

Density, orientation, solvation and adsorption effects on surface tension of mixtures

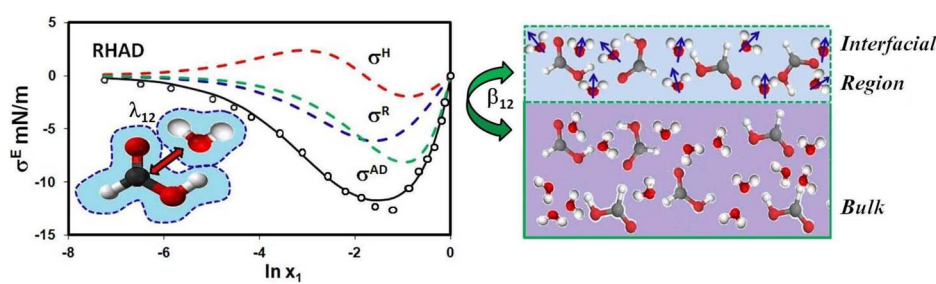


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GRAPHICAL ABSTRACT



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ABSTRACT

The present article offers a novel analysis tool that potentially can be used to describe and characterize the process of interfacial adsorption of both simple molecules and complex molecules (surfactants, biomolecules, etc). This analysis tool was developed for evaluating the influence of the density, orientation, solvation and adsorption effects on the surface tension of mixtures. We propose a procedure that consists in split the excess surface tension function into three additive contributions. That is, a residual function (R) based on the concept of elastic energy density in which both the interfacial density and the axial orientation are taken into account, an enthalpic function (H) considering the solvation effects, and a contribution that includes the preferential adsorption (AD) effects. This approach is referred in this work as RHAD. The AD contribution was assessed using the Langmuir isotherm model. In order to evaluate the reliability of the RHAD method, simple molecular approaches describing each contribution were chosen. Some experimental systems were employed as binary mixtures models for the evaluation of the descriptive capability of RHAD. The experimental data for both complexes and simple binary mixtures were successfully reproduced. Thus, this methodology allowed us to quantitatively and qualitatively incorporate the influence of molecular parameters on the experimentally observed behavior of this important physical property. Also, the results shown that when one of the contributions domains over the others, the overall behavior of the surface tension of the binary mixture is mainly led by the difference between the surface tensions (π_0) and the ratio of the molar volumes (V_2/V_1) of their pure components. Meaningful deviations from ideal behavior and the occurrence of aneutropy can be further interpreted employing RHAD. Finally, our results suggest that the adsorption process is better understood by considering the interfacial width.

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1. Introduction

Surface tension is a macroscopic physical property which has been the subject of uncountable studies. Variables as density, pressure and energy including its profiles have been explored at interface region through theoretical and simulation tools. However, computational simulations are limited by molecular models used. These models are developed for bulk properties, are nonpolarizable and some cases overestimates the diffusion constant. This situation is remarked for the case of the water molecule, where the most favorable results show differences between 5–10 mN/m with respect to the experimental values of surface tension [1], as consequence, aqueous mixtures also show important deviations respect to experimental behavior [2].

In terms to the thermodynamic connections between these variables and the interfacial properties are incipient. In the case of a pure compound in equilibrium, the surface and bulk densities have been related to the standard chemical potential difference between interface and bulk by means of the inclusion of an elastic field concept [3,4]. Thus, it was possible to derive an expression for the fugacity at the interface, which in turn is the platform of all residual functions associated with this region. Consequently, surface tension can be written as a function of the interfacial fugacity [5–7]. More recently, it has been demonstrated for systems that are not in thermodynamic equilibrium that density changes can generate considerable differences between the surface tension and the surface energy [8]. Thus, in this work, it is established that the net motion of the molecules driven by the chemical potential difference between the surface and the bulk will remove the differences between both surface properties upon reaching equilibrium.

In the case of mixing, the surface density is affected by the values of the interface composition. If each mixing state is treated as a pseudo-compound, any associated residual function will depend on the partial molar density of the species immersed in the interfacial region. The pseudo-compound strategy requires establishing a mixing rule and this should be expressed in terms of surface composition, e.g. molar fraction or other variables weighted as volume or mass fraction.

Similar to the case of pure compounds, the surface tension of mixing keeps a dependence on the surface density. This dependence is the reason why semi-empirical equations such as those proposed by Laaksonen and Kulmala (L-K model) [9] show successful results in several water-alcohol binary mixtures, in which the enrichment of the component with lower surface tension is known to take place. In that model, surface volume fractions (ϕ^s) are used to calculate the surface tension of the binary mixtures from the surface tension of their pure components (σ_i)

$$\sigma_m = \phi_1^s \sigma_1 + \phi_2^s \sigma_2 \quad (1)$$

where molar volumes of pure compounds are used to estimate surface volume fractions.

Other approach proposed where similar dependencies are considered is the Parachor model. In that model a proportionality constant known as the Parachor, \wp [10], which can be also estimated e.g. using groups contribution method [11], is defined for one pure compound i as a function of their density, ρ_i , and molecular weight, M_i

$$\wp_i = \frac{\sigma_i^{1/4} M_i}{\rho_i} \quad (2)$$

For multicomponent mixtures, a direct relation with the composition of the bulk is frequently used to calculate the Parachor of mixing [12], thus

$$\wp_m = \sum_i x_i \wp_i \quad (3)$$

A modified version of the above approach [13] explicitly suggests the use of surface density and surface molar fraction to relate the mixing surface tension to the surface tension of the pure components through of the expression

$$\frac{\sigma_m^{1/4} M^s}{\rho_m^s} = \sum_i x_i^s \frac{\sigma_i^{1/4} M_i}{\rho_i^s} \text{ or equivalently } \frac{1}{\sigma_m^{1/4}} = \sum_i \phi_i^s \frac{1}{\sigma_i^{1/4}}, \quad (4)$$

where M^s and M_i are the molecular weight of the mixture and the component i , respectively. In this equation, the surface volume fractions, ϕ^s , are evaluated taken into account the partial molar surface density. Eq. (4) was used to describe aqueous systems by Tamura, et al. [14] who developed a semi-empirical method for mixtures composed of liquids differing widely in polarity.

Another important feature that must be considered, which defines the molecular structure in the interface, is the orientation molecular. This aspect has been constantly neglected in the thermodynamic treatment of the interface, since the interface is usually described as a plane with zero thickness that divides two phases (Gibbs analysis). The quantification of this effect on surface tension was initially proposed by Irving Langmuir [15,16] at the beginning of the last century. In his work, he applied some approximations on the distribution of molecular orientation, thus, assuming that each section of molecules has an independent surface action; Langmuir was able to calculate the surface tension and the dominant molecular arrangement for simple systems. Recently, through the analytical tools provided by molecular simulations, this aspect has been considered; for example, for pure water, it has been observed that surface molecules have H-bonds pointing towards the vapor phase. Although the average angle of such bonds was not exactly 90°, is also recognized that the molecular orientation may be a mechanism to maximize its energy of mutual interaction and to provide a gradual transition from one phase to another. Besides, Phan et al. [2] found that the molecular structure of the interfacial zone was deterministically correlated to the alcohol concentration in water-alcohol mixtures. The molecular orientation was associated with the dipole moment profile of the water molecules along the z-direction that allows defining an interfacial boundary. This boundary was used to calculate the amount of water and alcohol in the interfacial zone necessary to accurately determine the surface tension variation. In addition, it is important to highlight that in those works, the dipole moment profiles of interfacial water are graphically reported as a function of the percentage of alcohol (see Fig. 4 in Ref. [15]). In addition, it is appreciate a significant augment of the interfacial width with the increase of alcohol concentration. In the present work, we explore the preferential orientation taking into account its effect on thickness of interfacial region.

Let us now consider the effect of solvency at interfacial region; these effects are accompanied of solvation processes, cross associations, segregations, among others. Just as in a pure fluid, we expect a dependence between the surface tension and the association strength [17]. In that case, it is shown that molecular models must incorporate an explicit association interaction in order to describe the surface-tension behavior of a real associated fluid. However, in the mixtures cases, cross-association and auto-association can lead to different contributions depending on the spatial arrangement that the functional groups ultimately reach. Moreover, when the solute concentration at the surface is higher than in the bulk, it is possible that a phase segregation process leads to the formation of two surface phases at the liquid–air interface [18].

In the simplified Extended Langmuir (EL) [19] the solvency effects are incorporated through an approximation of mean field equivalent to the Scatchard–Hildebrand [20] free energy function

$$\sigma_m = \phi_1^s \sigma_1 + \phi_2^s \sigma_2 + \lambda \phi_1^s \phi_2^s \pi_0 \quad (5)$$

where $\pi_0 = \sigma_1 - \sigma_2$ and λ is an energetic dimensionless parameter. Under this approach, the behavior of interfacial mixture is considered as a regular solution (see Eq.(5)). Despite the simplifications, good agreement with experimental data are reached for many cases of binary mixtures [21].

The solvency effects are considered similar to regular solution

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