Application of group contribution SAFT equation of state (GC-SAFT) to model phase behaviour of light and heavy esters

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Abstract

The group contribution SAFT approach developed for pure compounds in an earlier work [S. Tamouza, J.-P. Passarello, J.-C. de Hemptinne, P. Tobaly, Fluid Phase Eq. 222–223 (2004) 67] is here extended for the treatment of ester series. Parameters for groups CH_2 and CH_3 previously determined were reused for the alkyl chains while new parameters were determined for COO and HCOO groups. The polarity of these molecules was taken into account by the addition to the equation of state (EOS) of a dipole–dipole interaction term due to Gubbins and Twu [K.E. Gubbins, C.H. Twu, Chem. Eng. Sci. 33 (1978) 863]. This term requires an additional parameter, the dipole moment which was correlated to the COO chemical group position in the ester chain.

Three different versions of SAFT were used here to test the validity of the method: the original SAFT [W.G. Chapman, G. Jackson, K.E. Gubbins, M. Radosz, Ind. Eng. Chem. Res. 29 (1990) 1709], VR-SAFT [A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, J. Chem. Phys. 106 (1997) 4168] and PC-SAFT [J. Gross, G. Sadowski, Fluid Phase Eq. 168 (2000) 183; J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 40 (2001) 1244]. In all three cases, similar and encouraging results are obtained. Reasonable predictions are found on heavy esters that were not included in the regression database.
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1. Introduction

Esters are today widely studied compounds. They are used in many areas such as for instance food industry (Mishra et al. [1]), petroleum industry (Bureau et al. [2]), . . . and by those who deal with environmental problems [3]. In the above cited areas, long chain esters are of particular importance.

Engineering studies concerned with esters processing often require reliable physical property data. Especially vapor pressure appears as a key property. But only a few experimental data are available, and mainly for small esters. Thus, a reliable method to predict such a property for both small and long chain esters is needed. Such a method should also apply to ester isomers that

have a different thermodynamic behavior. This is the purpose of this work.

Methods are available for correlating vapor pressure data, and to some extent for predicting them in the case of heavy esters [4,5]. These methods are based on empirical or semi-empirical vapor pressure equations that allow a good fit of the data and sometimes allow to determine other thermodynamic properties (vaporization enthalpy, . . .). For those purposes, they are very useful. But on the other hand, such equations cannot generally be easily extended to the representation of mixtures, which is a thermodynamic problem of industrial importance. EOSs are more adapted to such a task. This is a reason why such an approach is proposed here. Group-contribution (GC) methods appear in that case especially well appropriate.

Here, the method used is based on a SAFT EOS combined with a built-in group contribution method already tested with some success to model vapor–liquid equilibria (VLE) of hydro-

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carbons and alcohols. SAFT EOSs were chosen because of their good capability for representing various thermodynamic systems such as those containing long chain molecules.

2. Description of the equation of state

The SAFT equation of state was first developed by Chapman et al. [6], and this work was followed by a large number of attempts to improve this original EOS. Many versions of this equation thus exist today. In most of these SAFT approaches, a molecule is seen as a chain of spherical segments that may interact through an addition of repulsion, dispersion, association and in some cases [7] polar terms. The general form of the residual free energy may then be written as follows:

$$a - a^{\circ} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}} + a^{\text{polar}} \tag{1}$$

The terms a^{seg} and a^{chain}, respectively take into account segment interactions (repulsive + attractive) and segment chain formation. For non-associating compounds such as esters, the third term a^{assoc} that deals with associative interaction (H bond for instance) is set to zero.

The last term a^{polar} accounts for multi-polar interactions, such as dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, . . ., etc., that are long range and in that respect, at least, differ from associative interaction.

We used here three different versions of the SAFT equation. The first one is the original SAFT equation [6] slightly modified (Benzaghou et al. [8]). In the remainder of this article, it will be denoted by SAFT-0. It was chosen because it is one of the most simple version from a mathematical point of view and at the same time it appears efficient for the representation of vapor–liquid equilibria of rather different chemical compounds [8–11]. The second version of SAFT used here is due to Gil-Villegas et al. [12] and is known as VR-SAFT. One of the main differences if compared to SAFT-0 is that VR-SAFT allows a variable range for dispersion interaction. An additional parameter is therefore involved. PC-SAFT [13,14] is the third Version used for this work. It applies particularly well to hydrocarbons and their chemical derivatives. The exact expressions of these equations are not recalled here but the interested readers may find all the details in the original papers of Chapman et al. [6], Benzaghou et al. [8], Gil-Villegas et al. [12], and Gross and Sadowski [13,14].

In these expressions, three or four adjustable parameters are involved per species: the diameter σ and the energy ε of a segment, the chain length m and the range parameter λ (only in the case of VR-SAFT). The chain molecule is assumed to be made of identical segments. This may seem a limitation of the models but, as shown in previous works (see Müller and Gubbins [15]), non-homogeneous molecules in term of chemical groups may nevertheless be treated using such models, as also in the group contribution method [9,10] which will be recalled in a paragraph below.

In the case of polar molecules such as esters (dipole moment in the gas phase about 1.5 Debye), the dipole moments do have a significant effect on the thermodynamic bulk properties. For not too strongly oriented interactions (as expected in the case of esters) this effect may be quantified by using the perturbation theory of Gray and Gubbins [16], rather than using the association term of SAFT EOS. Here only dipole–dipole interactions are considered, and other multipolar interactions are neglected. Free molar energy corresponding to dipole–dipole interactions may be computed using a Padé approximant expression:

$$\frac{a^{\text{dd}}}{\text{NK}\tilde{T}} = \frac{a_2^{\text{dd}}}{1 - (a_3^{\text{dd}}/a_2^{\text{dd}})} \tag{2}$$

where a_2^{dd} and a_3^{dd} are, respectively, the second and third order perturbation term. Their expressions are given by Gubbins and Twu [17]:

$$a_2^{\text{dd}} = -\frac{2\pi}{3} \cdot \frac{\mu^{*4} \cdot \rho^*}{T^*} \cdot J^{(6)} \tag{3}$$

$$a_3^{\text{dd}} = \frac{32\pi^3}{135} \sqrt{\frac{14\pi}{5}} \frac{\mu^{*6} \cdot \rho^{*2}}{T^{*2}} \cdot K_{(222)}^{(333)} \tag{4}$$

with the reduced dipole moment μ^* defined by Kraska and Gubbins [7] as:

$$\mu^{*2} = \frac{\mu^2}{\varepsilon m \sigma^3} \tag{5}$$

where μ is the dipole moment. The chain length appears in the definition of μ^* because one assumes that the dipole moment belong to the whole molecule, not to one segment.

The reduced density ρ^* is given by $\rho^* = \rho \cdot N_{\text{AV}} \cdot \sigma^3$. The reduced temperature is $T^* = kT/\varepsilon$ and $\tilde{T} = \varepsilon/k$. $J^{(6)}$ and $K_{(222)}^{(333)}$ are integrals over two and three-body correlation functions for the Lennard-Jones fluid. Their variation with ρ^* and T^* that were used in this work may be found in Gubbins and Twu [17].

Strictly speaking, there is no adjustable parameter in expressions (2)–(5) if the true value of the dipole moment is known. But in the literature, only a few data are available and those were measured mainly in the gas phase. Furthermore, in the liquid phase, polarizability effects may increase this value up to 20–50% as emphasized by theoretical works of Wertheim [18,19] and simulation results of Sprik and Klein [20]. Kraska and Gubbins [9] have proposed a linear dependence of μ with density that is based on theoretical studies (Wertheim [18,19]). However, for the sake of simplicity, it was decided here to treat the dipole moment as a constant for each ester compound (it may differ from one ester to another) and to determine it by data regression. This procedure reduces the predictive value of the method but probably allows a more accurate computation of phase equilibria.

3. Parameters estimation for pure esters

Often, EOS parameters of a given species are determined by regression on its specific data. One set of specific parameters is therefore determined for each species. Instead of this classical approach, we want here to apply and extend a group contribution developed earlier [9] and use it as a predictive tool. In that perspective the segment parameters ε, σ, λ, and m of each ester

are obtained by appropriate averages of chemical group parameters using relations inspired by the Lorentz–Berthelot combining rules. The latter assume geometrical average of energy parameters and arithmetical average of size parameters for chemical groups parameters. All the details about the procedure applied in the case of the esters are given below.

3.1. Modeling esters using a group contribution method

Such a thermodynamic treatment of esters requires first a definition of the chemical groups found in an ester molecule. Let us recall that the general chemical formulas of esters are either HCOOR (formates) or RCOOR$'$ where R and R$'$ are hydrocarbon chains. In this work, we have considered only the case when R and R$'$ were linear alkyl chains. This means that R and R$'$ may be explicitly written as CH_3-$(CH_2)n$ and CH_3-$(CH_2)n'$ with n, $n' \geq 0$. Therefore, four different chemical groups are used in this work: CH_3, CH_2, COO and HCOO.

In the spirit of the GC method mentioned above, the EOS parameters of a given ester RCOOR$'$ are computed by the following relations:

$$\varepsilon = \sqrt[n^T]{(\varepsilon_{CH_2})^{n_{CH_2}}.(\varepsilon_{CH_3})^{n_{CH_3}}.(\varepsilon_{COO})^{n_{COO}}} \qquad (6)$$

$$\sigma = \frac{\sigma_{CH_2} \cdot n_{CH_2} + \sigma_{CH_3} \cdot n_{CH_3} + \sigma_{COO} \cdot n_{COO}}{n^T} \qquad (7)$$

$$\lambda = \frac{\lambda_{CH_2} \cdot n_{CH_2} + \lambda_{CH_3} \cdot n_{CH_3} + \lambda_{COO} \cdot n_{COO}}{n^T} \qquad (8)$$

where n_{CH2}, n_{CH3} and n_{COO} are, respectively, the numbers of groups CH_2, CH_3, COO in the ester molecule and $n^T = n_{CH2} + n_{CH3} + n_{COO}$ is the total number of groups in the molecule. As noticed in earlier works [7–9], the chain parameter m rarely fits an integer value. Rather, it may be correlated through a simple linear correlation to the different group numbers, involving a chain contribution parameter denoted R_i for each group i.

$$m = R_{CH_2} \cdot n_{CH_2} + R_{CH_3} \cdot n_{CH_3} + R_{COO \cdot n COO} \qquad (9)$$

In order to treat an ester HCOOR$'$, group COO should be simply substituted by group HCOO in Eqs. (6)–(9) above. In this work, HCOO is defined as a different group because it would be questionable to consider the hydrogen atom as a group by itself.

If one provides the value of the dipole moment, the model of a given ester is then apparently complete.

But, as a consequence of relations (6)–(9), and if the dipole moment is not considered, our GC method cannot distinguish between two different isomers since only the numbers of groups are introduced and not their relative positions. For instance, at this stage, the method cannot distinguish between the following isomer compounds: $CH_3CH_2COOCH_2CH_3$, $CH_3COOCH_2CH_2CH_3$ and $CH_3CH_2CH_2COOCH_3$. However, experimental data clearly show that two isomers may have a significantly different thermodynamic behavior [8]. This problem had to be addressed here since our database involves several ester isomers.

As suggested by a similar approach [8,11] proposed to model n-alkane and 1-alkanol isomers, we tried to make a distinction between two isomers using the chain lengths m of the two molecules i.e. through the corresponding R_i group parameters. All the other group parameters ε_i, σ_i and λ_i were assumed to depend only on the nature of the chemical group and not on their position in the molecule: consequently they have the same unique values for all the molecules. Therefore, all the parameters values ε_i, σ_i, and λ_i for the two groups CH_2 and CH_3 that were determined earlier (in a previous work on a n-alkane series [9]) were re-used here without further adjustment. The group parameters ε_{COO}, σ_{COO} and λ_{COO} that have unique values too were determined by data regression on a series of selected compounds. The same procedure was used to determine ε_{HCOO}, σ_{HCOO} and λ_{HCOO} by regression on a series of alkyl-formates.

As shown by the general chemical formulas of esters RCOOR$'$, such a molecule may be viewed as a hydrocarbon skeleton with a group COO inside the chain. In other words, using n_R and $n_{R'}$ (the total number of groups in chains R and R$'$), we can make a distinction between two different isomers. In this work, we further assume that values of R_{CH_2} and R_{CH_3} are constant: the values determined earlier [9] were thus re-used. R_{COO} is regarded as a function of the COO group position p in the ester chain, defined by $p = \min(n_R, n_{R'}) + 1$. In the case of HCOOR esters, the latter additional assumption means that a unique value for R_{HCOO} is sufficient to model the whole series.

But in these conditions, one may notice that the symmetrical molecules RCOOR$'$ and R$'$COOR have the same value for $R_{COO}(p)$. Therefore, an additional distinction was used: the dipole moment μ was introduced to make the difference between two symmetrical esters. Here, the dipole moment was supposed as a first approximation to follow an empirical linear relation with $n_R - n_{R'}$ that is written for RCOOR$'$ as:

$$\mu = \mu^\circ + \alpha.(n_R - n_{R'}) \qquad (10)$$

For HCOOR, we set n_R to 0:

$$\mu = \mu^{\circ\prime} - \alpha'.n_{R'} \qquad (11)$$

Such relations assume that substitutes R and R$'$ have opposite influences on the value of the dipole moment.

Notice that dipole moment values calculated using relations (10)–(11) are not bounded: when n_R or $n_{R'}$ goes to infinity, so does μ. However this does not appear as a problem of practical importance for the molecules investigated in this work (up to C30). The influence of dipolar interaction indeed decreases with the size of the molecule, and as we will see in the next paragraph the values of α and α' are small enough so that μ varies slowly with n_R and $n_{R'}$.

The reader may find some examples for calculating parameters in Appendix A.

In summary, the distinction between two esters isomers is made through the two parameters R_{COO} and μ.

3.2. Database for pure esters and regression results

As discussed above, the esters considered here contain linear hydrocarbon chains R and R$'$. In Table 1, vapor pressure and liquid molar volume at saturation data for esters available in

Table 1
Regression database (accepted data in DIPPR) and results

Compound	Vapor pressures						Saturated liquid volumes				
	T range (K)	Npt	AAD P^{sat} (%)				T range (K)	Npt	AAD v^{liq} (%)		
			SAFT-0	VR-SAFT	PC-SAFT				SAFT-0	VR-SAFT	PC-SAFT
Formates HCOOR′											
HCOOC	253.15–483.15	24	2.54	2.37	4.86		273.15–463.15	20	1.56	1.81	5.69
HCOOC2	250.45–503.15	27	1.38	2.98	3.29		273.15–503.15	23	1.77	2.02	2.04
HCOOC3	263.15–538.00	28	3.43	1.18	3.83		273.15–523.15	26	2.09	2.02	4.17
HCOOC4	246.75–559	18	4.30	3.08	4.27		273.15–373.15	11	0.93	1.11	5.09
HCOOC5	240.00–490.00	26	6.59	6.51	5.77		273.15–393.15	13	1.38	0.98	4.56
HCOOC6	254.58–607.00	9	9.88	9.58	9.62		273.15–363.15	10	2.11	2.01	4.56
HCOOC7	262.67–514.08	10	9.71	9.13	10.45		273.15–303.15	6	3.15	3.41	4.37
HCOOC8	306.15–558.15	9	11.84	12.03	14.93		273.15–303.15	6	3.73	4.03	3.74
HCOOC9	308.89–515.56	8	13.42	10.55	18.64		293.15	1	4.59	4.82	2.70
HCOOC10	316.67–516.67	8	11.49	7.69	17.22		293.15	1	4.03	4.30	3.22
Acetates CH₃COOR′											
CCOOC	253.15–503.15	14	6.62	5.34	12.43		273.1–503.15	13	2.36	3.42	6.98
CCOOC2	233.15–522.15	16	2.91	2.00	3.56		273.15–503.15	13	1.52	1.92	1.35
CCOOC3	273.15–543.15	15	4.48	1.67	4.04		273.15–533.15	14	2.43	2.31	1.96
CCOOC4	326.19–410.04	8	6.49	2.68	5.69		273.15–393.15	12	0.99	1.55	3.34
CCOOC5	281.88–599.90	12	3.83	3.37	2.14		273.15–417.65	12	1.36	1.72	3.63
CCOOC6	304.16–441.15	7	4.76	3.68	5.06		273.15–363.15	10	1.13	0.99	3.58
CCOOC7	349.15–462.15	10	6.06	4.87	4.69		273.15–303.15	5	2.29	1.81	3.37
CCOOC8	334.65–484.95	8	2.93	2.64	3.13		293.15–368.15	7	1.62	1.11	3.15
CCOOC9	293.13–661.00	11	17.90	14.48	16.75		298.15	1	3.01	2.56	2.65
CCOOC10	348.65–518.15	9	10.57	10.02	12.08		293.15–368.15	6	2.23	1.45	2.55
Propanoates CH₃CH₂COOR′											
C2COOC	253.15–530.55	29	3.52	2.12	3.52		273.15–523.15	26	3.58	3.73	1.72
C2COOC2	273.15–543.15	28	3.69	2.38	3.19		273.15–543.15	29	2.05	1.99	1.62
C2COOC3	258.95–420.35	17	2.93	1.18	1.45		273.15–393.15	13	1.27	0.96	1.96
C2COOC4	265.82–553.5	17	4.83	4.98	5.39		273.15–363.15	11	1.94	1.44	2.41
Butanoates CH₃(CH₂)₂COOR′											
C3COOC	273.15–553.15	29	3.09	1.07	2.80		273.15–373.15	11	1.43	2.60	3.80
C3COOC2	288.45–422.65	14	9.68	10.64	9.63		273.15–393.15	13	1.58	1.24	1.74
C3COOC3	295.25–445.15	16	4.27	3.16	3.35		273.15–413.15	14	3.42	2.84	0.18
C3COOC4	290.00–610.00	17	4.47	2.19	2.10		273.15–358.65	8	4.29	3.80	0.51
Other esters											
C4COOC4	262.35–508.35	8	7.29	5.00	6.00		273.15–358.45	4	4.69	4.01	0.57
C9COOC	308.65–671.00	17	6.18	4.98	4.70		293.15–372.05	7	1.26	1.15	3.49
C11COOC	295.41–452.00	17	4.47	3.32	4.78		293.15–372.05	10	2.05	1.44	2.88

the DIPPR database [21,22] are shown. We used in this work only the data considered as acceptable by DIPPR i.e. data with uncertainties generally lower than 10% except for instance in the case of CCOOC9 and CCOOC10 for which uncertainties are assumed to be lower only than 25%.

As it appears clearly from the table, data are mainly available for small R′, especially for formates (HCOOR) and acetates (CH₃COOR).

The parameters of CH_3 and CH_2 chemical groups are given by Tamouza et al. [9] for SAFT-0 and VR-SAFT. In the case of PC-SAFT, they were determined in this work in the same way as previously by VLE data regression of the *n*-alkane family nC_2–nC_{10}. Average deviations on pressure and saturation liquid volume fall within the 0.5–1.5% range, which compare very well to those obtained using SAFT-0 and VR-SAFT. All the parameters for CH_3 and CH_2 are recalled or given in Table 2.

Table 2
Parameters values for the CH₃ and CH₂ chemical groups

	CH₃					CH₂			
	ε/k (K)	σ (Å)	λ	R		ε/k (K)	σ (Å)	λ	R
SAFT-0	167.9	3.51	–	0.86		208.1	3.42	–	0.51
VR-SAFT	202.9	3.54	1.47	0.80		136.4	3.42	1.90	0.47
PC-SAFT	190.0	3.49	–	0.79		261.1	3.93	–	0.38

Table 3
Parameters values for the HCOO chemical group

	ε/k (K)	σ (Å)	λ	R	μ_0' (D)	α' (D)
SAFT-0	234.75	2.923	–	1.465	2.753	-2.099×10^{-01}
SAFT-VR	161.17	3.015	1.849	1.240	2.773	-2.542×10^{-01}
PC-SAFT	289.27	3.191	–	1.229	2.697	-1.994×10^{-01}

Table 4
Parameters values for the COO chemical group

	ε/k (K)	σ (Å)	λ	$R(2)$	$R(3)$	$R(4)$	$R(5)$	μ_0 (D)	α (D)
SAFT-0	238.19	2.417	–	1.398	1.327	1.236	1.239	3.416	2.099×10^{-02}
SAFT-VR	164.88	2.730	1.994	1.099	1.018	0.938	0.962	3.295	2.872×10^{-02}
PC-SAFT	318.79	3.106	–	1.016	0.962	0.886	0.894	3.468	1.994×10^{-02}

$R(2)$–$R(5)$ are values of R_{COO} at different symmetrical position i.e. $R(i)$ for $i = \min(n_R, n_{R'}) + 1$.

All the SAFT parameters for the COO and HCOO groups were determined by simultaneous regression of all the available data on esters (vapor pressure and saturated liquid volume) using a procedure presented earlier [8,9].

The resulting parameters values are given in Tables 3 and 4.

The regressed values of μ°, α, μ'° and α' (for computing dipole moments) are substantial. Indeed preliminary attempts to model ester compounds without polar terms led to unsatisfactory results (error larger than 15% on vapor pressure).

The values of average deviations are reported in Table 1 and Figs. 1 and 2. The agreement between experimental and calculated vapor pressures is generally better than 5% which is a reasonable accuracy for such a method, especially if compared to previous results obtained for hydrocarbons and alkanols. Note that the accuracy is of the same order as the experimental uncertainty, indicating that it would not be reasonable to search for a lower deviation. The representation of liquid molar volume at saturation is good. The three versions of SAFT seem to give almost equivalent results, but VR-SAFT provides generally the best ones. Note that PC-SAFT appears less accurate than the other equations for small esters (see especially saturated liquid molar volume).

For some compounds, significantly larger deviations are observed, especially for those with long alkyl chains and also in the case of methyl acetate CH_3COOCH_3 (PC-SAFT equation). Note however that the data for these heavy compounds were evaluated by DIPPR as containing large uncertainties.

4. Prediction and discussion

The parameters determined above were used to make pure predictions of vapor pressure of heavy esters that were not included in the regression database. Data from several authors were considered. Our inspection of the literature shows that only a few are available, mainly for methyl esters.

First, we compared our predictions to the data from Bureau [23] and Bureau et al. [2]. Vapor pressure values are very low especially in the case of methyl tetracosanoate (from 1.16 to 17.5 Pa).

The results of predictions are presented in Table 5. For the sake of comparison, results obtained by Bureau [23] using other methods are also given. They are based on the Peng–Robinson [30] and Elliott–Suresh–Donohue [29] (ESD) equation of state with parameters calculated using critical coordinates evaluated by three different group contribution methods (Constantinou-Gani [24], Elliott [25], Somayajulu [26]).

Our prediction errors by GC-SAFT may appear important at first sight in the case of methyl stearate and methyl tetracosanoate, but they are in fact reasonable when compared to
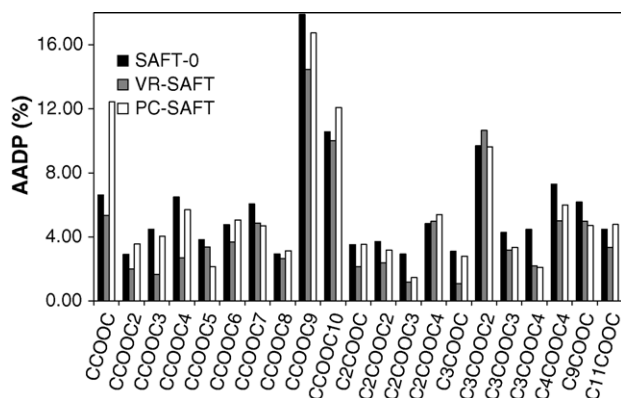

Fig. 1. Absolute average deviation on regressed vapor pressure AADP (%) of RCOOR′ esters. Data from DIPPR [21,22].
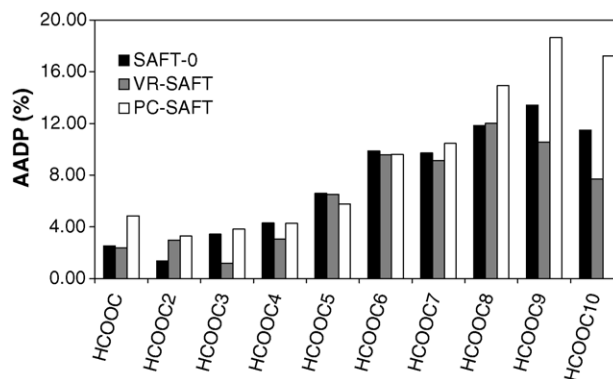

Fig. 2. Absolute average deviation on regressed vapor pressure AADP (%) of HCOOR′ esters. Data from DIPPR [21,22].

Table 5
Prediction of vapor pressure of some heavy esters

Equation of state	Method for estimation of critical parameters			GC-SAFT
	Constantinou-Gani	Elliott	Somayajulu	
Methyl palmitate (C15COOC)				
PR	38.87	72.19	13.91	
ESD	44.15	69.94	8.76	
SAFT-0				10.54
PC-SAFT				15.82
VR-SAFT				4.58
Methyl stearate (C17COOC)				
PR	38.81	74.73	45.41	
ESD	44.06	76.72	29.31	
SAFT-0				13.31
PC-SAFT				15.25
VR-SAFT				17.33
Methyl tetracosanoate (C23COOC)				
PR	>500	>500	103	
Willman-Tejà	>500	>500	34	
SAFT-0				48.94
PC-SAFT				36.24
VR-SAFT				70.13

Standard deviation are shown (all values are given in percent).
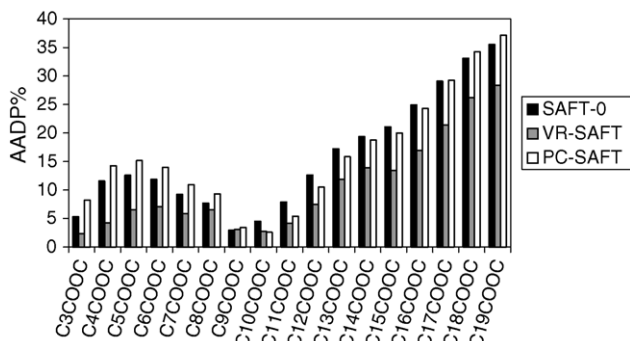
Fig. 3. Absolute average deviation on predicted vapor pressure AADP (%) of methyl esters series up to eicosanoate. Data from van Genderen et al. [27].
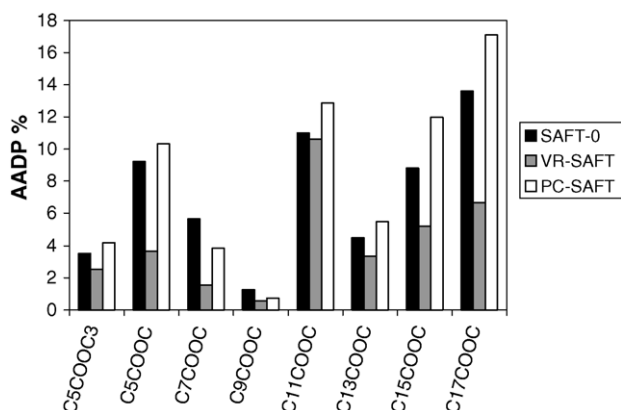

Fig. 4. Absolute average deviation AADP (%) on predicted vapor pressure of some esters. Data from NIST [28].
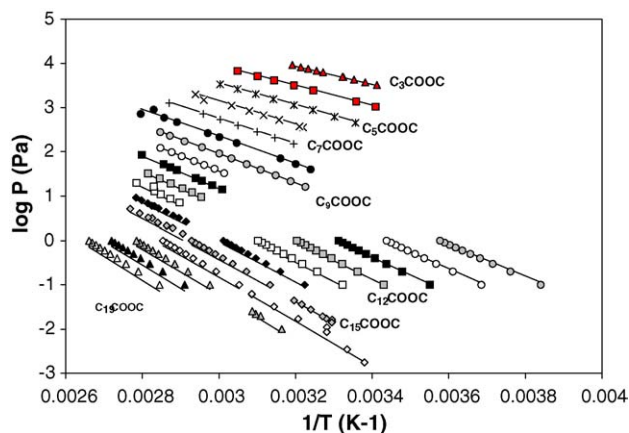

Fig. 5. Prediction of vapor pressure of methyl esters series from propanoate up to eicosanoate using VR-SAFT. Data from van Genderen et al. [27].
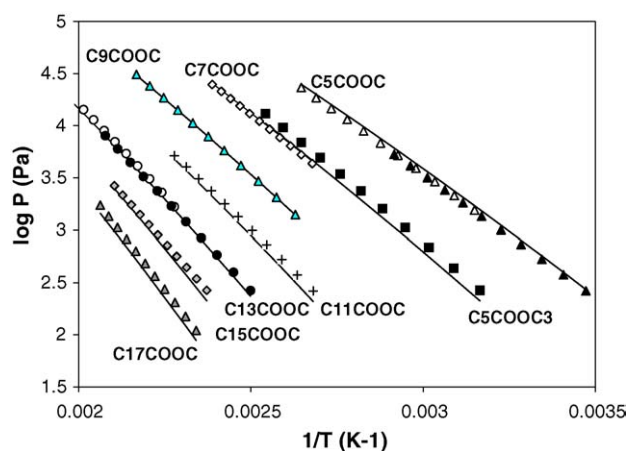

Fig. 6. Prediction of vapor pressure of some esters. Data from NIST [28].

those obtained using the other prediction methods. Such large errors are also observed in the case of other heavy esters (Bureau [2,23]) that are not considered here.

Other tests of prediction were made using GC-SAFT on data taken from Van Genderen et al. [27] and NIST [28]. The agreement between prediction and measurement appears satisfactory (see Figs. 3 and 4) in a wide pressure range: up to seven orders of magnitude (see Figs. 5 and 6), pressures ranging from 10^{-3} to 10^4 Pa. The overall best results are obtained using VR-SAFT. The calculation errors seem to increase with the size of the esters, but probably so do the experimental errors. Indeed, the larger the size of the ester, the lower the corresponding vapor pressure value and hence, the larger the expected error.

5. Conclusion

The GC-SAFT approach [9] has been here extended to the estimation of VLE properties of esters. In addition to the usual terms, a dipole–dipole contribution is used. Predictions of vapor pressure up to C25 by this approach compare well with other methods based on an EOS combined with a GC method for estimating critical coordinates.

The GC-SAFT method has already been tested on simple mixtures [10] and work is in progress to test this extended GC-SAFT (i.e. with polar terms) on mixtures containing polar compounds including esters.

List of symbols

a	reduced molar Helmholtz free energy (res, seg, hs, assoc, etc.)
a_0	segment reduced molar Helmholtz free energy (seg), per mole of segments
AAD	average absolute deviation
DIPPR	design institute for physical property data
EOS	equation of state
ESD	equation of Elliott–Suresh–Donohue [29]
GC	group contribution method
k	Boltzmann's constant $\approx 1.381 \times 10^{-23}$ J/K
m	effective number of segments within the molecule (segment number)
N_{Av}	Avogadro's number $\approx 6.023 \times 10^{23}$ molecules/mol
Npt	number of data points
P	pressure (Pa)
PR	equation of Peng–Robinson
PC-SAFT	perturbed chain SAFT [13,14]
R	gas constant
R_i	contribution of group i to the chain parameter
SAFT	statistical associating fluid theory
SAFT-0	original version of the SAFT equation of state [8,10]
T	temperature (K)
v	molar volume, v_{liq} = liquid molar volume
VR-SAFT	SAFT with a variable range potential [12]

Greek letters

ε	dispersion energy of interaction between segments (J)
η	pure component reduced density
λ	range parameter of the SAFT-VR equation of state
ρ	molar density (mol m^{-3})
σ	segment diameter (Å)

Subscripts

liq	liquid
reg	regression

Superscripts

assoc	association
cal	calculated
disp	dispersion
dd	dipole–dipole
exp	experimental
hs	hard sphere
res	residual
seg	segment
*	reduced property

Appendix A

Consider the three following different esters compounds in Fig. A.1.
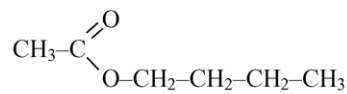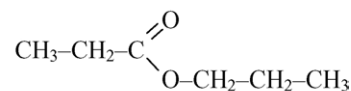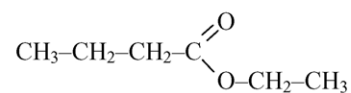
Fig. A.1. Molecular structure of the three example molecules.

They all contain three CH$_2$ groups, two CH$_3$ groups, and one COO group. Thus, for all these three compounds, the SAFT parameters ε, σ and λ values are given by:

$$\varepsilon = \sqrt[6]{(\varepsilon_{CH_2})^3.(\varepsilon_{CH_3})^2.(\varepsilon_{COO})^1}$$

$$\sigma = \frac{3\sigma_{CH_2} + 2\sigma_{CH_3} + \sigma_{COO}}{6}$$

$$\lambda = \frac{3\lambda_{CH_2} + 2\lambda_{CH_3} + \lambda_{COO}}{6}$$

In the case of butyl acetate: $n_R = 1$ and $n_{R'} = 4$. The position of the COO group as defined above is $2 = \min(1;4) + 1$. Hence, for this compound:

$$m = 3R_{CH_2} + 2R_{CH_3} + R_{COO}(2)$$

$$\mu = \mu^\circ - 3.\alpha$$

In the case of both propyl ethanoate ($n_R = 2$ and $n_{R'} = 3$) and ethyl propanoate ($n_R = 3$ and $n_{R'} = 2$), the position of the COO group is $3 = \min(2;3) + 1$. We have for these two compounds:

$$m = 3R_{CH_2} + 2R_{CH_3} + R_{COO}(3)$$

But they have different dipole moment, respectively:

$$\mu = \mu^\circ - \alpha$$

and

$$\mu = \mu^\circ + \alpha.$$

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