



# Surface tensions of esters from a combination of the gradient theory with the CPA EoS

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## ABSTRACT

Ester compounds are widely used in applications such as solvents, plasticizers, polymers, lubricants, cosmetics, medicinals, agrochemicals, soaps and other surface active agents, to mention a few. In many of these applications the simultaneous knowledge of the phase behavior and interfacial properties is an advantage for designing better products and improved processes. The van der Waals density gradient theory is an interesting theory providing such information. In this work it is applied for the first time to compute the surface tension of esters in a broad temperature range. A total of 37 ester compounds were evaluated, including formates, acetates, methyl, ethyl, propyl, butyl and unsaturated methyl esters.

For calculating the Helmholtz energy density and the bulk properties, the cubic-plus-association equation of state was used. It is demonstrated that ester surface tensions can be estimated within 1.5% deviation to the experimental data using a simple correlation for the temperature dependence of the gradient theory influence parameter. Whenever the influence parameters are considered to be temperature independent only slightly higher deviations, below 5%, were obtained.

The results suggest that the proposed methodology can be a valuable tool for modeling surface and interfacial tensions of esters and ester mixtures such as biodiesels.

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## 1. Introduction

Knowledge about ester surface tension is important to ensure the efficiency of industrial operation units involving chemical reactions and extractive processes that use these compounds as solvents.

Esters are broadly available in nature and also widely used in different industries. Just to mention a few of their applications, they can be used as flavorings in the food industry [1], as plasticizers in the rubber industry [2] and as lubricants in the metalworking industry [3]. Esters also have widespread use as emollients in the cosmetics [4] and pharmaceutical [5] industries.

The importance of surface tension in the oil industry is also widely recognized. Surface tension strongly influences the capillary pressure, relative permeabilities and the residual liquid saturation

important to many processes in chemical and reservoir engineering applications [6].

Considering other recent fuels such as biodiesel (a blend of fatty acid alkyl esters), surface tension is one of its physical properties that influence the design of purification processes and the fuel performance. Surface tension controls the formation of oil drops that determine the fuel atomization on the engine combustion chamber. A higher surface tension disables the formation of small droplets from the liquid fuel [7]. Surface tension is thus a key property to be taken into consideration while designing new injection systems [8]. However, the available experimental data for biodiesels surface tension are still very scarce, especially data accounting for their temperature dependence. Generally, data are only available at a single temperature.

Considerable more information is available for pure ester surface tensions, but the available data can still be considered limited for the heavier esters. The development of surface tension predictive schemes is thus of importance.

There are many approaches for computing the surface tensions of simple fluids and mixtures. The most basic approach is the parachor method [9] and its developments. In fact, up to now, only the Gibling's parachor equivalents have been calculated for ester compounds [10–12]. Gibling assigned parachor values to groups of atoms based on composition and linkage [13].

**Abbreviations:** AAD, average absolute deviation (%AAD =  $(1/NP) \sum_{i=1}^{NP} \text{ABS}((\text{exp}_i - \text{calc}_i)/\text{exp}_i) \times 100$ ); APACT, associated-perturbed-anisotropic-chain theory; CPA, cubic-plus-association; DFT, density functional theory; EoS, equation of state; PR, Peng–Robinson; QCHB, quasi-chemical hydrogen-bonding equation of state; SAFT, statistical associating fluid theory; SRK, Soave–Redlich–Kwong.

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Allen et al. suggested an empirical correlation based on the parachor method that is commonly used to compute surface tensions of biodiesels from their fatty acid composition [8,14,15].

Shu et al. [16] proposed a topological index that uses a combination of the distance matrix and adjacency matrix of the molecular structure to predict the surface tension of a biodiesel fuel from the molecular structure of its fatty acid methyl ester components.

Several thermodynamic correlations [17–19], namely the corresponding-state principle [20,21], are alternative approaches to the description of surface tensions. Actually, a generalized version of a corresponding states model for pure fluids and mixtures was developed, using a simple cubic EoS as a reference EoS, allowing an excellent representation of the surface tension of several pure alkanes and their mixtures with water [22].

More theoretically sound approaches account for interfacial properties include the perturbation theory [23], integral and density functional theories [23–26] or the density gradient theory [27,28]. Panayiotou [29] extended the QCHB (quasi-chemical hydrogen-bonding) equation of state model to interfaces obtaining a satisfactory agreement between experimental and calculated surface tensions of pure fluids. The density functional theory (DFT) can also be used for the prediction of surface tensions [30].

The density gradient theory of fluid interfaces was first proposed by van der Waals [28] and reformulated by Cahn and Hilliard [27]. This theory converts the statistical mechanics of inhomogeneous fluids into a non-linear boundary value problem that can be solved to compute the density and the stress distributions in the interface. Cahn and Hilliard made possible the calculation of the surface/interfacial tension by a theory that describes a continuous evolution of the Helmholtz energy along the interface. The physical consistency of this approach was confirmed by the regular solution theory for qualitatively describing the properties of planar interfaces [27].

One of the gradient theory inputs is the Helmholtz free energy density that can be computed by any thermodynamic model. When using an equation of state a simultaneous modeling of interfacial tensions and phase equilibria is possible.

Standard cubic EoSs, the Peng–Robinson EoS and the SRK EoS, with quadratic mixing rules were successfully used to describe the interfacial properties of simple mixtures containing hydrocarbons [16,31–35].

The well known difficulties of cubic EoS for describing liquid phase densities of longer chain molecules were corrected using a volume translation [34,36,37]. However, that approach cannot solve the problems found for systems containing polar and associating compounds [38]. Alternatively, complex mixing rules, such as the Wong–Sandler or the modified Huron–Vidal mixing rules, have to be applied for these systems as previously done by Mejia et al. [39,40] or, instead, more theoretical sound models that explicitly incorporate association due to hydrogen bonding and other polar effects can be used. An example of the last mentioned approach is the coupling of the gradient theory with the associated-perturbed-anisotropic-chain theory (APACT) that was used to compute interfacial tensions of systems composed of n-alkanols and water in agreement with the experimental data [41]. Panayiotou combined the gradient theory of fluid interfaces with the QCHB EoS model to compute surface tensions of pure fluids and mixtures of non polar, weakly polar and associating compounds [42].

Another associating model that can be used to describe interfacial properties of polar mixtures is the statistical associating fluid theory (SAFT). Kahl and Enders [38] and Fu [43] showed that the SAFT EoS can be successfully applied to the alcohol family.

Several issues were found when applying the above mentioned associating models to compute interface properties. The good prediction of water surface tension depends on the number of

association sites, significant problems were detected for polar compounds in the critical region and it was found that the SAFT and the APACT EoSs give different results depending on the temperature range selected [38].

Queimada et al. [44] used a combination of the gradient theory with the CPA EoS to describe hydrocarbon, ethanol and water liquid–vapor interfaces, with very good results. Oliveira et al. [45] applied that approach to the modeling of the surface tensions of the homologue families of n-alkanes (C<sub>2</sub>–C<sub>36</sub>), n-fluoroalkanes (C<sub>3</sub>–C<sub>9</sub>) and n-alkanols (C<sub>1</sub>–C<sub>20</sub>), and to the prediction of vapor–liquid interfacial tensions of five mixtures (methane + pentane, ethane + nonane, methanol + ethanol, octane + heptanol and octane + octanol) with very good results.

In this work it is intended to extend the excellent ability of the coupling of the gradient theory with the CPA EoS to describe surface tensions to compute that property for several ester families. 7 methyl esters, 4 ethyl esters, 2 propyl esters, 4 butyl esters, 10 acetates, 10 formates and two unsaturated methyl esters will be here considered.

## 2. Model

The gradient theory is based on the phase equilibria of the fluid phases separated by an interface [37,44,46]:

$$\sigma = \int_{n^{vap}}^{n^{liq}} \sqrt{2c\Delta\Omega(n)} dn \quad (1)$$

$$\Delta\Omega(n) = f_0(n) - \sum_i n_i \mu_o + p \quad (2)$$

where  $p$  is the equilibrium pressure,  $\sigma$  is the interfacial tension,  $f_0(n)$  is the Helmholtz energy density of the homogeneous fluid,  $\mu_i$  are the pure-component chemical potentials,  $n^{liq}$  and  $n^{vap}$  are the liquid and vapor phase molar densities and  $c$  is the so-called influence parameter.

The theoretical definition of the pure-component influence parameter,  $c$ , can hardly be implemented. As an alternative, after the vapor–liquid equilibrium is determined, this is correlated from surface tension data:

$$c = \frac{1}{2} \left[ \frac{\sigma_{exp}}{\int_{n^{vap}}^{n^{liq}} \sqrt{f_0(n) - n\mu + pdn}} \right]^2 \quad (3)$$

To use the gradient theory, it is necessary to determine the equilibrium densities of the coexisting phases, the chemical potentials and the Helmholtz energy using an adequate model. In this work, the CPA equation of state will be used for these purposes.

The CPA EoS presents several advantages over conventional cubic equations and other association models. As will be explained afterwards, the CPA EoS allows an accurate description of saturated liquid densities without any need for a volume correction, in contrast of what succeeds with traditional cubic EoS. The CPA EoS is also mathematically simpler than other association equations of state such as SAFT, being previously accessed to be the most adequate model to describe the phase equilibria of systems containing polar compounds with strong associative interactions that appear during the biodiesel production, purification and use, considering its accuracy, range of applicability, simplicity and predictive character [47–52].

The CPA EoS, in terms of the compressibility factor, can be expressed as the sum of two contributions: one accounting for physical interactions, that in the current work is taken as the SRK EoS, and another accounting for association, the Wertheim associ-

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