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Prediction of the solubility of aromatic components of wine in carbon dioxide

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Abstract

The possibility of using group contribution methods to predict the solubility of the most important families of aromatic compounds of wine—alcohols, esters and aldehydes—in carbon dioxide (CO_2) is analyzed in this work by comparing the results obtained with three different predictive methods, which couple equations of state and mixing rules based on the concept of the excess Gibbs free energy. The methods studied are the Predictive Soave–Redlich–Kwong (PSRK), the Linear Combination of the Vidal and Michelsen mixing rules (LCVM) and the Wong–Sandler mixing rule (WS). In all these models the excess Gibbs free energy is calculated by the UNIFAC method. For the WS mixing rule, interaction parameters between the groups CO_2/CH_2, CO_2/OH, $CO_2/CCOO$ and CO_2/CHO are obtained. For the LCVM mixing rule, interaction parameters are calculated for the groups CO_2/CHO, and revised values for the groups CO_2/OH are suggested. Finally, for the PSRK mixing rule, revised values are proposed for the interaction parameters between the groups CO_2/OH and CO_2/CHO. The results of this work show that the PSRK is the method that best predicts the phase equilibria for the systems studied, with a quadratic mean deviation lower than 5.5%.

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Keywords: Phase equilibria; Prediction; Mixing rules; Wine; Carbon dioxide

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1. Introduction

Wine is one of the most complex alcoholic beverages, mainly due to the presence of numerous volatile organic compounds, of which more than 800 have already been identified [1,2]. These compounds belong to a wide variety of chemical families, namely, acids, esters, alcohols, aldehydes, lactones, terpenes, nor-isoprenoids, pyrazines, and many others. The characteristic bouquet of a wine is largely the balance of the contribution of these different compounds and not the result of an individual impact. Therefore, it seems clear that the implementation of a dealcoholization process, in which the main goal is to remove the ethanol while preserving the organoleptic properties of the wine, is a very complex and challenging problem.

In recent years, supercritical fluid extraction with carbon dioxide has been suggested as a promising alternative to other conventional dealcoholization

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Nomenclature

$a(T)$	equation of state attractive parameter ($\mathrm{Pa\,m^6\,mol^{-2}}$)
$a_{c,i}$	equation of state attractive parameter for component i at the critical conditions ($\mathrm{Pa\,m^6\,mol^{-2}}$)
$a_i(T)$	equation of state attractive parameter for component i ($\mathrm{Pa\,m^6\,mol^{-2}}$)
A_{km}	UNIFAC group interaction parameter (K)
b	equation of state parameter ($\mathrm{m^3\,mol^{-1}}$)
$B(T)$	second virial coefficient ($\mathrm{m^3\,mol^{-1}}$)
b_i	equation of state parameter for component i ($\mathrm{m^3\,mol^{-1}}$)
$B_{ij}(T)$	cross virial coefficient ($\mathrm{m^3\,mol^{-1}}$)
B_{km}	UNIFAC group interaction parameter
c_1, c_2	EOS characteristic constants
C_1, C_2, C_3	Mathias–Copeman equation constants
C_{km}	UNIFAC group interaction parameter ($\mathrm{K^{-1}}$)
$C_{1,\mathrm{LCVM}}$, $C_{2,\mathrm{LCVM}}$	LCVM mixing rule constants
C_{PSRK}	PSRK mixing rule constant
C_{WS}	WS mixing rule constant
FOB	objective function
G^{E}	excess molar Gibbs free energy ($\mathrm{J\,mol^{-1}}$)
G_0^{E}	excess molar Gibbs free energy at low pressure ($\mathrm{J\,mol^{-1}}$)
k_{ij}	molecular interaction parameter of the WS mixing rule
$m_{0,i}$, $m_{1,i}$, m_i	Stryjek–Vera equation constants
nc	number of components
NRES	number of results
p	Pressure (Pa)
$P_{c,i}$	critical pressure of component i (Pa)
Q_k	UNIFAC area parameter for the functional group k.
R	ideal gas constant ($\mathrm{Pa\,m^3\,mol^{-1}\,K^{-1}}$)
R_k	UNIFAC volume parameter for the functional group k
T	temperature (K)
$T_{c,i}$	critical temperature of component i (K)
$T_{r,i}$	reduced temperature of component i ($T/T_{c,i}$)
V	molar volume ($\mathrm{m^3\,mol^{-1}}$)
$x_{\mathrm{CALC},i}$	calculated value of liquid phase mole fraction
$x_{\mathrm{CO_2}}$	mole fraction of CO_2 in the liquid phase
$x_{\mathrm{EXP},i}$	experimental value of liquid phase mole fraction
x_i	component i mole fraction
$y_{\mathrm{CALC},i}$	calculated value of vapor phase mole fraction
$y_{\mathrm{CO_2}}$	mole fraction of CO_2 in the vapor phase
$y_{\mathrm{EXP},i}$	experimental value of vapor phase mole fraction

Greek letters

α	dimensionless equation of state parameter, $\alpha = a(T)/(bRT)$
α_i	dimensionless equation of state parameter for component i, $\alpha_i = a_i(T)/(b_iRT)$
ε	mean quadratic deviation
ω_i	acentric factor
ψ_{km}	UNIFAC interaction parameter

Abbreviations

EOS	equation of state
EOS/G^{E}	equation of state and excess Gibbs free energy models
LCVM	linear combination of the Vidal and Michelsen mixing rules
NRTL	non-random two liquids
PR	Peng–Robinson
PRSV	Peng–Robinson–Stryjek–Vera
PSRK	Predictive Soave–Redlich–Kwong
SRK	Soave–Redlich–Kwong.

UNIFAC	UNIQUAC functional group activity coefficients
UNIQUAC	Universal QuasiChemical
WS	Wong–Sandler

techniques [3–5], such as: distillation [6–9], evaporation [10–12], osmosis [6,13–17] and solvent extraction [18]. The design of the dealcoholization process by supercritical fluid extraction with CO_2 requires information on the solubility of the aromatic compounds of wine in carbon dioxide. However, the experimental measurement of phase equilibria is a difficult, time consuming, and expensive process, which, for complex mixtures such as wine, becomes an endless task. Thus, the development of predictive methods, which allow overcoming the lack of experimental data, is of the uppermost importance for the design of this type of processes. These predictive methods are less precise than the alternative correlation methods, however, the correlation methods have the disadvantage of needing experimental data to be applied.

The prediction of phase equilibria at high pressures is commonly accomplished by coupling cubic equations of state (EOS), such as the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR), with mixing rules based on the concept of the excess Gibbs free energy (G^E), as was first suggested by Huron and Vidal [19]. These models are usually referred to as EOS/G^E models. The G^E is typically obtained by using expressions of the excess Gibbs free energy developed for liquid solutions at moderate pressures, such as the Wilson, NRTL and UNIQUAC equations. If the interaction parameters for the G^E model are available, the EOS/G^E models allow the prediction of phase equilibria at high pressures by using parameters obtained from data at low pressures. The EOS/G^E models can be made totally predictive if the excess Gibbs free energy is calculated by a group contribution method, such as the UNIFAC.

In this work, three EOS/G^E methods, based in three different mixing rules, are studied, and their capability for predicting the solubility of the most important families of aromatic compounds of wine in CO_2 is analyzed. These methods are the PSRK [20], which has been one of the most extensively used and for which there are a large number of interaction parameters published, the LCVM [21], that has been suggested to give very good results for polar and asymmetric systems, and for which there are also some parameters published, and the WS mixing rule [22,23], which has the advantage of being theoretically consistent, because it gives rise to a quadratic dependence on composition for the second virial coefficient, but for which there are no parameters published for the group CO_2.

These methods can be used to predict phase equilibria at high pressures using the UNIFAC parameters obtained at low and moderate pressures for vapor–liquid equilibrium. At most, there is only need to extend the existing table of parameters to account for the new groups introduced, such as CO_2 and other gases. This is, by far, the most important feature of these models.

2. PSRK mixing rule

The PSRK [20] has been one of the most extensively used methods to predict phase equilibria at high pressures, which associates an equation of state with a mixing rule based in an excess Gibbs free energy model. This method uses the SRK–EOS

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{1}$$

The a and b parameters of the EOS for pure component i (i.e. a_i and b_i) are given by the following equations

$$a_i(T) = a_{c,i} f(T, T_{c,i}, \omega_i) \tag{2}$$

and

$$b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \tag{3}$$

where

$$a_{c,i} = 0.42747 \frac{R^2 T_{c,i}^2}{P_{c,i}} \tag{4}$$

The subscript c indicates that the properties are evaluated at the critical point. For non-polar substances, $f(T, T_{c,i}, \omega_i)$ is given by

$$f(T, T_{c,i}, \omega_i) = [1 + (0.480 + 1.574\omega_i - 0.176\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \tag{5}$$

where $T_{r,i}$ is the reduced temperature of pure component i. The critical properties and the acentric factor for the components used in this study are given in Appendix A (Table A.1).

For polar substances, and in order to improve the quality of the prediction, the function $f(T, T_{c,i}, \omega_i)$ is obtained by the Mathias–Copeman method [24], which means that $f(T, T_{c,i}, \omega_i) = f(T, T_{c,i})$, where

$$f(T, T_{c,i}) = \begin{cases} [1 + C_1(1 - \sqrt{T_{r,i}}) + C_2(1 - \sqrt{T_{r,i}})^2 + C_3(1 - \sqrt{T_{r,i}})^3]^2, & T_{r,i} \le 1 \\ [1 + C_1(1 - \sqrt{T_{r,i}})]^2, & T_{r,i} > 1 \end{cases} \quad (6)$$

The constants C_1, C_2 and C_3 are adjustable parameters obtained by fitting the EOS to pure component vapor pressure data. The values of these constants, for the components used in this work, are summarized in Appendix A (Table A.2).

When applied to mixtures, the PSRK model calculates the parameter b as a linear combination of the pure component parameters, b_i

$$b = \sum_{i=1}^{nc} x_i b_i \quad (7)$$

and the parameter a is obtained by calculating the dimensionless quantity α, defined as $\alpha = a(T)/(bRT)$, for mixtures, and $\alpha_i = a_i(T)/(b_i RT)$, for pure component i. According to the PSRK model, α is given by

$$\alpha = \frac{1}{C_{PSRK}} \left[\frac{G_0^E}{RT} + \sum_{i=1}^{nc} x_i \ln \frac{b}{b_i} \right] + \sum_{i=1}^{nc} x_i \alpha_i \quad (8)$$

where C_{PSRK} is a constant that takes the value of -0.647, and G_0^E is the excess molar Gibbs free energy obtained by a low pressure solution model. In order to use the PSRK mixing rule in a totally predictive form, the Gibbs energy must be calculated by a group contribution method, such as UNIFAC.

In the PSRK model, the UNIFAC interaction parameters are assumed to be temperature dependent, and the parameter ψ_{km} of the UNIFAC method is calculated by the expression

$$\psi_{km} = \exp\left(-\frac{A_{km} + B_{km}T + C_{km}T^2}{T} \right) \quad (9)$$

However, for the UNIFAC main groups up to number 44, the parameters for the original UNIFAC method published for vapor–liquid equilibria are used by the PSRK method [20,25–27] and, therefore, the constants B_{km} and C_{km} are equal to zero. To extend the predictive capabilities of the PSRK model, some authors [20,25] calculated the UNIFAC interaction parameters for mixtures containing gases, such as N_2, H_2, H_2S, CH_4, CO and CO_2.

The data for the UNIFAC method, necessary to study the applicability of the PSRK model, are presented in Appendix B (Tables B.1 and B.2).

3. LCVM mixing rule

Another common method for the prediction of phase equilibria at high pressure is based on the LCVM mixing rule [21], which is a linear combination of the Vidal [28] and Michelsen [29] mixing rules. The LCVM mixing rule is usually used associated with the PR–EOS

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \quad (10)$$

For pure component i, the parameter b of the PR–EOS is given by

$$b_i = 0.07780 \frac{RT_{c,i}}{P_{c,i}} \quad (11)$$

and the parameter $a(T)$ is calculated by

$$a_i(T) = a_{c,i} f(T, T_{c,i}) \quad (12)$$

with

$$a_{c,i} = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \quad (13)$$

being $f(T, T_{c,i})$ obtained by the method of Mathias–Copeman (Eq. (6)). In Appendix A (Table A.2), the Mathias–Copeman constants are listed for the PR–EOS.

For the LCVM model, the parameters b and α of the mixture are obtained by Eqs. (7) and (14), respectively

$$\alpha = \frac{1}{C_{1,LCVM}} \frac{G_0^E}{RT} + C_{2,LCVM} \sum_{i=1}^{nc} x_i \ln \frac{b}{b_i} + \sum_{i=1}^{nc} x_i \alpha_i \quad (14)$$

The constants $C_{1,LCVM}$ and $C_{2,LCVM}$ take the values of -0.558 and -1.213, respectively.

The LCVM mixing rule has also been applied with the original UNIFAC group contribution model, using the published interaction parameters for vapor–liquid equilibrium and the new parameters obtained for gases, such as CO_2 [30].

The LCVM model considers also that the UNIFAC interaction parameters are temperature dependent, and that the UNIFAC parameter ψ_{km} is given by Eq. (15)

$$\psi_{\mathrm{km}} = \exp\left(-\frac{A_{\mathrm{km}} + B_{\mathrm{km}}(T - 298.15)}{T}\right) \tag{15}$$

To study the applicability of the LCVM model to predict the solubility for aromatic components of wine in CO_2, the interaction parameters for the groups CO_2/CHO had to be determined, because no published values could be found in the literature. All other parameters needed for using the UNIFAC model associated with the LCVM mixing rule can be found in Appendix B (Tables B.1 and B.3).

4. WS mixing rule

The PSRK and LCVM models do not give rise to a quadratic dependence on composition for the second virial coefficient, and therefore are not theoretically consistent. To overcome this inconsistency, Wong and Sandler [22] proposed a new mixing rule that predicts the correct composition dependence for the second virial coefficient. Indeed, expanding a cubic EOS in a Taylor's series, the following relationship can be found between the second virial coefficient, B(T), and the parameters a and b of the cubic EOS [31],

$$B(T) = b - \frac{a(T)}{RT} \tag{16}$$

Since $B(T)$ has a quadratic dependence on composition, it can be written that

$$B(T) = b - \frac{a(T)}{RT} = \sum_{i=1}^{\mathrm{nc}}\sum_{j=1}^{\mathrm{nc}} x_i x_j \left(b - \frac{a(T)}{RT}\right)_{ij} \tag{17}$$

The value of $(b - (a(T)/(RT)))_{ij}$, which is the cross virial coefficient B_{ij}, is only a function of temperature, and cannot be composition dependent. For the calculation of the cross virial coefficient, Wong and Sandler proposed the following combining rule

$$B_{ij}(T) = \left(b - \frac{a(T)}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i(T)}{RT}\right) + \left(b_j - \frac{a_j(T)}{RT}\right)}{2}(1 - k_{ij}) \tag{18}$$

where k_{ij} is a binary interaction parameter, independent of composition. For pure component i, this interaction parameter takes the value of zero (i.e. $k_{ii} = 0$).

To calculate the parameter α of a mixture, Wong and Sandler proposed the following mixing rule

$$\alpha = \frac{G_0^{\mathrm{E}}}{RTC_{\mathrm{WS}}} + \sum_{i=1}^{\mathrm{nc}} x_i \alpha_i \tag{19}$$

which, combined with Eqs. (17) and (18), gives rise to the following expression for obtaining the parameter b of the mixture

$$b = \frac{\sum_{j=1}^{\mathrm{nc}}\sum_{i=1}^{\mathrm{nc}} x_j x_i \left(b - \frac{a(T)}{RT}\right)_{ij}}{1 - \frac{G_0^{\mathrm{E}}}{RTC_{\mathrm{WS}}} - \sum_{i=1}^{\mathrm{nc}} x_i \alpha_i} \tag{20}$$

Eqs. (19) and (20) completely define the WS mixing rule. The value of the constant C_{WS} depends on the equation of state used, taking the values of −0.693 and −0.623, for the SRK and PR equations of state, respectively.

In its original form, the WS mixing rule cannot be used as a totally predictive method because the value of the molecular interaction parameter k_{ij} must be known, which means that experimental phase equilibrium data must be available. To overcome this difficulty, Coutsikos et al. [23] proposed the evaluation of the interaction parameter k_{ij} by setting equal the values of the excess Gibbs free energy calculated from the equation of state ($G_{\mathrm{EOS}}^{\mathrm{E}}$) and the value of G^{E} obtained by a solution model (G_0^{E}) for fixed values of composition and temperature (i.e. $G_{\mathrm{EOS}}^{\mathrm{E}} = G_0^{\mathrm{E}}$, for fixed values of x_i and T). For a binary mixture, it can be shown that k_{12} is given by

$$k_{12} = \frac{x_1 B_{11}(T) + x_2 B_{22}(T) - (1 - \alpha)\exp[x_1 \ln b_1 + x_2 \ln b_2 + q(\alpha) - x_1 q(\alpha_1) - x_2 q(\alpha_2)]}{x_1 x_2 (B_{11}(T) + B_{22}(T))} \tag{21}$$

where

$$q(\alpha) = -\ln(u-1) - \frac{\alpha}{c_1 - c_2}\ln\frac{u+c_1}{u+c_2} - C_{\text{WS}}\alpha \tag{22}$$

and

$$u = \frac{(\alpha - c_1 - c_2) - \sqrt{\alpha^2 - 2\alpha(2 + c_1 + c_2) + (c_1 - c_2)^2}}{2} \tag{23}$$

The constants c_1 and c_2 are characteristic of the EOS being considered, taking the values of 1 and 0, for the SRK–EOS, and $1+\sqrt{2}$ and $1-\sqrt{2}$, for the PR–EOS, respectively, and α is given by Eq. (19). In this work, the value of k_{12} was calculated for an equimolar mixture (i.e. $x_1 = x_2 = 0.5$) at a temperature of 273.15 K. As suggested by Wong and Sandler [22], the WS mixing rule was applied coupled with the PR–EOS according to the modification proposed by Stryjek and Vera [32] (i.e. PRSV–EOS). Therefore, the parameter a_i must now be obtained by the expression

$$a_i(T) = a_{\text{c},i}\, f(T, T_{\text{c},i}, \omega_i) \tag{24}$$

where

$$f(T, T_{\text{c},i}, \omega_i) = [1 + m_i(1 - \sqrt{T_{\text{r},i}})]^2 \tag{25}$$

with

$$m_i = m_{0,i} + m_{1,i}(1 + \sqrt{T_{\text{r},i}})(0.7 - T_{\text{r},i}) \tag{26}$$

and

$$m_{0,i} = 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3 \tag{27}$$

with $a_{\text{c},i}$ given by Eq. (13). The parameter $m_{1,i}$ is an adjustable parameter characteristic of each component whose value, for the substances used in this study, are summarized in Appendix A (Table A.2). This parameter is obtained by fitting the PRSV–EOS to vapor pressure data for pure components.

In this work, to study the applicability of the WS mixing rule, the modified UNIFAC model [33–35] is used to calculate the excess Gibbs energy, with the parameters given in Appendix B (Table B.4).

5. Prediction of phase equilibria

To study the capability of the WS mixing rule to predict the solubility of aromatic compounds of wine in CO_2, it was necessary to calculate the interaction parameters between the characteristic group of each family to be studied and the group CO_2. The optimization procedure to obtain these interaction parameters used the method of Roth–Meyer [36], based in the second order Levenberg–Marquardt algorithm [37], to minimize the objective function,

$$\text{FOB} = \frac{\sum_{i=1}^{\text{NRES}}(x_{\text{EXP},i} - x_{\text{CALC},i})^2 + \sum_{i=1}^{\text{NRES}}(y_{\text{EXP},i} - y_{\text{CALC},i})^2}{2\text{NRES}} \tag{28}$$

from which the following expression of the mean quadratic deviation, ε, is obtained

$$\varepsilon = \sqrt{\frac{\sum_{i=1}^{\text{NRES}}[(x_{\text{EXP},i} - x_{\text{CALC},i})^2 + (y_{\text{EXP},i} - y_{\text{CALC},i})^2]}{2\text{NRES}}} \tag{29}$$

The references for the experimental data used to obtain the interaction parameters calculated in this work are given in Table C.1. A more detailed description of the optimization procedure is given by Vázquez Silva [38].

In the following paragraphs the predictive capability of the PSRK, LCVM and WS mixing rules will be analyzed for the different families of aromatic compounds of wine considered.

6. Systems CO_2/alkane

Since, for the WS mixing rule, there are no published parameters for the group CO_2, it was necessary to begin by obtaining the interaction parameters between the groups CO_2/CH_2, because all the compounds used in this study are formed by the characteristic group of the family being considered—OH (alcohol), CHO (aldehyde), and CCOO (ester)—and groups CH_2 (alkane).

The interaction parameters for the groups CO_2/CH_2 are given in Table 1. These parameters were obtained by fitting 244 experimental points, covering a temperature range of 244–511 K, pressures from 0.03 to

Table 1
Calculated interaction parameters for the WS mixing rule

Group k/group m	A_{km} (K)	A_{mk} (K)	B_{km}	B_{mk}	C_{km} (K^{-1})	C_{mk} (K^{-1})
CO_2/CH_2	−9.889	45.016	0.00999	−0.49380	-1.000×10^{-3}	3.1142×10^{-3}
CO_2/OH	0	0	0	0	0.669243	0.597693
CO_2/CCOO	4.470	−7.623	−0.02558	0.19992	−0.00398	0.09229
CO_2/CHO	289.385	−100.000	0.00180	−0.01242	0.105138	-1.2313×10^{-3}

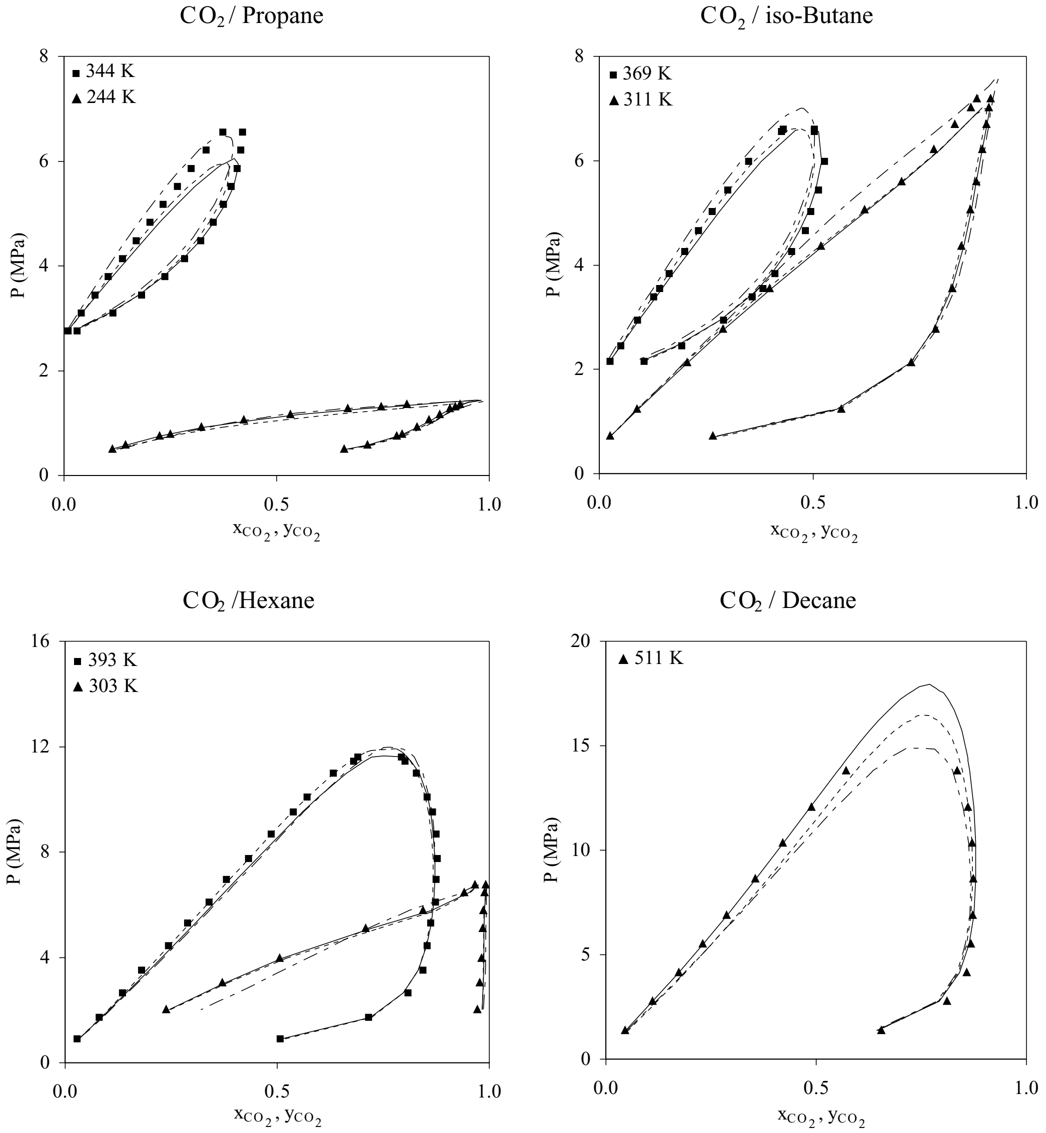

Fig. 1. PSRK (—), LCVM (---) and WS (– – –) predictions for systems CO_2/alkane.

Table 2
Revised interaction parameters for the PSRK mixing rule

Group k/group m	A_{km} (K)	A_{mk} (K)	B_{km}	B_{mk}	C_{km} (K^{-1})	C_{mk} (K^{-1})
CO_2/OH	0	0	0	0	0.0017815	0.0035507
CO_2/CHO	174.298	−157.188	0	0	-2.528×10^{-3}	-2.247×10^{-4}

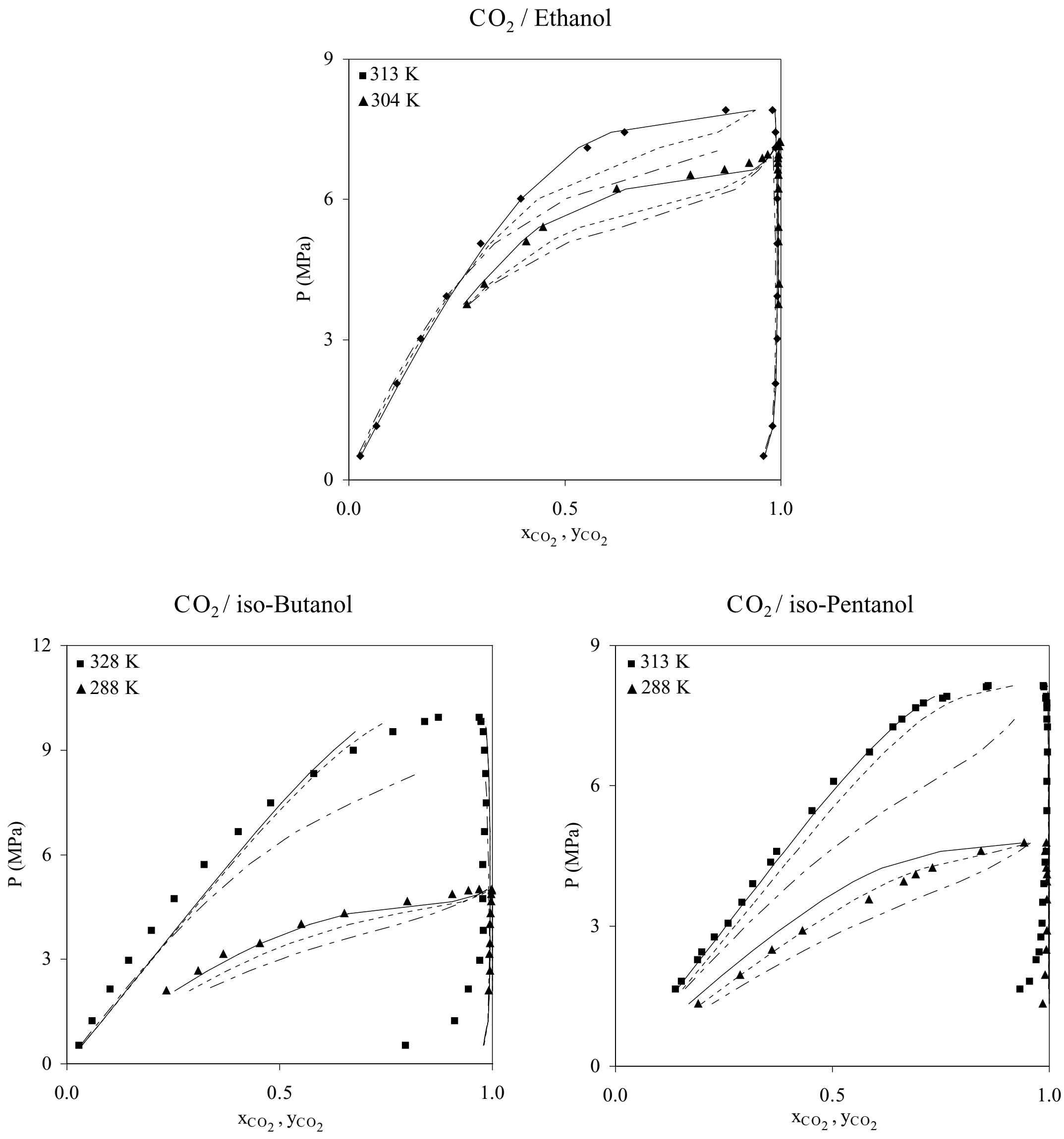

Fig. 2. PSRK (—), LCVM (---) and WS (– – –) predictions for systems CO_2/alcohol.

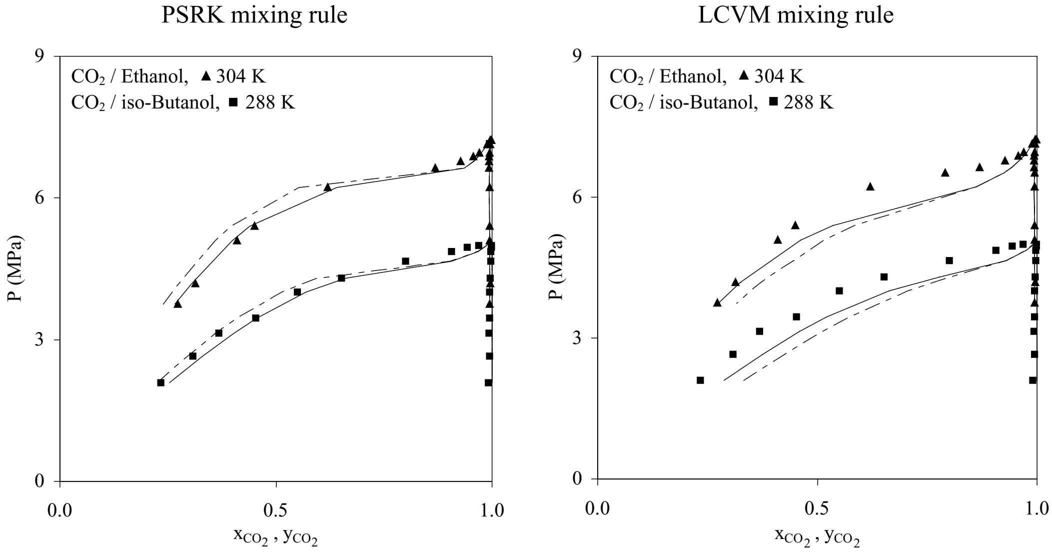

Fig. 3. Comparison between the results obtained with the published (- - -) and the revised (—) interaction parameters for the groups CO_2/OH.

17.2 MPa, and including alkanes with a number of carbon atoms between 3 and 10.

In Fig. 1, the predictions by the PSRK, LCVM and WS models are compared for binary mixtures of propane, *iso*-butane, hexane and decane with carbon dioxide. An analysis of this figure shows that the WS mixing rule predicts satisfactorily the phase equilibria for the systems CO_2/propane and CO_2/*iso*-butane, but the quality of the prediction decreases with the increasing of the number of carbon atoms of the alkane. The PSRK and LCVM models fail to correctly predict the phase equilibria for the CO_2/propane system at high pressures and temperatures, but give better results than the WS mixing rule for the other systems studied.

The mean quadratic deviation, ε, for all the systems CO_2/alkane studied (i.e. for all 244 experimental data points), show that the PSRK is the method that best predicts the equilibrium data for these systems ($\varepsilon_{\mathrm{PSRK}} = 0.016$), and the WS mixing rule is the one that gives the worst results ($\varepsilon_{\mathrm{WS}} = 0.029$), having the LCVM an intermediate quality ($\varepsilon_{\mathrm{LCVM}} = 0.024$).

7. Systems CO_2/alcohol

The prediction of phase equilibria for the systems CO_2/alcohol by the PSRK and LCVM models with the parameters published in the literature [20,25,30] gives rise to a mean quadratic deviations of 0.076 and 0.085, respectively. Since these values are slightly high, it was attempted the calculation of new interaction parameters for these models using the same data bank used to obtain the parameters for the WS mixing rule. This data bank has 257 experimental data points, covering temperatures from 288 to 395 K, pressures from 0.5 until 19.0 MPa, and contains alcohols with a maximum of eight carbon atoms.

The calculated and revised interaction parameters between the groups CO_2/OH are given in Tables 1–3, for the WS, PSRK and LCVM mixing rules, respectively. Fig. 2 shows the prediction for the solubility of ethanol, *iso*-butanol and *iso*-pentanol in CO_2, according to the PSRK, LCVM and WS mixing rules. As it would be expected, due to the polarity of these compounds, the predictions are worse than for the alkane systems. The PSRK and LCVM models give identical results ($\varepsilon_{\mathrm{PSRK}} = 0.055$, $\varepsilon_{\mathrm{LCVM}} = 0.053$), which

Table 3
Revised and calculated$^{(*)}$ interaction parameters for the LCVM mixing rule

Group k/group m	A_{km} (K)	A_{mk} (K)	B_{km}	B_{mk}
CO_2/OH	87.100	943.660	1.96365	2.58830
CO_2/CHO$^{(*)}$	−110.933	6.972	8.2838	−8.1331

are much better than the predictions obtained with the WS mixing rule ($\varepsilon_{WS} = 0.111$).

The improvement obtained for the PSRK and LCVM models with the revised parameters calculated in this study is shown in Fig. 3, for the systems CO_2/ethanol and CO_2/*iso*-butanol, where the predictions with the parameters published earlier in the literature and with the revised parameters proposed in this study are compared. It can be seen that the revised parameters improve slightly the predicted results.

8. Systems CO_2/ester

The interaction parameters between the groups CO_2/CCOO for the WS mixing rule are given in

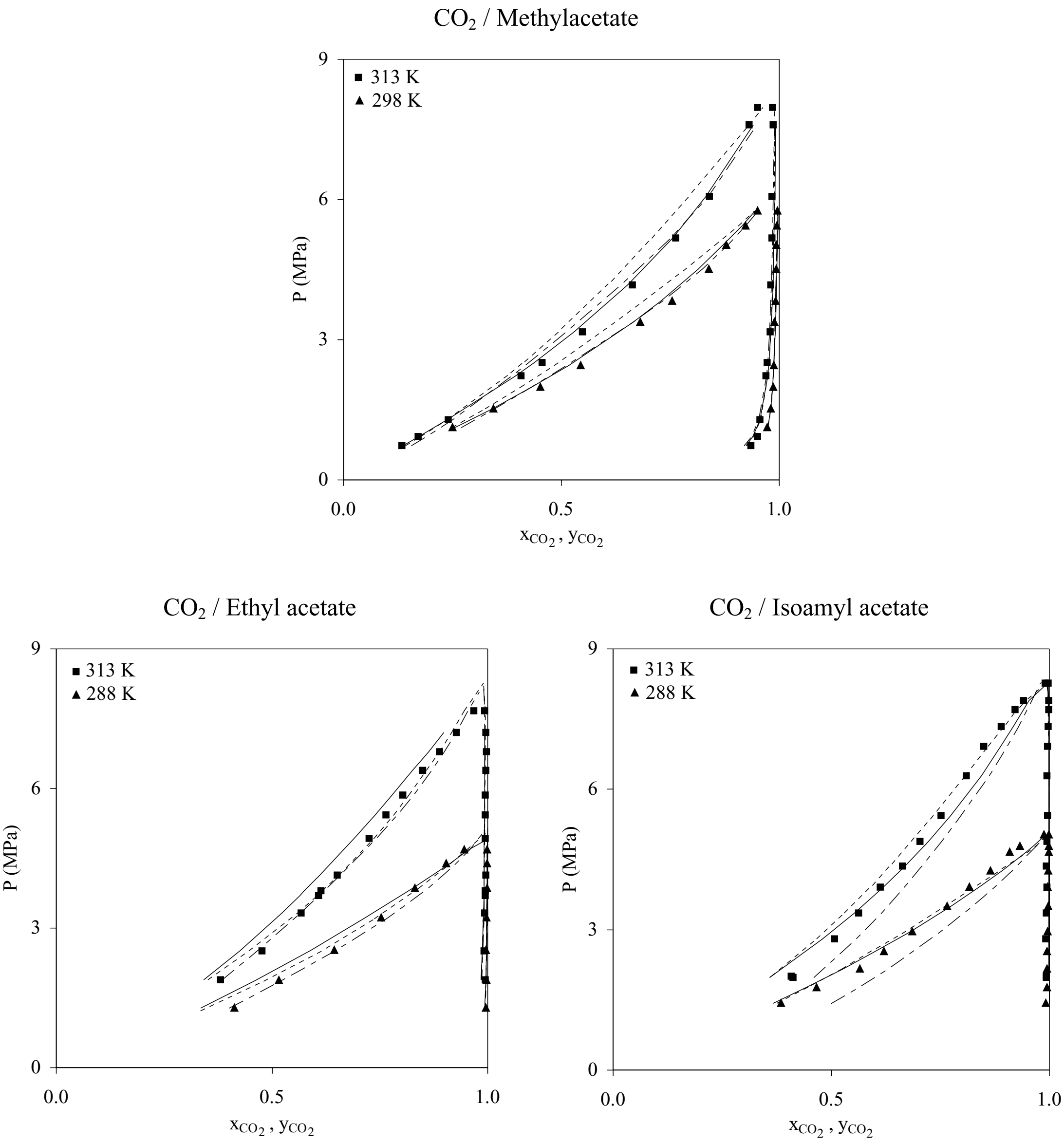

Fig. 4. PSRK (—), LCVM (---) and WS (– – –) predictions for systems CO_2/ester.

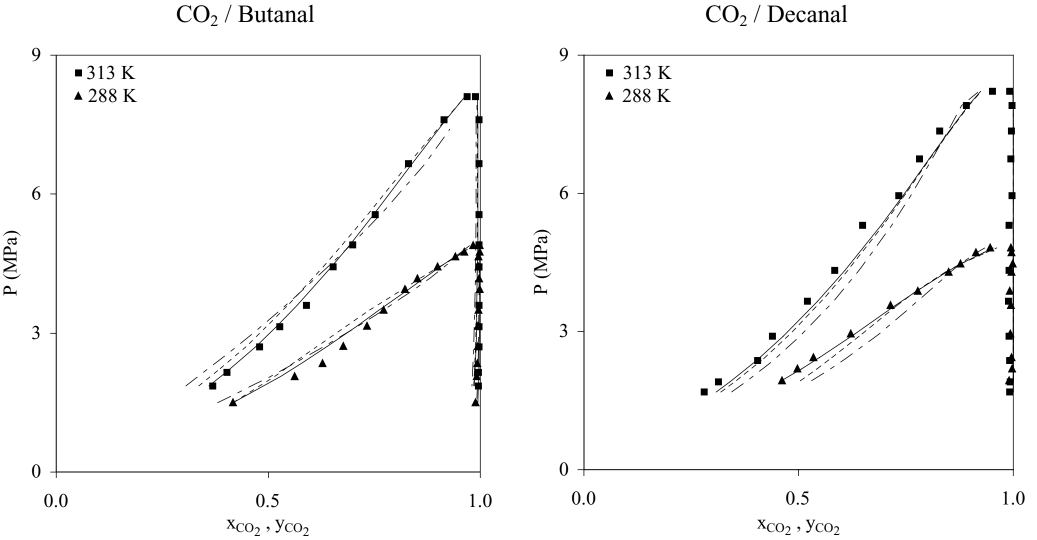

Fig. 5. PSRK (—), LCVM (---) and WS (–––) predictions for systems CO_2/aldehyde.

Table 1, and were obtained by fitting 238 experimental data points, for a temperature range of 288–323 K, pressures between 1.1 and 9.2 MPa, and for esters having between 3 and 7 carbon atoms.

In Fig. 4, the predictions by the PSRK, LCVM and WS mixing rules are compared with the experimental data for some CO_2/esters systems (i.e. CO_2/methyl acetate, CO_2/ethyl acetate and CO_2/isoamyl acetate). Analyzing the mean quadratic deviations for these systems ($\varepsilon_{PSRK} = 0.035$, $\varepsilon_{LCVM} = 0.047$, $\varepsilon_{WS} = 0.035$), it is verified that the PSRK and WS models predict equally well the phase

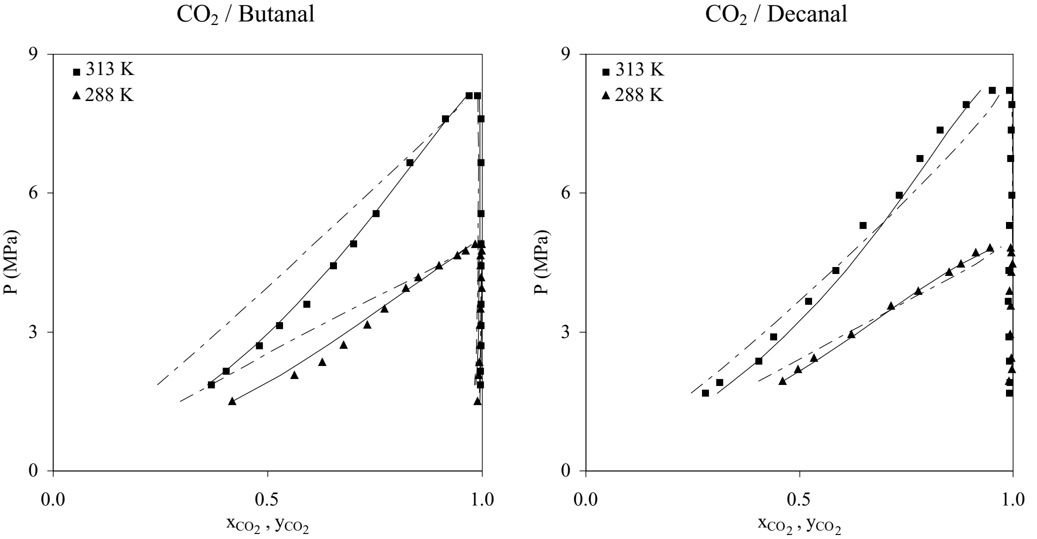

Fig. 6. Comparison between the results obtained with the published (–––) and the revised (—) interaction parameters for the groups CO_2/CHO.

equilibria, giving the LCVM model slightly worse results.

9. Systems CO_2/aldehyde

As for the systems containing alcohols, it was found that the existing parameters for the PSRK model [25] gave poor phase equilibria predictions for the CO_2/aldehyde systems ($\varepsilon_{PSRK} = 0.056$), which led to the calculation of a new set of interaction parameters for the groups CO_2/CHO in an attempt to improve the quality of the predicted results. A data bank with 68 experimental points, covering a temperature range of 288–313 K, pressures between 1.5 and 8.2 MPa, and having aldehydes with 4 and 10 carbon atoms was used to obtain the revised parameters for the PSRK model, and to calculate the parameters for the LCVM and WS mixing rules. These parameters are given in Tables 1–3 for the WS, PSRK and LCVM models, respectively.

In Fig. 5, the experimental data is compared with the predictions by the PSRK (with the revised parameters), LCVM and WS mixing rules. Once again, the WS model is the one that gives the worst results ($\varepsilon_{WS} = 0.034$), giving the PSRK and LCVM models almost identical results ($\varepsilon_{PSRK} = 0.016$, $\varepsilon_{LCVM} = 0.023$). The improvement gained with the revised parameters proposed for the PSRK model can be seen in Fig. 6, where the predictions for the systems CO_2/butanal and CO_2/decanal with the published and revised parameters are compared. This comparison shows a clear improvement obtained with the use of the revised parameters.

10. Conclusions

In this work, the PSRK, LCVM and WS mixing rules, associated with the UNIFAC group contribution model to calculate the excess Gibbs free energy, are compared as to their capability for predicting the phase equilibria of binary systems containing carbon dioxide and compounds belonging to the main families of the aromatic compounds of wine. Since for the WS mixing rule there are no interaction parameters published for the group CO_2, the interaction parameters between the groups CO_2/CH_2, CO_2/OH, CO_2/CHO and CO_2/CCOO were determined. For the LCVM mixing rule, the interaction parameters between the groups CO_2/CHO were also calculated, because there are no parameters in the literature for these groups.

An initial attempt to predict the phase equilibria for the systems CO_2/alcohol and CO_2/aldehyde with the PSRK model, and for the system CO_2/alcohol with the LCVM mixing rule, gave rise to significant errors. Therefore, the published parameters for these systems were revised and new values were proposed.

The results obtained with these three mixing rules for the systems CO_2/alkane, CO_2/alcohol, CO_2/ester and CO_2/aldehyde show that the WS mixing rule is the method that gives worse results, ex-

Table A.1
Critical properties and acentric factor for pure components

	T_c (K)	P_c (MPa)	ω	Reference
Inorganic compounds				
CO_2	304.2	7.39	0.239	[39]
Alkanes				
Propane	369.8	4.25	0.154	[32]
Butane	425.2	3.80	0.201	[32]
iso-Butane	408.1	3.65	0.176	[40]
Pentane	469.7	3.36	0.251	[32]
iso-Pentane	460.4	3.38	0.227	[40]
Hexane	507.3	3.01	0.301	[32]
Heptane	540.1	2.74	0.350	[32]
Decane	617.5	2.10	0.491	[32]
Alcohols				
Ethanol	513.9	6.15	0.644	[32]
1-Propanol	536.7	5.17	0.620	[32]
2-Propanol	508.4	4.76	0.664	[32]
1-Butanol	563.0	4.41	0.590	[32]
iso-Butanol	547.7	4.30	0.588	[40]
1-Pentanol	588.2	3.91	0.578	[32]
iso-Pentanol	579.5	3.85	0.580	[40]
1-Octanol	684.8	2.86	0.324	[32]
Esters				
Methyl acetate	506.8	4.69	0.254	[40]
Ethyl acetate	524.1	3.85	0.362	[39]
Propyl acetate	549.4	3.33	0.392	[40]
Isoamyl acetate	599.2	2.82	0.408	[41]
Ethyl propionate	546.0	3.36	0.395	[40]
Aldehydes				
Butanal	545.4	5.38	0.352	[39]
Decanal	652.0	2.26	0.634	[39]

cept for the system CO_2/propane at high pressures and temperatures, and the systems CO_2/ester, for which the errors are identical to those of the PSRK. This is not a surprising result, because, even though the WS mixing rule has the advantage of being consistent with the quadratic dependence on composition of the second virial coefficient, it is well known that this mixing rule fails for polar and asymmetric systems, as is the case for most of the systems studied. To make this method completely predictive the binary interaction parameter k_{12} (Eq. (21)) had to be estimated for fixed values of temperature and composition, which restricts the applicability of the model. Therefore, it may be expected that the molecular version of the WS mixing rule would give better results for these systems.

The PSRK and LCVM mixing rules give similar results, although the PSRK model is the one that best predicts the phase equilibria for the systems studied, with a quadratic mean deviation always lower than 5.5%. The improvement in the prediction obtained with the revised parameters for the PSRK and LCVM models is only slight for the systems CO_2/alcohol, but significant for the systems CO_2/aldehyde.

The lack of reliable experimental data for multicomponent mixtures is, at present, an obstacle to the extension of this analysis to mixtures of industrial interest.

Table A.2
Mathias–Copeman constants (C_1, C_2 and C_3) for the SRK and PR–EOS, and m_1 parameter for the PRSV–EOS

	SRK–EOS			PR–EOS			PRSV–EOS
	C_1	C_2	C_3	C_1	C_2	C_3	m_1
Inorganic compounds							
CO_2	0.5984	2.3820	0.0316	0.4633	2.4202	0.0838	0.0429*
Alkanes							
Propane	0.7250	−0.0678	0.0365	0.5923	0.0577	0.0362	0.0314 [32]
Butane	0.7820	0.0097	0.0000	0.6668	0.0246	0.0190	0.0344 [32]
iso-Butane	0.7630	−0.0168	−0.0071	0.6509	−0.0085	0.0000	0.1701*
Pentane	0.8612	−0.0078	0.0000	0.7425	−0.0182	0.1093	0.0395 [32]
iso-Pentane	0.8287	−0.0141	0.0000	0.6605	0.2740	−0.0055	0.0697*
Hexane	0.9406	−0.0319	−0.0170	0.8067	0.0318	0.0000	0.0510 [32]
Heptane	1.0072	0.0059	0.0000	0.8777	0.0194	−0.0053	0.0465 [32]
Decane	1.2123	0.0084	0.0000	1.0688	0.0126	0.0310	0.0451 [32]
Alcohols							
Ethanol	1.4401	−0.1044	−0.0179	1.2788	−0.0067	−0.1009	−0.0337 [32]
1-Propanol	1.3600	0.1917	0.0596	1.2075	0.2326	0.0409	0.2142 [32]
2-Propanol	1.4173	0.1903	0.0076	1.2392	0.3356	0.1512	0.2326 [32]
1-Butanol	1.2356	0.6834	0.0790	1.0532	0.8950	0.1475	0.3343 [32]
iso-Butanol	1.2690	0.4701	0.1897	1.0578	0.8310	0.3845	0.2742*
1-Pentanol	1.2440	0.5000	0.1000	1.0995	0.5000	0.1000	0.3678 [32]
iso-Pentanol	1.1896	0.7203	0.0613	1.0049	0.9686	0.0666	0.3568*
1-Octanol	0.6592	1.9410	0.0500	0.5424	1.8863	0.0500	0.8294 [32]
Esters							
Methyl acetate	0.9693	−0.0092	0.0000	0.8378	0.0351	0.0470	0.4560*
Ethyl acetate	1.0159	0.0093	0.0000	0.8908	0.0002	0.0395	0.0228*
Propyl acetate	1.0612	0.0151	0.0859	0.9077	0.1640	0.0239	0.7134*
Isoamyl acetate	0.9316	0.5451	0.0560	0.7856	0.6663	0.0253	0.0592*
Ethyl propionate	1.0655	0.0100	0.0010	0.9202	0.1000	0.0019	0.0278*
Aldehydes							
Butanal	0.9170	0.0100	0.0000	0.8002	0.0060	0.0000	−0.4348*
Decanal	1.4344	0.0064	0.1049	1.2699	0.0536	0.2130	0.1822*

* Value obtained in this work.

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Appendix A. Pure component properties

In this appendix the pure component properties needed for the implementation of the PSRK, LCVM and WS mixing rules are summarized. The critical properties and acentric factor are given in Table A.1. The Mathias–Copeman constants (for the SRK–EOS and PR–EOS) and the parameter m_1 of the PRSV–EOS are presented in Table A.2. These values were obtained by fitting the respective EOS to vapor pressure data for the pure components. The references for the vapor pressure data used in the fitting procedure are given by Vázquez Silva [38]. The parameter m_1 was only calculated if its value was not available in the literature.

Table B.1
Area (Q_k) and volume (R_k) parameters for the original UNIFAC model [27]

Group number	Group	Sub-group	R_k	Q_k
1	CH_2	CH_3	0.9011	0.848
		CH_2	0.6744	0.540
		CH	0.4469	0.228
		C	0.2195	0.000
5	OH	OH	1.0000	1.200
10	CHO	CHO	0.9980	0.948
11	CCOO	CH_3COO	1.9031	1.728
		CH_2COO	1.6764	1.420
56	CO_2	CO_2	1.3000 [20]*	0.982 [20]*
			1.296 [30]**	1.261 [30]**

* Value used in the PSRK model.

** Value used in the LCVM model.

Table B.3
Group interaction parameters for the LCVM mixing rule [26,30]

Group k	Group m	A_{km} (K)	A_{mk} (K)	B_{km}	B_{mk}
CO_2	CH_2	110.6	116.7	0.5003	−0.9106
CO_2	OH	87.1	471.8	3.9270	2.588
CO_2	CCOO	−126.9	102.75	−1.8187	−0.4999
CH_2	OH	986.5	156.4	0	0
CH_2	CHO	677.0	505.7	0	0
CH_2	CCOO	232.1	114.8	0	0

Appendix B. UNIFAC parameters

The excess Gibbs free energy (G^E) for the PSRK and LCVM models was calculated by the original UNIFAC method, with different expressions for the temperature dependence of the UNIFAC interaction parameter, Ψ, given by Eqs. (9) and (15), respectively. The group and sub-group interaction parameters for the original UNIFAC method are presented in Table B.1, and the published interaction parameters of interest are summarized in Tables B.2 and B.3, for the PSRK and LCVM models, respectively. For the LCVM mixing rule, the parameters for the group CO_2 published by Voutsas et al. [30] were used (i.e. $R_k = 1.296$ and $Q_k = 1.261$).

For the WS mixing rule, the G^E was obtained by the modified UNIFAC method, whose group and

Table B.2
Group interaction parameters for the PSRK mixing rule [20,25,26]

Group k	Group m	A_{km} (K)	A_{mk} (K)	B_{km}	B_{mk}	C_{km} (K^{-1})	C_{mk} (K^{-1})
CO_2	CH_2	−38.672	919.8	0.8615	−3.913	-1.791×10^{-3}	4.631×10^{-3}
CO_2	OH	148.2	510.6	0	0	0	0
CO_2	CHO	340.0	−162.0	0	0	0	0
CO_2	CCOO	−742.2	818.72	2.9173	−3.5627	0	0
CH_2	OH	986.5	156.4	0	0	0	0
CH_2	CHO	677.0	505.7	0	0	0	0
CH_2	CCOO	232.1	114.8	0	0	0	0

Table B.4
Area (Q_k) and volume (R_k) parameters for the modified UNIFAC model [33]

Group number	Group	Sub-group	R_k	Q_k
1	CH_2	CH_3	0.6325	1.0608
		CH_2	0.6325	0.7081
		CH	0.6325	0.3554
5	OH	OH (p)	1.2302	0.8927
		OH (s)	1.0630	0.8663
10	CHO	CHO	0.7173	0.7710
11	CCOO	CH_3COO	1.270	1.6286
		CH_2COO	1.270	1.4228
56	CO_2	CO_2	1.296 [30]	1.261 [30]

sub-group parameters used in this work are summarized in Table B.4.

Appendix C. Experimental data

In Table C.1 is given a compilation of the bibliographic references for the experimental data used in this work to obtain the necessary interaction parameters and to analyzed the predictive quality of the three models studied. For each system, the temperature and pressure range of the experimental data used is indicated.

Table C.1
Experimental data for the systems CO_2 + X used in this work

X	*T* (K)	*P* (MPa)	Reference
Propane	244–344	0.5–6.6	[42,43]
Butane	278–387	0.03–8.1	[44–46]
iso-Butane	311–369	0.7–6.6	[47,48]
Pentane	273–438	0.3–6.9	[49,50]
iso-Pentane	278–408	0.15–8.2	[50,51]
Hexane	303–393	0.9–11.6	[52,53]
Heptane	352–394	0.4–13.3	[54]
Decane	378–511	1.4–17.2	[55]
Methyl acetate	298–313	1.1–8.0	[56]
Ethyl acetate	288–313	1.3–7.7	[57]
Propyl acetate	303–323	2.1–9.2	[58]
Isoamyl acetate	288–313	1.4–8.3	[57]
Ethyl propionate	303–323	1.7–9.1	[59]
Ethanol	304–333	0.5–10.6	[60,61]
1-Propanol	313–333	0.5–10.8	[60]
2-Propanol	335–395	1.4–12.4	[62]
1-Butanol	313–333	0.5–11.2	[63]
iso-Butanol	288–328	0.5–9.9	[63,64]
1-Pentanol	315–337	5.2–12.0	[65]
iso-Pentanol	288–313	1.2–8.1	[64]
1-Octanol	313–348	4.0–19.0	[66]
Butanal	288–313	1.5–8.1	[57]
Decanal	288–313	1.7–8.2	[67]

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