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Invited Article. Calculation of the interfacial tension in multicomponent liquid-vapor systems by the density gradient theory

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Abstract.-
A good knowledge of interfacial properties is required in many applications of the oil and gas industry, where multiphase flows are encountered like in the acid gases injection and Enhanced Oil Recovery operations. The density gradient theory, combined with the Peng-Robinson equation of state, was used to estimate the interfacial tension for binary and ternary mixtures in liquid-vapor systems, avoiding the use of experimental techniques, with maximum deviation of 15% for values above 1 mN/m. The new criterion of using the equilibrium K values for selecting the reference component, instead of the surface tension of the pure component, has been successfully tested. We have performed calculations of systems composed by carbon dioxide and hydrocarbons. The calculated interface thickness increases as the system equilibrium pressure increases. It is proposed to evaluate other liquid-vapor systems and other equations of state. Also, the study could be extended to liquid-liquid systems.

Keywords: interfacial tension; gradient theory; multicomponent mixtures.

1. Introduction

In oil industry, the interfacial tension (IFT) is required for the design of extraction processes in refineries and in the oil enhanced recovery operations, because this property controls the fluid...
displacement in porous media [11].

At present, two methods can be used to predict this property without using the experimental techniques: the density gradient theory (DGT) and the density functional theory (DFT) [2, 3, 4]. Both methods carry the need to solve iterative algorithms to determine the density profile of each component inside the interface, so any calculation implies the use of some computational tool for its solution.

The density gradient theory [5] is based on an approximation of mean field that describes a constant evolution of the density of the Helmholtz energy along the interface, allowing to know such interfacial properties as the density profile and the interfacial tension. The DGT was validated by Sahimi [6], who considered it to be more efficient and precise than other methods. The main advantage of this method is that the applied equation of state (EOS) can be used for the interfacial properties and for the phase equilibrium.

The DGT has been combined with different equations of state. This method has been employed with different versions of the SAFT (Statistical Associating Fluid Theory) equation of state, for describing the interfacial behavior of the mixture CO₂ + H₂O [7, 8, 9, 10].

On the other hand, the DGT has been used with the classical cubic EOS, like Redlich-Kwong-Soave (RKS) [11], and its more recent modifications to study associating components, the Cubic-Plus-Association (CPA) EOS, who is a generalized cubic EOS with an additional associating term [12].

The Peng-Robinson (PR) EOS, with different mixing rules, has also been used to study not only hydrocarbon mixtures [13] but also a polar system like the mixture of a saturated hydrocarbon with an alcohol or an ether (fuel mixtures). For these systems, the PR EOS has been used with the Stryjek-Vera thermal cohesion function and the Huron-Vidal mixing rule [14].

2. Methodology

According to the density gradient theory, in the absence of external potentials, the differential equation that governs the density distributions ρ(z) through a planar interface is the equation [1] [11, 13], where n_c is the number of components in the mixture and Φ(ρ) is the grand thermodynamic potential. Considering that the influence parameters c_{jk} are independent on composition, the second term in the right side of the equation [11] vanished and the Φ(ρ) is related to chemical potential μ, leading to the equation [2].

\[
\frac{\partial \Phi(\rho)}{\partial \rho_i} = \sum_{j=1}^{n_c} \frac{d}{dz} \left[ c_{i,j} \frac{d\rho_j}{dz} \right]
\]

\[
-\frac{1}{2} \sum_{j=1}^{n_c} \sum_{k=1}^{n_c} \left[ \frac{\partial c_{jk}}{\partial \rho_i} \frac{d\rho_j}{dz} \frac{d\rho_k}{dz} \right]
\]

\[
\sum_{j=1}^{n_c} c_{i,j} \left[ \frac{d^2 \rho_j}{dz^2} \right] = \mu_i(\rho) - \mu_{i}^c
\]

The influence parameter contains the information of the intermolecular geometry of the interface and it relates the deviation of the Helmholtz energy density and the chemical potential. In equation [2], μ_{i}^c is the chemical potential of component i at the equilibrium conditions, μ_i(ρ) is the chemical potential of component i inside the interface.

The differential equation [2] have boundary conditions on the infinite interval [−∞, +∞]. An easier approach is to define a new density independent variable ρ_s to eliminate the variable z (position inside the interface). The transformation will be done with the equation [3]. The independent variable ρ_s (known like density of the reference component) will increase monotonically from its value in the low density phase to its value in the high density phase as z changes from −∞ to +∞.

\[
\frac{d\rho_i}{dz} = \frac{d\rho_i}{d\rho_s} \frac{d\rho_s}{dz}
\]

The differential equation [2] are then transformed to the new independent variable ρ_s. For example, for a binary mixture (components 1 and 2) the equation [2] will result in 2 equations (equations [4] and [5]):

\[
c_{11} \left[ \frac{d^2 \rho_1}{dz^2} \right] + c_{12} \left[ \frac{d^2 \rho_2}{dz^2} \right] = \mu_1(\rho) - \mu_{1}^c
\]
\[ c_{21} \frac{d^2 \rho_1}{dz^2} + c_{22} \frac{d^2 \rho_2}{dz^2} = \mu_2 (\rho) - \mu_s^2 \]  

(5)

If \( c_{12} = c_{21} = (c_{11} \times c_{22})^{1/2} \), by multiplying the equation (5) by \((c_{11})^{1/2}\) and the equation (4) by \((c_{22})^{1/2}\), both equations are the same and the equation (6) is obtained:

\[ \sqrt{c_1} (\mu_2 (\rho_1, \rho_2) - \mu_s^2) = \sqrt{c_2} (\mu_1 (\rho_1, \rho_2) - \mu_1^s) \]  

(6)

The algebraic equation (6) is solved for the component 1, because the component 2 is the reference component (the independent variable for the densities).

For multicomponent systems, the binary interaction parameter is \( c_{i,j} = (1 - \beta_{i,j})(c_{i}c_{j})^{1/2} \). When \( \beta_{i,j} = 0 \), the \( n_c \) differential equations from equation (2), can be reduced to a set of \((n_c - 1)\) algebraic equations showed by equation (7), where \( s \) is the index for the reference component:

\[ \sqrt{c_1} (\mu_s (\rho_1, \rho_2, .. \rho_n) - \mu_s^s) \]  

\[ - \sqrt{c_s} (\mu_i (\rho_1, \rho_2, .. \rho_n) - \mu_i^s) = 0 \]  

(7)

The solution of the equation (7) gives us the density of each component \( i \) as a function of \( \rho_s \) and the derivative \( d\rho_i / d\rho_s \). When the density profile of the reference component \( \rho_s(z) \) is calculated and it is verified its monotonic behavior, the density profiles of the \( i \) components inside the interface \( \rho_i(z) \) can be obtained with the equation (5). This allows to access to the Helmholtz energy profile in the interface which is necessary to calculate the interface tension. In this work, the multicomponent mixtures were studied when \( \beta_{i,j} = 0 \), solving the set of \((n_c - 1)\) algebraic equations from equation (7), following the calculation sequence showed here:

1. Select the components, the equation of state (with its parameters) to be used and the conditions (T, P, global compositions).
2. Determine the equilibrium data: molar fractions \( x \) and \( y \) and bulk densities of each phase at T & P (\( x_i \rho_L \) in liquid phase and \( y_i \rho_V \) in vapor phase).
3. For each component, determine the pure component \( i \) data: the saturation pressure (\( P_{i,s}^{sat} \)), the saturation densities (\( \rho_{i,V}^{sat}, \rho_{i,L}^{sat} \)) and the experimental surface tension, \( \sigma_{i,exp}^{(i)} \), at the reference temperature \( T_{ref,i} = NBP_i \) (according to Mejía [14]). Other Tref, different from the Normal Boiling Point (NBP) can be chosen if the effect of the temperature on the parameter \( c_i \) is going to be evaluated. When the NBP is not available for some component, the triple point temperature (TPT) can be used.
4. Determine the pure component interaction parameter \( c_i \) with the equation (8), using only the chemical potential for calculating the grand thermodynamic potential. The definition of the chemical potential for pure component, is shown in equation (9).

\[ H = \left( P_{i,s}^{sat} \sqrt{2 \rho_i (\mu_{ipure} - \mu_{ipure}^{sat}) - (P(\rho_i) - P_{i,s}^{sat})} \right)^2 \]  

(8)

\[ c_i \left( T^{NBP}_i \right) = \sigma_{i,exp}^{(i)} \left( T^{NBP}_i \right) H \]  

\[ \mu_{ipure} = \mu_{ipure}^{res} - RT \ln \left( \frac{P_{ref}}{\rho_{i,RT}} \right) + RT \]  

(9)

Where,
\( \mu_{ipure}^{res} \): residual contribution of the chemical potential for the pure component \([kJ/kmol]\).
\( P_{ref} \): reference pressure 100 kPa.
\( R \): gas universal constant 8, 314\([kJ/(kmolK)]\).
5. Calculate the equilibrium \( K \) values of each component; \( K_i = y_i / x_i \). The heavy compound (smallest \( K_i \) value) will be for the reference component \( s \). (As alternative, some authors propose to calculate the surface tension of the pure components and the highest one is for the reference component [15]).

The selection of the reference component is automatic in the code but it is possible to do it manually.
6. Determine the equilibrium molar concentrations of component \( i \) in each phase with equation (10) (these are the limits of the density profiles) for example for a liquid-vapor equilibrium:

\[ \rho_{i,L}^e = x_i \rho_L \quad \text{and} \quad \rho_{i,V}^e = y_i \rho_V \]  

(10)
7. Determine the $\Delta \rho_s$ for the step change in the density of the reference component $\rho_s$, ($N_p = 500$, [13]), with equation (11).

$$\Delta \rho_s = \frac{\rho_{s,L}^i - \rho_{s,V}^i}{N_p}$$  (11)

8. Solving the set of equations (7):

$$F (i) = \sqrt{c_i}(\mu_s(\rho_1, \rho_2, .., \rho_{nc}) - \mu_s^e)$$

$$- \sqrt{c_i}(\mu_i(\rho_1, \rho_2, .., \rho_{nc}) - \mu_i^e) = 0$$  (12)

For the solution of the $n_c - 1$ algebraic equations, (equation (12)), the initialization of the $\rho_i$ ($i \neq s$) is required at each k step (sequence from 8a to 8c).

a) The matrix equation (14) is used for finding the first estimate of the $n_c - 1$ derivatives $\frac{d\mu_i}{d\rho_j}$

$$\sum_{i=1}^{n_c-1} \sum_{j=1}^{n_c-1} \left\{ \left[ \sqrt{c_i} \frac{\partial \mu_s}{\partial \rho_j} - \sqrt{c_s} \frac{\partial \mu_i}{\partial \rho_j} \right] \frac{d\rho_j}{d\rho_s} - \sqrt{c_s} \frac{\partial \mu_{is}}{\partial \rho_s} \right\} = 0$$  (13)

$$\left[ \sqrt{c_s} \frac{\partial \mu_s}{\partial \rho_j} - \sqrt{c_i} \frac{\partial \mu_i}{\partial \rho_j} \right] \frac{d\rho_j}{d\rho_s} = \sqrt{c_i} \frac{\partial \mu_{is}}{\partial \rho_s}$$  (14)

b) The $n_c$ derivatives $\frac{d\mu_i}{d\rho_j}$ required in equation 14 are evaluated numerically with $\delta \rho_j = 1 \times 10^{-6}$ using the equation 15 for the chemical potential of the component $i$ in the mixture:

$$\mu_i = \mu_{i res}^e + RT \left[ 1 - \ln \left( \frac{P_{ref}}{\rho_i RT} \right) \right]$$  (15)

Where, $\mu_{i res}^e$ is residual contribution of the chemical potential of $i$ in the mixture, [kJ/kmol]

c) The first estimation for the k step concentrations will be done with equations 16 and 17:

$$\rho_s^k = \rho_s^{k-1} + \Delta \rho_s$$  (16)

$$\rho_i^k = \rho_i^{k-1} + \left( \frac{d\mu_i}{d\rho_s} \right) \Delta \rho_s$$  (17)

$d) With this first estimate for concentrations $\rho_i$, the system of algebraic equations is solved by Newton-Raphson method, with $N$ iterations (until in equation 19 the biggest of the $|\Delta \rho_i| < 1 \times 10^{-7}$). (The definitive concentrations for the k step are then achieved).

$$\begin{pmatrix} \frac{\partial F(1)}{\partial \rho_1} & \frac{\partial F(1)}{\partial \rho_{nc-1}} \\ \vdots & \vdots \\ \frac{\partial F(n_c-1)}{\partial \rho_1} & \frac{\partial F(n_c-1)}{\partial \rho_{nc-1}} \end{pmatrix} \begin{pmatrix} \rho_1^k \\ \vdots \\ \rho_{nc-1}^k \end{pmatrix} = -\begin{pmatrix} F(1) \\ \vdots \\ F(n_c-1) \end{pmatrix}$$  (18)

$$\begin{pmatrix} \frac{\partial F(1)}{\partial \rho_1} & \ldots & \frac{\partial F(1)}{\partial \rho_{nc-1}} \\ \vdots & \ldots & \vdots \\ \frac{\partial F(n_c-1)}{\partial \rho_1} & \ldots & \frac{\partial F(n_c-1)}{\partial \rho_{nc-1}} \end{pmatrix} \begin{pmatrix} \Delta \rho_1 \\ \vdots \\ \Delta \rho_{nc-1} \end{pmatrix} = -\begin{pmatrix} F(1) \\ \vdots \\ F(n_c-1) \end{pmatrix}$$  (19)

For the next k, the procedure from step 8a is repeated.

9. Once the iterative process for getting “$\rho_i$” is finished, the density profile for the reference component “$\rho_s(z)$” must be verified and for doing that, the grand thermodynamic potential, $\Phi(\rho)$ is needed and it can be calculated by equation 20.

$$\Delta \Phi (\rho_1, \rho_2, .., \rho_{nc}) = \Phi(\rho) - \Phi^e$$

$$= \frac{A}{V} - \sum_{i=1}^{nc} (\rho_i \mu_i^e) + P^e$$

$$a_0 = \sum_{i=1}^{nc} (\rho_i \mu_i^e) + P^e$$  (20)

Where $\Phi^e = -P^e$, the equilibrium pressure, [Pa]

$A = \text{Helmholtz energy} [J]$

$V = \text{volume} [m^3]$

$a_0 = \text{Helmholtz energy density} [J/m^3]$.

The Helmholtz energy density $a_0$ can be calculated with equation (21).

$$a_0 (\rho) = \rho \mu(\rho) - P(\rho)$$  (21)
10. Calculate the concentration profile for the reference component, “ρₛ(z)” with equation (22).

\[
J = \sum_{i=1}^{n_c} \left[ \rho_i (\mu_i(\rho_i) - \mu_f) \right] - (P(\rho) - P^e) = 2J \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} Y_{i,j} \frac{d\rho_i}{d\rho_s} \frac{d\rho_j}{d\rho_s} = \frac{2J}{\sum_{i=1}^{n_c} \sum_{j=1}^{n_c} Y_{i,j}} \frac{d\rho_s}{dz}^2 \tag{22}
\]

If \(d\rho_s/dz \geq 0\), the concentration profile of the reference component (\(\rho_s\)) is monotonic as it was stated for doing the independent variable change according equation (3), the interface position can be calculated from step 11. On the contrary, other reference component has to be selected and the calculation process must be repeated from step 7.

11. The interface position is calculated with \(d\rho_s/dz = B\). For example, for the first point \(z_1\) from an arbitrary origin \(z_0\), using the equation (23).

\[
\int_{z_0}^{z_1} dz = \int_{\rho_{s0}}^{\rho_{s1}} \frac{1}{B} d\rho_s \tag{23}
\]

By the trapezoid method, the equation (24) is obtained:

\[
z_1 - z_0 = \frac{(\rho_{s1} - \rho_{s0})}{2} \left( \frac{1}{B_0} + \frac{1}{B_1} \right) \tag{24}
\]

The general expression for the interface position “z” at step “k” is in equation (25):

\[
z_k = z_{k-1} + \frac{\Delta \rho_s}{2} \left( \frac{1}{B_k} + \frac{1}{B_{k-1}} \right) \tag{25}
\]

12. Calculate the interfacial tension “σ”, with the equation (26) (if the concentration profile of the reference component from the step 10 is monotonic):

\[
J = \sum_{i=1}^{n_c} \left[ \rho_i (\mu_i(\rho_i) - \mu_f) \right] - (P(\rho) - P^e) = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} Y_{i,j} \frac{d\rho_i}{d\rho_s} \frac{d\rho_j}{d\rho_s} \tag{26}
\]

\[
\sigma = \int_{\rho_f}^{\rho_s} \sqrt{2J \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} Y_{i,j} d\rho_s} \tag{26}
\]

3. Analysis and Discussion of Results

Two binary and one ternary mixtures were studied using the Peng-Robinson (PR) equation of state. The pure components are n-butane (nC₄), n-decane (nC₁₀) and carbon dioxide (CO₂).

Table 1: \(T_c\), \(P_c\), acentric factor of pure components.

<table>
<thead>
<tr>
<th>Component(*)</th>
<th>(T_c) [K]</th>
<th>(P_c) [Pa]</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>304.21</td>
<td>7.383 × 10⁶</td>
<td>0.223621</td>
</tr>
<tr>
<td>nC₄</td>
<td>425.12</td>
<td>3.796 × 10⁶</td>
<td>0.290164</td>
</tr>
<tr>
<td>nC₁₀</td>
<td>617.7</td>
<td>2.110 × 10⁶</td>
<td>0.49328</td>
</tr>
</tbody>
</table>

(*) : Experimental value from Diadem Pro Gold®

3.1. Binary mixtures

The critical properties of pure components (critical temperature \(T_c\), critical pressure \(P_c\) and acentric factor \(w\)) are shown in Table 1. The expressions of the saturation pressure \(P^sat_i\) and saturation density \(\rho^sat_i(T)\) of pure components can be calculated with equations (27) and (28):

\[
P^sat_i(T) = \frac{A}{B^{1/(1 - \xi)^{\nu}}} \tag{27}
\]

\[
\rho^sat_i(T) = \exp \left[ A + \frac{B}{T} + ClnT + DT^E \right] \tag{28}
\]

The parameters A, B, C, D and E are shown in Table 2 and 3.

Table 2: Parameters of saturation liquid pressure of pure components.

<table>
<thead>
<tr>
<th>Saturation pressure (Pa)</th>
<th>CO₂</th>
<th>nC₄</th>
<th>nC₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>47.0169</td>
<td>66.343</td>
<td>112.73</td>
</tr>
<tr>
<td>B</td>
<td>-2839</td>
<td>-4363.2</td>
<td>-9749.6</td>
</tr>
<tr>
<td>C</td>
<td>-3.86388</td>
<td>-7.046</td>
<td>-13.245</td>
</tr>
<tr>
<td>D</td>
<td>0.52158</td>
<td>0.223621</td>
<td>0.00000094509</td>
</tr>
<tr>
<td>E</td>
<td>15.2286</td>
<td>0.290164</td>
<td>0.0000071266</td>
</tr>
</tbody>
</table>

Values from Diadem Pro Gold®

The calculated influence parameters for the pure components used in the mixtures are shown in Table 4.
Table 3: Parameters of saturation liquid density of pure components

<table>
<thead>
<tr>
<th>Saturation density (kmol/m³)</th>
<th>CO₂</th>
<th>nC₄</th>
<th>nC₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2.768</td>
<td>1.0677</td>
<td>0.41084</td>
<td></td>
</tr>
<tr>
<td>B 2.62612</td>
<td>0.27188</td>
<td>0.25175</td>
<td></td>
</tr>
<tr>
<td>C 304.21</td>
<td>425.12</td>
<td>617.7</td>
<td></td>
</tr>
<tr>
<td>D 0.2908</td>
<td>0.28688</td>
<td>0.28571</td>
<td></td>
</tr>
<tr>
<td>E 0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Values from Diadem Pro Gold®

Table 4: Calculated influence parameter cᵢ of pure components (PR).

<table>
<thead>
<tr>
<th>Component</th>
<th>Tref [K]</th>
<th>σₜₚₜₜ [mN/m] (٭)</th>
<th>Jₚₑ [m²/kmol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>216.58 (٭)</td>
<td>16.6924</td>
<td>2.6147E-14</td>
</tr>
<tr>
<td>nC₄</td>
<td>272.65</td>
<td>14.90103</td>
<td>1.75337E-13</td>
</tr>
<tr>
<td>nC₁₀</td>
<td>447.305</td>
<td>10.26487</td>
<td>1.2415E-12</td>
</tr>
</tbody>
</table>

(٭): Experimental value from Diadem Pro Gold®
(٭): TPT is used for CO₂ instead NBP

Mixture CO₂/nC₁₀ at T = 344.3K. For this mixture, the PR binary interaction parameter kᵢⱼ=0.12 was used. The IFT was calculated at four different pressures. The results are shown in Table 5 and in Figures 1, 2 and 3.

Table 5: Interfacial tension vs pressure at 344.3K for CO₂/nC₁₀ mixture (PR).

<table>
<thead>
<tr>
<th>P [bar]</th>
<th>IFT [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.4</td>
<td>7.24</td>
</tr>
<tr>
<td>103.4</td>
<td>2.77</td>
</tr>
<tr>
<td>117.3</td>
<td>1.37</td>
</tr>
<tr>
<td>125.5</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Figure 1 shows that the IFT values obtained by the density gradient theory for the CO₂/nC₁₀ mixture are very close to the experimental data with an absolute average deviation (AAD) below 10 %, when the experimental values are above 1 mN/m. For low experimental IFT values, the AAD increases abruptly over 60 %. This behavior was obtained also by other author [11] working DGT with RKS equation of state with a binary mixture methane + butane and it was stated the limitation of this cubic equation for the estimation of the liquid equilibrium values at high pressure.

The monotonic trend of the density profile inside the interface, for the n-decane is observed in Figure 2. This behavior confirms the correct choice of the nC₁₀ as the reference component.

Mixture CO₂/nC₄ at T = 344.3K. For this mixture, the PR binary interaction parameter kᵢⱼ=0.15 was used. The IFT was calculated at three different pressures. The results are shown in Table 6 and in Figures 4, 5 and 6.

In Figure 4, the IFT values obtained by DGT for the CO₂/nC₄ mixture are close to the experimental data (15 %), but there is a bigger deviation (24 %) in the interfacial tension value below 1mN/m, like in the previous case. The monotonic trend of the density profile for the n-butane inside the interface...
Figura 3: Density profiles at 344.3K and different pressures for CO₂. (CO₂/nC₁₀ mixture, PR).

Table 6: Interfacial tension vs pressure at 344.3K for CO₂/nC₄ mixture (PR).

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>IFT [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.05</td>
<td>2.79</td>
</tr>
<tr>
<td>55.3</td>
<td>1.57</td>
</tr>
<tr>
<td>73</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Figura 4: Interfacial tension vs pressure at 344.3K, (CO₂/nC₄ mixture, PR). Experimental data [17].

is observed in Figure [5]. Like it was obtained for the nC₁₀ in the previous mixture, the selection of the nC₄ as the reference component was the correct.

In Figures [5] and [6] it is observed that the interface thickness increases as the equilibrium pressure increases. This behavior is the same for the binary mixture CO₂/nC₁₀ (Figures [2] and [3]).

3.2. Ternary mixture CO₂/nC₄/nC₁₀ at T = 344.3K

The kij binary interaction parameters used for the Peng-Robinson (PR) equation of state are presented in Table [7].

Table 7: kij parameter for PR equation of state in mixture CO₂/nC₄/nC₁₀.

<table>
<thead>
<tr>
<th>kij</th>
<th>CO₂</th>
<th>nC₄</th>
<th>nC₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0</td>
<td>0.08</td>
<td>0.1</td>
</tr>
<tr>
<td>nC₄</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>nC₁₀</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

In this case, the influence parameters were calculated using a reference temperature different from the normal boiling point and the values are shown in Table [8]. This mixture has a global molar composition 90.2 % CO₂/5.9 % nC₄/3.9 % nC₁₀ and it was evaluated at five pressures. The results are shown in Figures [7][8][9][10].

The Figure [7] shows the interfacial tension calculated values are similar to the experimental ones for the studied mixture, with a maximum

Figura 5: Density profiles, at 344.3K and different pressures, reference component, nC₄. (CO₂/nC₄ mixture, PR).

Figura 6: Density profiles at 344.3K and different pressures for CO₂ (CO₂/nC₄ mixture, PR).

Figura 7: Interfacial tension vs pressure at 344.3K, CO₂/nC₄/nC₁₀ mixture, PR. Experimental data [17].

In Figures 5 and 6, it is observed that the interface thickness increases as the equilibrium pressure increases. This behavior is the same for the binary mixture CO₂/nC₁₀ (Figures 2 and 3).

3.2. Ternary mixture CO₂/nC₄/nC₁₀ at T = 344.3K

The kij binary interaction parameters used for the Peng-Robinson (PR) equation of state are presented in Table 7.

Table 7: kij parameter for PR equation of state in mixture CO₂/nC₄/nC₁₀.

<table>
<thead>
<tr>
<th>kij</th>
<th>CO₂</th>
<th>nC₄</th>
<th>nC₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0</td>
<td>0.08</td>
<td>0.1</td>
</tr>
<tr>
<td>nC₄</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>nC₁₀</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

In this case, the influence parameters were calculated using a reference temperature different from the normal boiling point and the values are shown in Table 8. This mixture has a global molar composition 90.2 % CO₂/5.9 % nC₄/3.9 % nC₁₀ and it was evaluated at five pressures. The results are shown in Figures 7, 8, 9, and 10.

The Figure 7 shows the interfacial tension calculated values are similar to the experimental ones for the studied mixture, with a maximum
AAD of 10.9%. The IFT values below 1mN/m were in very good agreement with the experimental data. A possible explanation is that the ‘\(k_{ij}\)’ binary parameters used in the PR EOS for this mixture was adjusted with the experimental phase equilibrium data, for the range of the equilibrium pressure and temperature where the interfacial tension is going to be estimated. Also, the effect of the influence parameter ‘\(c_i\)’ could be evaluated, because in this case the reference temperature Tref was higher than the NBP of the pure components for the estimation of the ‘\(c_i\)’.

Table 8: Calculated influence parameter ‘\(c_i\)’ of pure components (PR) at Tref #NBP.

<table>
<thead>
<tr>
<th>Component</th>
<th>Tref [K]</th>
<th>(\sigma_{\text{pure}}) [mN/m] (*)</th>
<th>(c_i) [J m(^5)/kmol(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>285</td>
<td>2.44307</td>
<td>3.8909E-14</td>
</tr>
<tr>
<td>nC4</td>
<td>400</td>
<td>1.616567</td>
<td>3.1261E-13</td>
</tr>
<tr>
<td>nC10</td>
<td>590</td>
<td>0.951017</td>
<td>1.6178E-12</td>
</tr>
</tbody>
</table>

(*): Experimental value from Diadem Pro Gold®

Once again, the selection of the reference component was the correct as it is observed in the n-decane density profile (Figure 8). Also, the interface thickness increases when the pressure increases (Figures 8 to 10), as it was observed for the binary mixtures.

### 4. Conclusions

In this work, we have proposed an algorithm to calculate the interfacial tension with the Density Gradient Theory for multi-component mixtures. DGT, combined with the Peng-Robinson EOS, allows to estimate with good precision the interfacial tension for multicomponent mixtures in liquid-vapor systems, avoiding the use of experimental techniques. Only pure properties are
needed to calibrate the model.

The new criterion of using $K$ values for selecting the reference component, instead of the surface tension of the pure component, has been successfully proven for the studied mixtures. Other cases like the mixtures with non-volatile (or with not condensing) component can be studied. For more complex mixtures where there are similar components, like isomers, may be both criteria can be incorporated for selecting the reference component.

For the examined systems ($CO_2$ and hydrocarbons), the interface thickness increases as the system pressure increases and the model predicts the interfacial tension with a deviation below 15%, for values above 1 mN/m. The reduction of this deviation for lower IFT values may be studied in future works with a better adjustment of the PR $ki j$ binary parameters and the estimation of the influence parameters “ci” at reference temperatures in the interval NBP< Tref< $Tc$.

It is proposed to evaluate other liquid-vapor systems, like polar systems and other equations of state. Also, the study could be extended to liquid-liquid systems.

References


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