frontier conditions or coupling to phenomenological isotherms like in Feinerman's approach [5]. Alternatively, in the multi-cited work of Eberhart [6], the mixing rule for the surface tension of the mixture plays the main role before the establishment of bulk and surface equilibrium through partition coefficients. Among these models, the so-called Sprow and Prausnitz equation (Eq. (1)) [7], which in fact was first presented by Butler [8] and derived again in Refs. [1,3], has gained popularity since Sprow and Prausnitz paper [9]. It is widely used in metallurgy, in proteins, surfactants and organic solvents adsorption [10–13].

$$\sigma = \frac{a_i}{\bar{a}_i}\sigma_i + \frac{RT}{\bar{a}_i}\ln\frac{x_i^s\gamma_i^s(x_i^s)}{x_i^b\gamma_i^b(x_i^b)} \tag{1}$$

where σ is the surface tension of the liquid mixture, a_i is the molar area of pure component i, $\bar{a}_i$ is its partial molar area in the mixture, x_i^s and x_i^b are the molar fractions in the surface and in the bulk, respectively, and $\gamma_i^s\left(x_i^s\right)$ and $\gamma_i^b\left(x_i^b\right)$ are the corresponding activity coefficients. Several authors, like Rafati et al. [14] and Pstruś [15] have used a set of Eqs. (1), one for each component of the system, to reproduce surface tension data through different approximations for calculating the partial molar areas, the surface and bulk activity

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Nomenclature

σ	surface tension of the liquid mixture (N/m)
σ_i	surface tension of species *i* or solute (N/m)
a_i	molar area of species *i* (m^2/mol)
$\bar{a}_i$	partial molar area of *i* (m^2/mol)
x_i	molar fraction
γ_i	activity coefficient
L	geometric factor
N_{Av}	Avogadro's number
v_i	molar volume (m^3/mol)
μ_i	chemical potential
μ_i^0	standard chemical potential of pure component
π	surface pressure (N/m)
π^0	maximum surface pressure (N/m)
π^*	reduced surface pressure
α	intermolecular interaction constant
A	area per mole of component I in the surface (m^2/mol)
A_0	two-dimensional repulsive van der Waals-type constant (m^2/mol)
A	area of the surface (m^2)
Γ_i	two-dimensional surface concentration (mol/m^2)
Ni	number of moles
T	temperature
p	pressure
G	Gibbs energy
U	internal energy
S	entropy
V	volume

Subscripts or superscripts

s	surface
b	liquid bulk
i	species *i* or solute
solv.	solvent
sat.	saturation conditions

coefficients, and the molar fractions in the surface. For example, Pstruś computed the molar areas using the following equation:

$$a_i = L N_{Av}^{1/3} v_i^{1/3} \tag{2}$$

where v_i is the molar volume of pure component *i*, *L* is a geometric factor which sometimes considers a molecular packing, and N_{Av} is Avogadro's number. For the activity coefficients, it was assumed that surface activity coefficients were 17% smaller than bulk activity coefficients based on the ratio of the coordination numbers in bulk and surface.

In his seminal work in 1932, Butler arrived to the conclusion that the chemical potential in the surface μ_i^s and in the bulk μ_i^b are not equal (Eq. (3)) on the contrary of what many authors [16–20], including us [21,22], have assumed to be true.

$$\mu_i^s = \mu_i^b + \bar{a}_i\sigma \tag{3}$$

Expressing μ_i^s analogously to μ_i^b as a function of phase composition and activity coefficients (Eqs. (4) and (5)), the Butler (or Sprow and Prausnitz) equation is afforded (Eq. (1)).

$$\mu_i^s = \mu_i^{0,s} + RT\ \ln x_i^s \gamma_i^s(x_i^s) \tag{4}$$

$$\mu_i^b = \mu_i^{0,b} + RT\ \ln x_i^b \gamma_i^b(x_i^b) \tag{5}$$

where μ_i^0 is the surface chemical potential of the pure species, and $\mu_i^{0,s} = \mu_i^{0,b} + a_i\sigma_i$. From Eqs. (3) and (4), it is commonly said that the surface chemical potential is given by Eq. (6) and in this way, bulk and surface chemical potentials are equal, $\mu_i^b = \mu_i^s$ [16].

$$\mu_i^s = \mu_i^{0,s} + RT\ \ln x_i^s \gamma_i^s(x_i^s) - \bar{a}_i\sigma \tag{6}$$

Fainerman and Vollhardt [17] have substituted the so-called Butler's chemical potential (although Butler did not write Eq. (6), see Ref. [8]) into Gibbs adsorption equation for a binary system with Gibbs' dividing surface (Eq. (7)).

$$d\pi = \Gamma_i d\mu_i^s \tag{7}$$

After integration under different approximations, a version of the two-dimensional van der Waals' equation (Eq. (8)) and Volmer's equation (Eq. (9)) are obtained,

$$\pi = \frac{RT}{A - \bar{a}_i} - \frac{\alpha RT \bar{a}_i}{A^2} \tag{8}$$

$$\pi = \frac{-RT}{A - \bar{a}_i} - \pi^c \tag{9}$$

where π is the surface pressure defined as the difference between the surface tension of the pure solvent and of the solution ($\pi = \sigma_{\text{solv.}} - \sigma$), π^c is the cohesion pressure ($\pi^c = \sigma_{\text{solv.}} - \sigma_{\text{solute}}$), the area *A* is the reciprocal of the solute surface two-dimensional concentration Γ_i ($A = 1/\Gamma_i$), and α is an intermolecular interaction constant (denoted as *a* in Ref. [17]). Ruckenstein and Li [23] have also used Eq. (6) to arrive to Eqs. (8) and (9), and to a surface equation of state for clustering, aided by the relation between activity coefficients and the enthalpy of mixing.

Our purpose in this paper is to show that Butler's equation (Eq. (1)) is analogous to two equations presented by our research group for describing bulk–surface equilibrium [21,24], arising from the integration of Gibbs adsorption equation. In these models, the only variables are the experimental surface tension and solute molar fraction data, representing a notable advantage over Butler's equation (Eq. (1)) for which approximations for the estimation of partial molar areas, surface activity coefficients and surface composition are needed. For the derivation of the first of our equations, no assumptions were made except for considering Volmer's equation of state valid in the dilute region to obtain an expression for surface chemical potential. The final model has been probed to adequately describe experimental data, and the fitting provides the van der Waals-type constant of Volmer's equation and the solute activity coefficient. In the second model, we put aside the use of surface equations of state; Gibbs adsorption equation was integrated assuming that in the vicinity of the surface saturation region the solvent surface concentration approaches to zero, what is in fairly good agreement with the adsorption phenomena. The fitting of the model to the experimental data provides de solute surface saturation concentration and its activity coefficient. Both models were derived from the equilibrium criterion of *equality* of bulk and surface chemical potentials on the contrary to Butler's equilibrium criterion (Eq. (3)). It will be shown that the discrepancy between both criteria relies on the variables of the system that are taken as constant and/or independent. Rusanov presented a similar discussion, showing the inconsistency of Butler's theory with respect to Gibbs' theory, aiming to develop a master surface equation of state for insoluble monolayers [25]. Also Salonen et al. [26] have noticed the difference between both equilibrium criteria but they did not enquire profoundly in this matter. In the present paper, it is demonstrated that in Gibbs adsorption equation, the equality of chemical potentials is valid and that the models are thermodynamically consistent.