

# 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-

**Table 1**  
Correlation coefficients for calculating the influence parameters (Eq. (6)) and modeling results for esters.

| Family                    | Compound                         | 3 correlated parameters |                 |                 |                | 2 correlated parameters |                 |                | 2 averaged parameters<br>$D \times 10^6 = 0.6177$ ;<br>$E \times 10^6 = -0.4425$ |
|---------------------------|----------------------------------|-------------------------|-----------------|-----------------|----------------|-------------------------|-----------------|----------------|--|
|                           |                                  | $D \times 10^6$         | $E \times 10^6$ | $F \times 10^6$ | AAD $\sigma$ % | $D \times 10^6$         | $E \times 10^6$ | AAD $\sigma$ % | AAD $\sigma$ %   |
| Methyl esters             | C <sub>2</sub> COOC              | 0.7232                  | -0.7828         | 0.2819          | 0.98           | 0.6670                  | -0.5110         | 1.15           | 1.44   |
|                           | C <sub>3</sub> COOC              | 0.6271                  | -0.4052         | -0.0285         | 1.37           | 0.6329                  | -0.4360         | 1.51           | 3.36   |
|                           | C <sub>9</sub> COOC              | 0.6526                  | -0.6197         | 0.1635          | 0.61           | 0.6242                  | -0.4812         | 0.81           | 0.91   |
|                           | C <sub>11</sub> COOC             | 0.3263                  | 0.4404          | -0.7469         | 0.55           | 0.4533                  | -0.1865         | 1.32           | 9.83   |
|                           | C <sub>13</sub> COOC             | 0.5784                  | -0.4560         | 0.0000          | 0.90           | 0.5784                  | -0.4560         | 1.24           | 6.92   |
|                           | C <sub>15</sub> COOC             | 0.5720                  | -0.4537         | 0.0000          | 0.07           | 0.5720                  | -0.4537         | 1.25           | 7.95   |
|                           | C <sub>17</sub> COOC             | 0.2207                  | 0.1577          | 0.0000          | 0.64           | 0.2207                  | 0.1577          | 0.64           | 7.13   |
| Ethyl esters              | C <sub>2</sub> COOC <sub>2</sub> | 0.5189                  | -0.0998         | -0.3006         | 0.88           | 0.5716                  | -0.3626         | 0.85           | 1.20   |
|                           | C <sub>3</sub> COOC <sub>2</sub> | 0.4582                  | 0.3042          | -0.7680         | 0.64           | 0.5866                  | -0.3360         | 0.98           | 2.29   |
|                           | C <sub>5</sub> COOC <sub>2</sub> | 1.4074                  | -3.7140         | 3.4800          | 1.16           | 0.8239                  | -0.8111         | 3.09           | 9.41   |
|                           | C <sub>7</sub> COOC <sub>2</sub> | 1.5005                  | -4.6090         | 4.6016          | 1.92           | 0.7133                  | -0.7358         | 5.15           | 8.16   |
| Propyl esters             | C <sub>2</sub> COOC <sub>3</sub> | 0.7354                  | -0.7813         | 0.3004          | 1.11           | 0.6829                  | -0.5260         | 1.45           | 5.00   |
|                           | C <sub>3</sub> COOC <sub>3</sub> | 0.5974                  | -0.2694         | -0.1787         | 0.31           | 0.6264                  | -0.4163         | 0.39           | 1.67   |
| Butyl esters              | C <sub>2</sub> COOC <sub>4</sub> | 0.6283                  | -0.5611         | 0.1300          | 0.25           | 0.6036                  | -0.4417         | 0.31           | 1.63   |
|                           | C <sub>3</sub> COOC <sub>4</sub> | 0.7007                  | -0.7120         | 0.2416          | 0.71           | 0.6583                  | -0.5062         | 0.99           | 2.81   |
|                           | C <sub>4</sub> COOC <sub>4</sub> | 0.4482                  | -0.0210         | -0.2765         | 0.83           | 0.5010                  | -0.2804         | 0.97           | 6.03   |
|                           | C <sub>8</sub> COOC <sub>4</sub> | 0.5400                  | 0.6753          | -1.2430         | 0.55           | 0.7536                  | -0.3740         | 1.22           | 13.45  |
| Formates                  | HCOOC                            | 0.5442                  | -0.0915         | -0.2774         | 0.58           | 0.5905                  | -0.3226         | 0.60           | 2.44   |
|                           | HCOOC <sub>2</sub>               | 0.9485                  | -1.6631         | 1.1097          | 1.49           | 0.7495                  | -0.6941         | 1.65           | 3.69   |
|                           | HCOOC <sub>3</sub>               | 1.0190                  | -2.0245         | 1.5521          | 1.22           | 0.7543                  | -0.7188         | 2.67           | 6.15   |
|                           | HCOOC <sub>4</sub>               | 0.9900                  | -1.8033         | 1.2719          | 1.15           | 0.7706                  | -0.7281         | 2.44           | 7.15   |
|                           | HCOOC <sub>5</sub>               | 0.7972                  | -0.9519         | 0.2827          | 1.06           | 0.7301                  | -0.6864         | 1.28           | 3.73   |
|                           | HCOOC <sub>6</sub>               | 0.8252                  | -1.2024         | 0.7098          | 1.73           | 0.7026                  | -0.6024         | 1.73           | 2.23   |
|                           | HCOOC <sub>7</sub>               | 0.4554                  | 0.2697          | -0.6757         | 0.96           | 0.5698                  | -0.2969         | 1.84           | 2.83   |
|                           | HCOOC <sub>8</sub>               | 0.3519                  | 0.8361          | -1.2755         | 0.48           | 0.5688                  | -0.2356         | 1.87           | 4.64   |
|                           | HCOOC <sub>9</sub>               | 0.5130                  | -0.0310         | -0.3970         | 0.20           | 0.5808                  | -0.3655         | 0.55           | 1.56   |
|                           | HCOOC <sub>10</sub>              | 0.4834                  | 0.1550          | -0.6094         | 0.81           | 0.5860                  | -0.3545         | 2.36           | 9.51   |
| Acetates                  | CCOOC                            | 1.1825                  | -2.4805         | 1.8978          | 0.81           | 0.8538                  | -0.8731         | 2.36           | 9.51   |
|                           | CCOOC <sub>2</sub>               | 0.7210                  | -0.8782         | 0.3698          | 1.80           | 0.6806                  | -0.6186         | 1.80           | 2.32   |
|                           | CCOOC <sub>3</sub>               | 0.6668                  | -0.6530         | 0.2229          | 0.71           | 0.6281                  | -0.4642         | 0.98           | 1.24   |
|                           | CCOOC <sub>4</sub>               | 0.6019                  | -0.3608         | -0.0885         | 1.43           | 0.6158                  | -0.4327         | 1.51           | 1.32   |
|                           | CCOOC <sub>5</sub>               | 0.8120                  | -1.2765         | 0.8895          | 1.49           | 0.6607                  | -0.5290         | 2.40           | 3.58   |
|                           | CCOOC <sub>6</sub>               | 0.4602                  | 0.1026          | -0.5017         | 0.88           | 0.5531                  | -0.3634         | 0.91           | 3.82   |
|                           | CCOOC <sub>7</sub>               | 0.3128                  | 0.5980          | -0.9254         | 0.42           | 0.4702                  | -0.1793         | 1.84           | 8.29   |
|                           | CCOOC <sub>8</sub>               | 0.3774                  | 0.2879          | -0.6535         | 1.23           | 0.4876                  | -0.2582         | 2.15           | 10.10  |
|                           | CCOOC <sub>9</sub>               | 0.3696                  | 0.3828          | -0.6979         | 0.60           | 0.4891                  | -0.2047         | 1.16           | 5.62   |
|                           | CCOOC <sub>10</sub>              | 0.4780                  | -0.0300         | -0.3786         | 0.47           | 0.5419                  | -0.3468         | 0.57           | 4.87   |
| Unsaturated esters        | Methyl oleate                    | 0.6730                  | -0.9460         | 0.5053          | 0.31           | 0.5870                  | -0.5212         | 0.84           | 6.45   |
|                           | Methyl linoleate                 | 0.8236                  | -0.4096         | 0.0000          | 0.40           | 0.8236                  | -0.4096         | 0.72           | 22.02  |
| Global average deviations |                                  |                         |                 |                 | 0.86           |                         | 1.48            | 5.44           |  |

ation term [53–55]:

$$Z = Z^{phys.} + Z^{assoc.} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2} \left( 1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (4)$$

where  $a$  is the energy parameter,  $b$  the co-volume parameter,  $\rho$  is the density,  $g$  a simplified radial distribution function [56],  $X_{A_i}$  the mole fraction of pure component  $i$  not bonded at site  $A$  and  $x_i$  is the mole fraction of component  $i$ .

The pure component energy parameter of CPA has a Soave-type reduced temperature dependency:

$$a(T) = a_0 [1 + c_1 (1 - \sqrt{T_r})]^2 \quad (5)$$

Esters are non-self-associating compounds and therefore there are only three pure compound parameters, the ones of the physical part ( $a_0$ ,  $c_1$ , and  $b$ ), to be regressed simultaneously from vapor pressure and liquid density data. Basically for these compounds the CPA EoS will reduce to the SRK EoS, but as SRK is well known for its

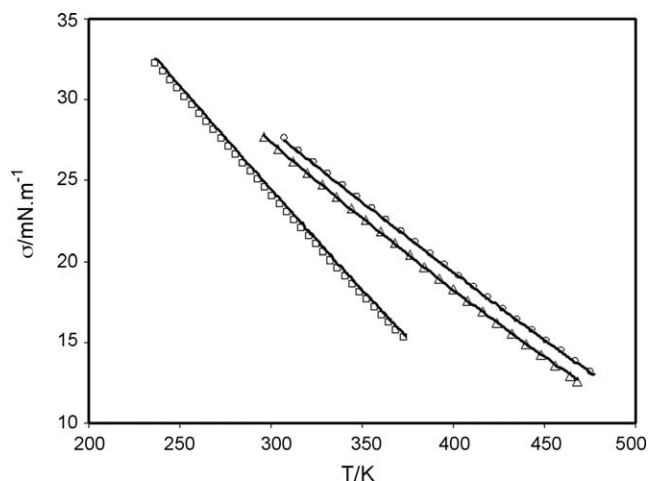
deficiencies in liquid phase density estimates, this is an alternative approach for providing better density estimates, while leaving the possibility for future modeling in associating systems.

### 3. Results and discussion

Literature data for surface tensions were available [10–12,57] for 7 methyl esters, 4 ethyl esters, 2 propyl esters, 4 butyl esters and also for 10 acetates and 10 formates and two unsaturated methyl esters.

The CPA parameters for esters were already estimated in a previous work, when modeling the water solubility in esters and in biodiesels [52]. Ester vapor pressures and liquid densities were described with global average deviations of 2.3% and 1.4%, respectively. Once the phase equilibria are correctly described, the gradient theory can be applied to calculate surface tensions.

The pure-component influence parameter,  $c$ , has a theoretical definition, but it is too complex to be easily implemented [46]. The theoretical definition of the influence parameter also performs poorly when predicting surface tensions [58]. Alternatively, the influence parameter is adjusted from surface tension data and plot-

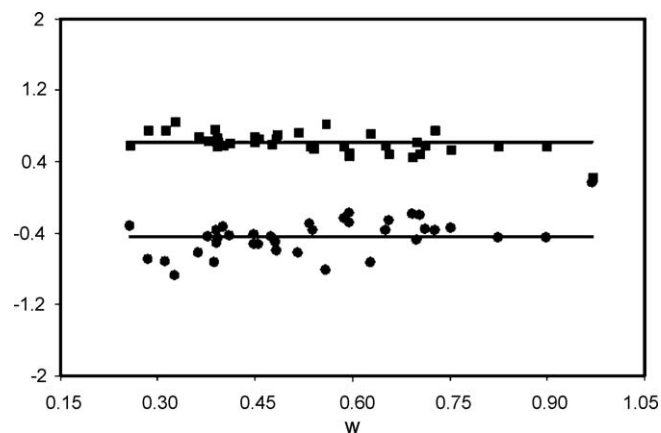


**Fig. 1.** Ester surface tensions. Experimental [57] ( $\square$ , methyl propanoate;  $\Delta$ , nonyl formate;  $\circ$ , methyl decanoate) and gradient theory results using a linear temperature dependency for the influence parameter (—).

ted (far from the critical point), using the energy and the co-volume parameters of the physical part of the CPA EoS (as  $c/ab^{2/3}$ ) as a function of  $(1 - T_r)$ , as already done in previous works [32,36,44].

Different approaches were previously considered for the temperature dependence of the influence parameter. The influence parameter can be taken either as temperature independent [38] or as temperature dependent [43] when combining the gradient theory with different versions of the SAFT EoS. When using cubic EoS a linear reduced temperature dependency for the influence parameter seemed to be more adequate [34,37]. The influence parameter can also be correlated as a function of the critical compressibility factor, the acentric factor, the reduced dipole moment and the reduced temperature, as recently shown by Lin et al. [58].

As discussed in Section 1, the coupling of the CPA EoS with the gradient theory was previously used for an accurate description of the surface tension of a series of n-alkanes, n-alcohols and perfluoralkanes [45]. It was shown that some of the components presented



**Fig. 2.** Coefficients  $D \times 10^6$  ( $\blacksquare$ ) and  $E \times 10^6$  ( $\bullet$ ) in Eq. (6) as a function of the acentric factor  $\omega$ . (—) Average values for  $D \times 10^6 = 0.6177$  and  $E \times 10^6 = -0.4425$ .

variations of  $c/ab^{2/3}$  that were quadratic with  $(1 - T_r)$ , others were linear and others still almost constant, which in some cases can be explained by the limited reduced temperature range of surface tension data available to correlate the influence parameters and their accuracy, especially for the heavier members of the series. A quadratic correlation was therefore proposed for the variation of the influence parameter with reduced temperature (Eq. (6)).

$$\frac{c}{ab^{2/3}} = D + E \times (1 - T_r) + F \times (1 - T_r)^2 \quad (6)$$

For esters, at first, the quadratic variation of the influence parameter was used within the reduced temperatures of 0.45–0.85. Using this approach surface tensions were computed with a global average deviation of 0.9% as shown in Table 1. The influence parameter dependency with temperature appears, however, to be linear up to a  $T_r$  of about 0.70. Taking into account these results, a linear approach was then considered, resulting in only two parameters to be correlated (Eq. (6)). That approach was already previously considered by Miqueu et al. [36], who justified it by stating that since equations of state are unable to describe the behavior of fluid

**Table 2**  
Surface thermodynamic functions for the ester families studied.

| Family                           | Compound                         | Experimental  |   | 2 correlated parameters                                   |   | Family           | Compound            | Experimental  |   | 2 correlated parameters                                   |   |      |
|----------------------------------|----------------------------------|---|---|---|---|------------------|---------------------|---|---|---|---|------|
|                                  |                                  | $S \times 10^{-5}$<br>( $\text{J m}^{-2} \text{K}^{-1}$ ) | $H \times 10^{-2}$<br>( $\text{J m}^{-2}$ ) | $S \times 10^{-5}$<br>( $\text{J m}^{-2} \text{K}^{-1}$ ) | $H \times 10^{-2}$<br>( $\text{J m}^{-2}$ ) |                  |                     | $S \times 10^{-5}$<br>( $\text{J m}^{-2} \text{K}^{-1}$ ) | $H \times 10^{-2}$<br>( $\text{J m}^{-2}$ ) | $S \times 10^{-5}$<br>( $\text{J m}^{-2} \text{K}^{-1}$ ) | $H \times 10^{-2}$<br>( $\text{J m}^{-2}$ ) |      |
| Methyl esters                    | C <sub>2</sub> COOC              | 1.20  | 6.01  | 1.21  | 6.09  | Formates         | HCOOC               | 1.58  | 7.17  | 1.57  | 7.11  |      |
|                                  | C <sub>3</sub> COOC              | 1.10  | 5.74  | 1.09  | 5.68  |                  | HCOOC <sub>2</sub>  | 1.18  | 5.85  | 1.22  | 5.99  |      |
|                                  | C <sub>9</sub> COOC              | 0.82  | 5.22  | 0.82  | 5.21  |                  | HCOOC <sub>3</sub>  | 1.09  | 5.63  | 1.10  | 5.66  |      |
|                                  | C <sub>11</sub> COOC             | 0.78  | 5.13  | 0.77  | 5.07  |                  | HCOOC <sub>4</sub>  | 1.00  | 5.45  | 1.02  | 5.47  |      |
|                                  | C <sub>13</sub> COOC             | 0.80  | 5.28  | 0.80  | 5.27  |                  | HCOOC <sub>5</sub>  | 0.98  | 5.51  | 0.95  | 5.34  |      |
|                                  | C <sub>15</sub> COOC             | 0.78  | 5.27  | 0.77  | 5.26  |                  | HCOOC <sub>6</sub>  | 0.94  | 5.45  | 0.95  | 5.52  |      |
|                                  | C <sub>17</sub> COOC             | 0.78  | 5.27  | 1.08  | 6.10  |                  | HCOOC <sub>7</sub>  | 0.92  | 5.39  | 0.91  | 5.38  |      |
| Ethyl esters                     | C <sub>2</sub> COOC <sub>2</sub> | 1.16  | 5.83  | 1.09  | 5.62  |                  | HCOOC <sub>8</sub>  | 0.88  | 5.36  | 0.86  | 5.28  |      |
|                                  | C <sub>3</sub> COOC <sub>2</sub> | 0.99  | 5.32  | 0.97  | 5.26  |                  | HCOOC <sub>9</sub>  | 0.83  | 5.18  | 0.83  | 5.16  |      |
|                                  | C <sub>5</sub> COOC <sub>2</sub> | 0.83  | 4.99  | 0.87  | 5.13  |                  | HCOOC <sub>10</sub> | 0.83  | 5.31  | 0.82  | 5.28  |      |
|                                  | C <sub>7</sub> COOC <sub>2</sub> | 0.70  | 4.66  | 0.77  | 4.91  | Acetates         | CCOOC               | 1.22  | 6.10  | 1.25  | 6.16  |      |
| Propyl esters                    | C <sub>2</sub> COOC <sub>3</sub> | 1.00  | 5.41  | 1.00  | 5.39  |                  | CCOOC <sub>2</sub>  | 1.13  | 5.69  | 1.14  | 5.75  |      |
|                                  | C <sub>3</sub> COOC <sub>3</sub> | 0.93  | 5.23  | 0.93  | 5.23  |                  | CCOOC <sub>3</sub>  | 1.09  | 5.63  | 1.09  | 5.63  |      |
|                                  | Butyl esters                     | C <sub>2</sub> COOC <sub>4</sub>                          | 0.94  | 5.23  | 0.94  |                  | 5.25                | CCOOC <sub>4</sub>  | 1.00  | 5.43  | 1.01  | 5.48 |
| C <sub>3</sub> COOC <sub>4</sub> |                                  | 0.89  | 5.12  | 0.89  | 5.12  |                  | CCOOC <sub>5</sub>  | 0.94  | 5.32  | 0.95  | 5.31  |      |
| Butyl esters                     | C <sub>4</sub> COOC <sub>4</sub> | 0.89  | 5.20  | 0.88  | 5.14  |                  | CCOOC <sub>6</sub>  | 0.89  | 5.14  | 0.87  | 5.08  |      |
|                                  | C <sub>8</sub> COOC <sub>4</sub> | 0.84  | 5.42  | 0.82  | 5.35  |                  | CCOOC <sub>7</sub>  | 0.90  | 5.32  | 0.88  | 5.27  |      |
|                                  |                                  | CCOOC <sub>8</sub>  | 0.85  | 5.23  | 0.86  |                  | 5.22                | CCOOC <sub>8</sub>  | 0.85  | 5.23  | 0.86  | 5.22 |
|                                  |                                  | CCOOC <sub>9</sub>  | 0.84  | 5.21  | 0.85  |                  | 5.27                | CCOOC <sub>9</sub>  | 0.84  | 5.21  | 0.85  | 5.27 |
|                                  | CCOOC <sub>10</sub>              | 0.80  | 5.15  | 0.81  | 5.19  |                  | CCOOC <sub>10</sub> | 0.80  | 5.15  | 0.81  | 5.19  |      |
| Unsaturated esters               | Methyl oleate                    | 0.77  | 5.38  | 0.73  | 5.21  | Methyl oleate    | 0.77                | 5.38  | 0.73  | 5.21  |   |      |
|                                  | Methyl linoleate                 | 1.12  | 6.31  | 1.11  | 6.30  | Methyl linoleate | 1.12                | 6.31  | 1.11  | 6.30  |   |      |

phases in the vicinity of critical points, there is no point in using them to predict surface tensions near the critical point. Using this approach global average deviations of only 1.5% were obtained, as seen in Table 1. Some results are depicted in Fig. 1 for two methyl esters and one formate.

Plotting the parameters of Eq. (6) against the acentric factor, it is possible to see in Fig. 2 that these parameters do not vary significantly, and average values were estimated for  $D$  and  $E$ . Using these average values higher deviations for the surface tensions are obtained, but nevertheless, the deviations are lower than 5% as reported in Table 1, which it is very promising for prediction purposes.

Using the linear approach for the temperature dependency of the influence parameter the surface thermodynamic properties, surface entropies and surface enthalpies, were derived using the quasi linear surface tension variation with the temperature [59,60]:

$$S = - \left( \frac{d\sigma}{dT} \right) \quad (7)$$

$$H = \sigma - T \left( \frac{d\sigma}{dT} \right) \quad (8)$$

Results for all the ester families here considered are reported in Table 2. As a general conclusion, both the surface entropy and surface enthalpy decrease with the chain length of the ester, and as expected, CPA EoS results are in very good agreement with the experimental data.

Unfortunately, surface tension data for biodiesels and other complex mixtures containing esters are limited. The gradient theory modeling of such mixtures is considerably more difficult than for pure compounds, as density profiles have to be calculated at each discrete point of the dividing interface limited by the upper and lower phase densities [37]. Such evaluation is expected to be performed as more experimental data become available.

#### 4. Conclusions

In this work the density gradient theory was applied to the description of the surface tensions of several ester families. The CPA EoS, with no need to perform any volume correction, as the parameters of the EoS were fitted on saturation pressure and liquid density data, was used to compute the phase equilibria. A linear correlation of the influence parameter in  $T_r$  allowed very accurate estimations of surface tensions, with global average errors of 1.5% in the  $0.45 < T_r < 0.70$  range.

The broad surface tension database that was evaluated in this work (for 7 methyl esters, 4 ethyl esters, 2 propyl esters, 4 butyl esters, 10 acetates, 10 formates and also for two unsaturated methyl esters) ensures that the proposed model can adequately be used for modeling the surface tension of esters in a wide temperature range.

It is shown that the gradient theory can be used as a predictive method allowing calculating the surface tensions with good agreement with the available experimental data using constant parameters for the linear temperature dependence of the influence parameter. Having already studied and established correlations for the influence parameters for calculating pure component ester surface tensions, surface and interfacial tensions of biodiesels and heterogeneous process mixtures are expected to be modeled with the coupling of the density gradient theory with the CPA EoS, as soon as new experimental data as a function of temperature appear in literature.

#### List of symbols

|       |  |
|-------|--|
| $a$   | energy parameter ( $\text{J m}^3 \text{mol}^{-2}$ )              |
| $a_0$ | parameter for calculating $a$ ( $\text{J m}^3 \text{mol}^{-2}$ ) |
| $A_i$ | site $A$ in molecule $i$   |

|           |  |
|-----------|--|
| $b$       | co-volume parameter ( $\text{m}^3 \text{mol}^{-1}$ )                   |
| $c$       | gradient theory influence parameter ( $\text{J m}^5 \text{mol}^{-2}$ ) |
| $c_1$     | parameter for calculating $a$  |
| $D, E, F$ | correlation coefficients for the influence parameter                   |
| $f_0$     | Helmholtz energy density ( $\text{J m}^{-3}$ )                         |
| $g$       | radial distribution function   |
| $H$       | surface enthalpy ( $\text{J m}^{-2}$ )                                 |
| $k$       | binary interaction coefficient   |
| $n$       | mole density   |
| $P$       | vapor pressure (Pa)  |
| $R$       | gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )                     |
| $S$       | surface entropy ( $\text{J m}^{-2} \text{K}^{-1}$ )                    |
| $T$       | temperature (K)  |
| $X_{A_i}$ | mole fraction of component $i$ not bonded at site $A$                  |
| $x$       | mole fraction.   |
| $Z$       | compressibility factor   |

#### Greek symbols

|               |   |
|---------------|---|
| $\beta$       | association volume                                    |
| $\varepsilon$ | association energy ( $\text{J mol}^{-1}$ )            |
| $\sigma$      | surface tension ( $\text{N m}^{-1}$ )                 |
| $\Omega$      | grand thermodynamic potential ( $\text{J m}^{-3}$ )   |
| $\mu$         | chemical potential ( $\text{J mol}^{-1}$ )            |
| $\rho$        | mole density ( $\text{mol m}^{-3}$ )                  |
| $\eta$        | reduced fluid density                                 |
| $\Delta$      | association strength ( $\text{m}^3 \text{mol}^{-1}$ ) |

#### Subscripts

|        |                        |
|--------|------------------------|
| $i, j$ | pure component indexes |
| $liq.$ | liquid                 |
| $r$    | reduced                |
| $c$    | critical               |

#### Superscripts

|          |             |
|----------|-------------|
| $assoc.$ | association |
| $phys.$  | physical    |

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