

# Application to Petroleum Engineering of Statistical Thermodynamics – Based Equations of State

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**Résumé — Application des équations d'état basées sur la statistique thermodynamique, aux besoins pétroliers** — L'utilité des équations d'état cubiques pour l'ingénieur pétrolier a été démontrée depuis de nombreuses années. Leur pouvoir prédictif reste cependant limité. De nouvelles équations d'état, basées sur des principes de mécanique statistique, ont été développées depuis environ 15 ans, et leur maturité est telle qu'elles sont maintenant de plus en plus utilisées par l'ingénieur. Dans cette publication, nous nous concentrerons essentiellement sur les équations qui ont pour base la théorie de Wertheim.

Nous aborderons trois thèmes :

Les mélanges associatifs tels l'eau et les alcools en présence d'hydrocarbures ont toujours représenté un défi majeur pour les équations d'état. Nous démontrons ici que l'équation CPA (SRK avec un terme associatif), tout en conservant les caractéristiques de la cubique pour les molécules non-associatives, améliore significativement le pouvoir prédictif de ces équations pour les mélanges contenant de l'eau, du méthanol et des hydrocarbures.

La signification physique des paramètres de l'équation SAFT rend possible l'élaboration d'une méthode de contribution de groupe pour la détermination des paramètres de cette équation. En utilisant cette approche, il est possible de prédire les tensions de vapeur et les volumes liquide des molécules lourdes avec une précision remarquable. Nous montrons cela sur les n-alcanes, les n-alcools et les 1-oléfines, ainsi que pour les isomères méthyls des alcanes.

Finalement, nous présenterons les prédictions d'équilibres liquide-vapeur de mélanges non-idéaux, obtenu par l'équation SAFT en incluant des termes polaires. Nous montrons ainsi clairement l'effet du quadrupole pour les mélanges aromatique-non-aromatique. Le fait de tenir compte ou non des interactions dipole-dipole permet de différencier le comportement des isomères cis- et trans oléfiniques.

**Abstract — Application to Petroleum Engineering of Statistical Thermodynamics – Based Equations of State** — Cubic equations of state (EOS) have proven their utility to the petroleum engineers for many decades. Their predictive power remains, however, limited. Statistical mechanical approaches have meanwhile grown allowing the development of powerful engineering equations of state. In particular, this paper investigates how equations that are based on the association term of Wertheim can improve significantly the predictive power in petroleum applications.

Three distinct issues are discussed.

Mixtures of associating components such as water or methanol with hydrocarbons have so far represented one of the main challenges for the predictive power of equations of state. It is shown that the CPA equation, that combines the classical SRK EOS with the association term of Wertheim, provides a significant improvement for both methanol-hydrocarbon and water-hydrocarbon mixtures.

The physical significance of the SAFT parameters makes it possible to develop a group contributions method for their determination. Using this approach, it becomes possible to predict vapour pressure and liquid volume of heavy molecules. This is shown for a number of families, such as n-alkanes, n-alcohols, 1-olefins as well as for isomers of methyl-alkanes.

Finally, the improved predictions resulting from the use of polar terms with SAFT are illustrated. The effect of the quadrupole is clearly shown with an aromatic-non aromatic mixture. Including a dipolar interaction makes it possible to differentiate the behaviour of the cis and the trans 2-butene isomers.

## NOMENCLATURE

### Latin lower case

$a$	molar Helmholtz energy	J/kmol
$a$	energy parameter of the cubic eos	J m <sup>3</sup> /kmol
$a_0$	energy parameter of the cubic eos at $T = T_c$	J m <sup>3</sup> /kmol
$b$	volume parameter of the cubic equation of state	m <sup>3</sup> /kmol
$c_1$	parameter of the cubic equation of state	–
$d$	hard sphere diameter of the segments	Å
$m$	parameter of the SAFT equation of state referring to the number of segments in the molecule	–
$f$	generalized function	–
$g$	radial distribution function	–
$k_{ij}$	binary interaction parameter	–
$k$	Boltzman constant = $R/N_{av}$	–
$qN$	canonical Partition Function	–
$s_l$	high pressure segment diameter for SAFT VR	Å
$v$	molar volume	m <sup>3</sup> /kmol
$x$	mole fraction in liquid phase	–
$y$	mole fraction in vapor phase	–
$z$	total mole fraction	–

### Latin Capitals

$A$	Helmholtz energy	J
$A_{nm}$	parameter in the Alder equation of state	–
$E$	reduced energy density = $e/RT$	1/m <sup>3</sup>
$G$	Gibbs energy	J
$N$	number of moles	kmol
$N_{av}$	Avogadro Number = $6.02 \cdot 10^{23}$	–
$P$	pressure	Pa
$Q$	quadrupole moment, eos parameter	–

$R$	ideal gas constant = 8314.5	J/kmol/K
$T$	temperature	K
$V$	total volume	m <sup>3</sup>
$X^{Ai}$	mole fraction of molecule i not bonded at site A	–
$Z$	compressibility Factor (= $PV/NRT = P_v/RT$ )	–

### Greek Letters

$\alpha$	attractive function of a cubic EOS	–
$\beta$	association volume for CPA EOS	–
$\sigma$	parameter of the SAFT EOS expressing the segment diameter	Å
$\epsilon/\kappa$	parameter of the SAFT EOS expressing the interaction energy between segments	K
$\mu$	dipole moment, EOS parameter	J/kmol
$\rho$	molar density	kmol/m <sup>3</sup>
$\kappa$	association volume for SAFT EOS	–
$\Delta$	association strength	–
$\omega$	acentric factor	–
$\lambda$	well width parameter in the SAFT-VR equation	–
$\eta$	compacity (= $v/v^*$ ), or non-dimensional volume	–

### Indices

1,2,3	indices of the degree of perturbation used
$att$	attractive contribution
$rep$	repulsive contribution
$hs$	hard sphere contribution (equivalent to repulsive contribution)
$disp$	dispersive contribution (equivalent to attractive contribution)
$dipole-dipole$	dipole-dipole interaction contribution

<i>quad-quad</i>	quadrupole - quadrupole interaction contribution
<i>chain</i>	contribution due to chain formation
<i>polar</i>	polar contribution, may be dipole-dipole, quadrupole-quadrupole or dipole - quadrupole
<i>c</i>	critical property
<i>ass</i>	contribution due to association
<i>i, k, j</i>	pure component index
<i>ij, ji</i>	parameter related to the interaction between components <i>i</i> and <i>j</i>
<i>r</i>	reduced property

### Superscript

*	characteristic property
0	segment property
<i>hs</i>	hard sphere property
<i>hc</i>	hard chain property (in the PC-SAFT EOS)
<i>sw</i>	square well property (in the SAFT-VR EOS)
<i>A<sub>j</sub></i>	refers to site <i>A</i> on molecule <i>j</i>
<i>A<sub>j</sub>B<sub>i</sub></i>	interaction parameter between sites <i>A</i> of molecule <i>j</i> and site <i>B</i> of molecule <i>i</i>

## INTRODUCTION

The use of equations of state (EOS) has been the generally accepted method for the calculation of many fluid physical properties since the famous van der Waals' proposal (1873) in the 19<sup>th</sup> century. The cubic equations are the most used equations, but over the last fifteen years, many new equations have been proposed, based on statistical mechanical concepts. Their use in the petroleum industry is not yet generally accepted. It is the purpose of this paper to show that they bring considerable advantages for a number of mixtures of industrial interest.

## 1 FROM CUBICS TO STATISTICAL MECHANICS

### 1.1 The Cubic Equations

An equation of state is a relation between the pressure *P*, the temperature *T* and the molar volume *v*. In the last century, the cubic equations of state have by far dominated in the description of such equations and their general form is:

$$P = \frac{RT}{v-b} - P_{att}(v,T)$$

with

$$P_{att}(v,T) = \frac{a}{v(v+d) + c(v-d)}$$

In these relations, *a*, *b*, *c* and *d* may be constant or function of the temperature and of some other properties of the fluid (acentric factor for example). These relations show the main concept developed by van der Waals: the separation of repulsive forces caused by molecular size from cohesive forces caused by molecular attraction. This approach is still used in recent modelling of fluid properties. This kind of equation allows the continuous description of the vapour and the liquid phase with the same tool. The most famous cubic equations of state are those of:

*Soave-Redlich-Kwong (1972)*

$$P = \frac{RT}{v-b} - \frac{a(T,\omega)}{v(v+b)}$$

*Peng and Robinson (1976)*

$$P = \frac{RT}{v-b} - \frac{a(T,\omega)}{v(v+b) + b(v-b)}$$

These equations have two parameters: *b* is the covolume and is a function only of critical properties (*T<sub>c</sub>* and *P<sub>c</sub>*) whilst the attractive parameter, *a*, is function of the temperature and of the acentric factor. These equations of state are included in all the computer process simulation packages. One of the main drawbacks of these equations is that the critical compressibility factor is constant regardless of the compound. Equations of state with three or four parameters overcome this deficiency.

The reason for the clear superiority of this kind of equations was not so much their accuracy, but rather their simplicity of use, and the development of many ways to "tune" the parameters for the specific application.

### For Pure Component Vapour Pressure Improvement

The attraction term, *a*, has been adapted several time (Redlich and Kwong, 1949; Soave, 1972). The simple forms are a function only of temperature or of acentric factor whereas the more complex forms (Behar *et al.*, 1985, 1986; Twu *et al.*, 1995) increase the number of parameters.

### For Volume Prediction

The cubic equations of state are known to give poor results for liquid molar volumes. However, one may add volume translation (Péneloux *et al.*, 1982; Ungerer and Batut, 1997; de Sant'Ana *et al.* 1999, etc.) to improve this information without modifying the phase equilibrium.

### For Mixture Prediction

One of the major advantages of the cubic equations is the wide variety of available mixing rules. These are more or less complex, and thus require more or fewer parameters. The classical mixing rules were proposed by van der Waals

(1873) and they should be applied to non-polar mixtures. Huron and Vidal (1979) have initiated a new type of mixing rule, which combines the power of Excess Gibbs energy models with the equation of state approach. Since then, many new models have been developed, the most known of which are the MHV2 (Dahl & Michelsen, 1990), Wong- Sandler (Wong *et al.*, 1992) and LCVm model (Boukouvalas *et al.*, 1994) models. These more complex mixing laws extend the use of the cubic EOS to mixtures with polar compounds such as water or alcohols. But in these cases, the number of adjustable parameters is typically twice the number used with the classical mixing rule (two per binary rather than one). The description of multiphase equilibria remains difficult with this approach (unless specific parameters are used for different liquid phases).

Many efforts have been made for making these equations more predictive (Coniglio *et al.*, 2000; Chen *et al.*, 2002; P neloux *et al.*, 1989), but the empirical nature of these equations results in a rather complex set of equations whose accuracy remains limited. This conclusion shows that other ways should be proposed to model the behaviour of fluids and improve the predictive character of the EOS.

### 1.2 Equations Based on the Thermodynamic Perturbation Theory - SAFT

With the advent of molecular simulation coupled with statistical physics, new approaches have been investigated for equations of state. These approaches develop an expression for the Helmholtz free energy, *A*, using what is called the “canonical partition function” ( $q_N$ ) for a system of *N* particles (Atkins and de Paula, 2002):

$$\frac{A}{NkT} = - \left( 1 + \ln \frac{q_N}{N} \right)$$

The partition function is approximated using a potential function that describes the potential energy of particles as a function of their distance. A simple derivation makes it possible to calculate the compressibility factor:

$$Z = \frac{PV}{NRT} = - \frac{V}{NRT} \left. \frac{\partial A}{\partial V} \right|_T$$

The best known of these models is the Carnahan-Starling equation for hard spheres (Carnahan & Starling, 1972). Using a derivation based on the interaction potential, they describe the compressibility factor as that of an ideal gas with a residual contribution (*Fig. 1*).

Of course, this equation cannot describe a real fluid behaviour, because it contains only a repulsive term. However, it is of great use for describing the deviation from the ideal gas behaviour at infinite temperature, *i.e.* when the attraction between molecules is negligible. An empirical approach is generally used for describing the attraction in a square well fluid (Alder *et al.*, 1972), (*Fig. 2*).

Prigogine’s theory (1957) postulating how the rotational and vibrational degrees of freedom could depend on density has resulted in the development of many equations of state for chain-like molecules (COR - Chien *et al.*, 1983; PHCT - Donohue and Prausnitz, 1978, PACT - Vilmachand and Donohue, 1985, APACT - Ikonomou and Donohue, 1986, SPHCT - Kim *et al.*, 1986). These equations are developed using the so-called “Thermodynamic Perturbation Theory” (TPT), because the fluid behaviour is described as a sum of a “reference” behaviour and a “perturbation”. The reference is taken at infinite temperature: the hard sphere behaviour.

Using Wertheim’s theory (1986), Chapman *et al.* published in 1988 and in 1990 the first papers applying the perturbation theory to associating fluids (SAFT: Statistical-Associating Fluid Theory). We consider two major contributions in their theory.

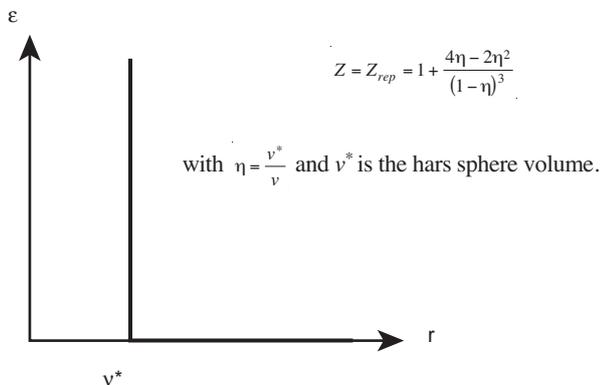


Figure 1  
Carnahan and Starling's equation for hard spheres.

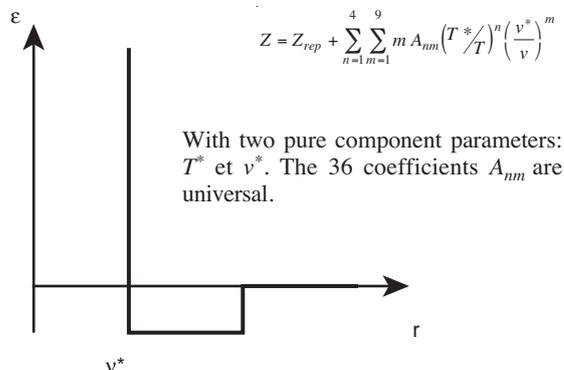


Figure 2  
The equation of Alder *et al.* for square well interactions.

**The Association Term**

The first contribution is based on Wertheim’s TPT and proposes an analytical expression for associating fluids:

$$Z_{ass} = \sum_i x_i \sum_j \rho_j \sum_{A_j} \left[ \left( \frac{1}{X^{A_j}} - \frac{1}{2} \right) \frac{\partial X^{A_j}}{\partial \rho_i} \right]$$

This expression has since then been found to be equivalent to the much simpler form (Michelsen and Hendriks, 2001):

$$Z_{ass} = -\frac{1}{2} \left( 1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X^{A_i})$$

where  $\rho_i = \frac{x_i}{v}$  is the molar density of component  $i$ , and  $X^{A_i}$  is the mole fraction of molecule  $i$  not bonded at site A. This last quantity must be computed based on following intrinsic set of equations:

$$X^{A_i} = \left[ 1 + \sum_i \left( \rho_i \sum_{B_i} X^{B_i} \Delta^{A_i B_i} \right) \right]^{-1}$$

The key parameter for calculating the amount of non-associating sites is the association strength which is defined by Chapman (1990) as:

$$\Delta^{A_i B_i} = d_{ij}^3 g_{ij}(d_{ij}) \kappa^{A_i B_i} \left[ \exp\left(\frac{\epsilon^{A_i B_i}}{kT}\right) - 1 \right]$$

The parameter  $\epsilon^{A_i B_i}$  represents the association energy between the two sites  $A_j$  and  $B_i$ , and the parameter  $\kappa^{A_i B_i}$  characterises the bonding volume. The radial distribution function  $g_{ij}(d_{ij})$  represents the probability that two molecules of type  $i$  and  $j$  are found at a distance  $d_{ij}$  from each other.

Huang and Radosz (1990) proposes to simplify the set of implicit equations in a number of often—encountered simple cases where a single association type exists in the fluid. They label these association types with a number (corresponding to the number of sites on the molecule) and a letter (A when any site can associate with any other; B when one site is electropositive, and the other(s) electronegative; C when two sites are electropositive, etc.).

**The Chain Term**

The second major contribution of Chapman *et al.* (1988, 1990) is their proposal to consider a chain molecule as a mixture of segments with infinite association strength (Fig. 3). Doing so, and using a Lennard-Jones type potential interaction, they write (for non-associating molecules):

$$Z = 1 + m \left( Z_{hs}^o + Z_{disp}^o \right) + Z_{chain}$$

where  $m$  is the number of segments in the molecule,  $Z_{hs}^o$  and  $Z_{disp}^o$  are the segment hard sphere (repulsion) and dispersion (attraction) terms and  $Z_{chain}$  is the contribution of the chain-forming to the compressibility factor. We will show further in this article how the physical basis of this equation may lead to an unexpectedly good extrapolation of fluid properties to heavy components, by using a group contribution approach for the pure component parameters.

Many authors have proposed improvements to the SAFT equation of state since it was initially proposed (Huang and Radosz, 1990; Banaszak *et al.*, 1993: SW-SAFT; Kraska and Gubbins, 1996a, 1996b: LJ-SAFT; Fu and Sandler, 1995: S-SAFT; Galindo *et al.*, 1996, 1997: HS-SAFT, Blas and Vega, 1998: Soft-SAFT; von Solms *et al.* (2003): simplified; PC-SAFT, etc.). Some reviews of these many versions and their applications have been written (Wei and Sadus, 2000; Muller and Gubbins, 2001; Economou, 2002). Further in this paper, we will discuss in some more details the original SAFT version (SAFT-0), SAFT-VR (Gil-Villegas *et al.*, 1997) and PC-SAFT (Gross and Sadowski, 2000, 2001).

**1.3 Hybrid Equations**

In the engineering community, hybrid equations of state have often been used. These equations combine energy interaction terms originating from different theories. As example, we can mention Carnahan and Starling (1972) who combine their own hard sphere repulsive equation with the attractive term of the cubic Redlich-Kwong equation.

Along these lines, Kontogeorgis *et al.* (1996) suggest using the association term proposed by Chapman *et al.* (1990) as an additional contribution to the classical cubic equation of state. Thus, their equation is written as (using the Redlich-Kwong version of the attractive

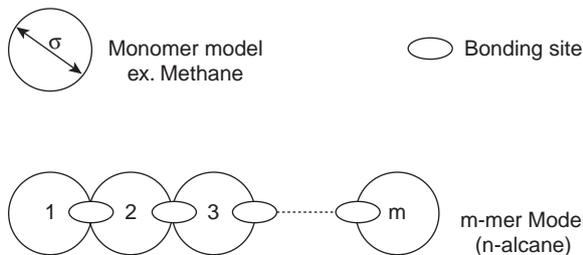


Figure 3

Hard sphere (monomer) and chain molecules (m-mer) model, with bonding sites (Chapman *et al.*, 1990).

term and the Michelsen and Hendricks formulation of the associative one):

$$Z = \frac{v}{v-b} - \frac{a}{RT(v+b)} - \frac{1}{2} \left( 1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum x_i \sum_{A_i} (1 - X^{A_i})$$

This equation is further discussed in this paper. The reason why it is of interest to petroleum engineers is that in the absence of associating compounds, the well-known cubic equation is recovered, and all the existing correlations can be used. The advantage of keeping the capability to work with complex hydrocarbon mixtures, including badly defined pseudo-components is the main reason why, despite its dubious physical basis, this approach remains attractive in the petroleum engineering community.

Although association among molecules clearly results in non-ideal behaviour that can now be described explicitly, other causes may also result in non-ideal behaviour. Among these, we can mention the presence of dipolar or quadrupolar moments. For these contributions, a thermodynamic perturbation theory has also been developed (Kraska and Gubbins, 1996a, 1996b; Gubbins and Twu, 1978). The contribution of these physical phenomena can be included in the SAFT-type approach, resulting in a more complex hybrid equation:

$$Z = 1 + m(Z_{hs}^o + Z_{disp}^o) + Z_{chain} + Z_{ass} + Z_{dipole-dipole} + Z_{quad-quad}$$

As we will show below, these additional contributions can improve significantly the predictions in the case of components of similar volatility.

In this article, we will show how these equations of state can be of use to industrial problems in the petroleum industry. The added value of the association term, as used in the CPA equation is clearly shown in the case of mixtures with polar compounds such as water and methanol. Binary interaction parameters for a number of binary mixtures are proposed. The power of the SAFT equation is its predictive capability for polar or long-chain molecules. This is illustrated by two additional examples. The first shows how group contributions can be used for predicting vapour pressures and liquid phase volume; the second uses polar terms for the prediction of the azeotropic behaviour of near-boiling mixtures.

## 2 SHORT DESCRIPTION OF THE EQUATIONS

It is not the purpose here to describe the equations in detail. The original articles can be consulted for that purpose. We only want to stress here some basic features that will help in understanding the strengths and weaknesses of these equations.

### 2.1 The Main Contributions

The two types of equations considered in this work are SAFT and CPA. Three different versions of SAFT are examined: SAFT-0, which is the original version of Chapman *et al.* (1988, 1990); SAFT-VR which has been proposed by Gil-Villegas *et al.* (1997), and which seems to be quite promising, at the expense of an additional parameter,  $\lambda$ , that describes the width of the square well; and PC-SAFT (Gross and Sadowski, 2000, 2001), which benefits from a growing popularity in the engineering world.

The common point between the SAFT equations and CPA is that the Helmholtz free energy expression (and therefore the compressibility factor) is written as a sum of energetic contributions. In both cases, a repulsive and an attractive contribution are identified. The former describes the repulsion between molecules when they approach each other; the latter is a combination of the long-range attractive forces. In addition, both equations take explicitly into account the short range association forces. Hence, they are written as:

$$Z(T, v) = Z_{rep}(T, v) + Z_{att}(T, v) + Z_{ass}(T, v)$$

The association contribution is identical in both equations of state. The repulsive and the attractive part are expressed differently in CPA or in the different SAFT versions. In CPA, they are directly taken from the cubic equation of Redlich-Kwong. In SAFT, the reference and the dispersive term can be considered equivalent to respectively the repulsive and attractive terms in CPA:

$$Z_{rep}(T, v) = 1 + mZ_{hs}^o(T, v) = 1 + Z_{hs}(T, v)$$

$$Z_{att}(T, v) = mZ_{disp}^o(T, v) = Z_{disp}(T, v)$$

Where the reference term is build starting from hard spheres (segments). An additional term resulting from the chain formation is added, yielding:

$$Z = 1 + Z_{hs} + Z_{disp} + Z_{chain} + Z_{ass}$$

The expressions for each of these terms are compared in Table 1. The parameters are compared later in Table 2. Two major differences can be noted between the equations.

#### The Radial Distribution Function

The first difference concerns the radial distribution function that appears both in the association term and, as a derivative, in the chain term (except for CPA that has no chain term). It

Table 1

Main expressions for the contributions to the compressibility factor of the three versions of the SAFT equation of state and CPA, used in this work

Expressions	Chapman <i>et al.</i> , 1990 (SAFT-0)	Gross and Sadowski, 2001 (PC-SAFT)	Gil-Villegas <i>et al.</i> 1997 (SAFT-VR)	Kontogeorgis <i>et al.</i> , 1996 CPA
$Z_{hs}$	$Z_{hs} = mZ_{hs}^0 = m \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}$ (Carnahan and Starling, 1969)			$Z_{rep} = \frac{v}{v - b}$
$Z_{chain}$	$Z_{chain} = -(m - 1)\rho \frac{\partial \ln(g^0(d))}{\partial \rho}$ (Chapman <i>et al.</i> 1988, 1990)			
	$g^0(d) = g^{hs}(d) = \frac{2 - \eta}{2(1 - \eta)^3}$ (Carnahan and Starling, 1969)	$g^0 = g^{sw}$ : Radial distribution function developed up to the first order for a square-well potential		
$Z_{disp}$	$Z_{disp} = mZ_{disp}^0 = m \left( \frac{Z_{disp}^{01}}{T_r} + \frac{Z_{disp}^{02}}{T_r^2} \right)$ (Cotterman <i>et al.</i> 1986)	$Z_{disp} = \rho \frac{\partial}{\partial \rho} (a_1 + a_2)$ $a_2$ is a function of $Z_{hc} = 1 + m(Z_{hs} - 1) + Z_{chain}$	$Z_{disp} = m \left[ \rho \frac{\partial}{\partial \rho} \left( a_1 + \frac{a_2}{RT} \right) \right]$	$Z_{att} = - \frac{a(T)}{RT(v + b)}$ (Soave, 1972)
$Z_{ass}$	$Z_{assoc} = \rho \sum_A \left[ \frac{1}{X^A} - \frac{1}{2} \right] \frac{\partial X^A}{\partial \rho}$ (Chapman <i>et al.</i> 1988, 1990)			
	$g^{hs}$ (Carnahan and Starling, 1969)	$g^{sw}$ (Gil-Villegas <i>et al.</i> , 1997)		$g^{hs}(d) = \frac{2 - \eta}{2(1 - \eta)^3}$
Comments	$\eta = \frac{\pi N_{Av}}{6} \rho d^3 m$ and $\rho = 1/v$			$\eta = \frac{b}{4v}$
	$d = \sigma f_1(T)$	$d = \sigma f_2(T)$	$d = \sigma$	$b = \sigma^3$

is generally taken from the hard sphere expression of Carnahan and Starling (1969):

$$g^{seg}(d) = g^{hs}(d) = \frac{2 - \eta}{2(1 - \eta)^3}$$

In the SAFT-VR equation, the radial distribution function is developed up to the first order and is taken from a square-well fluid. Its expression can be found in (Gil-Villegas, 1997) and is not given here.

The CPA equation is further used with a still simplified radial distribution function, as was proposed by Elliot *et al.* (1990) and applied to CPA by Kontogeorgis *et al.* (1999):

$$g(\eta) = \frac{1}{(1 - 1.9\eta)}$$

### The Dispersion Term

The dispersion expresses the attractive contribution that is generally not included in the reference term. The expressions are usually empirical in nature, as no exact theory exists. For the cubic equation (CPA), the expression is that proposed by

Soave (1972), with:

$$a = a_0(1 + c_1(1 - \sqrt{T_r}))^2$$

where both  $a_0$  and  $c_1$  are considered as adjustable parameters.

In TPT based equations of state, the expression is usually obtained by fitting on molecular simulation results. For single segments, the deviation from the reference can be made visible in a plot showing the energy potential as a function of the distance between segments. This is done in Figures 4 through 6 for the three SAFT equations discussed here.

In most versions of the SAFT equation, the dispersion term contribution to the molecular Helmholtz energy is proportional to the number of segments:  $a_{disp} = ma_{disp}^0$ . This is the case for the SAFT-0 and the SAFT-VR equations. In PC-SAFT, the dispersion term is originally written for chains of segments. A second major difference between PC-SAFT and the other SAFT versions is that the parameter fitting was done on physically measured data rather than molecular simulation data. This is probably one of the reasons for its rather good description of hydrocarbon fluids.

TABLE 2  
Parameters used in the equations considered

	Chapman <i>et al.</i> , 1990 (SAFT-0)	Gross and Sadowski, 2001 (PC-SAFT)	Gil-Villegas <i>et al.</i> , 1997 (SAFT-VR)	Kontogeorgis <i>et al.</i> , 1997 CPA
Size parameter $d^3m$	$d = \sigma f_1(T)$	$d = \sigma f_2(T)$	$d = \sigma$	$d = \sigma^3$
Shape parameter		$m$		$c_1$
Energy parameter		$\epsilon/k$		$a_0$
Well size parameter	not used		$\lambda$	not used
Association energy		$\frac{\epsilon^{A_j B_i}}{k}$		
Association volume		$d_{ij}^3 \kappa^{A_j B_i}$		$b \beta^{A_j B_i}$
Dipole moment		$\mu$		not used
Quadrupole moment		$Q$		not used

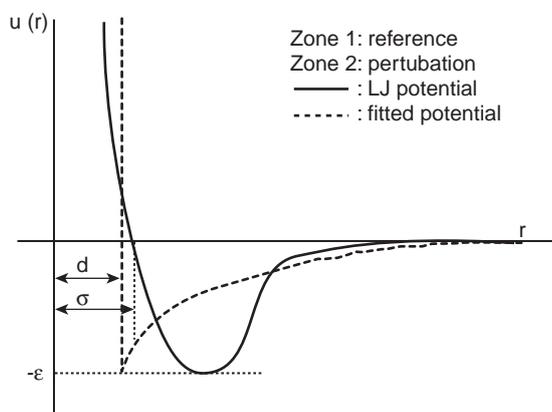


Figure 4

Lennard-Jones interaction potential described by the perturbation theory.

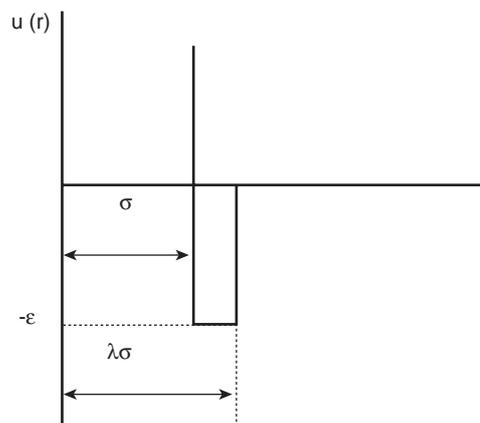


Figure 5

Variable-range square-well potential model.

#### SAFT-0 dispersion term

In the original version of SAFT, the Lennard-Jones potential is approximated as shown in Figure 4.

The expression for the dispersion term has been obtained by Cotterman *et al.* (1986), using a correlation on molecular simulation of Lennard-Jones spheres. The contributions  $Z_{01}^{disp}$  and  $Z_{02}^{disp}$  are simple polynomials as a function of reduced density.

#### SAFT-VR dispersion term

Here, the dispersion term is developed according to a perturbation development up to the first order, for a hard-sphere reference fluid. The equation used in this work is based on a square-well potential with a variable width (Fig. 5). The

attraction range width is characterised by an additional parameter, denoted by  $\lambda$ .

The dispersion term is written as a development in  $\beta = 1/kT$ , where the Helmholtz energy contributions,  $a_1$  and  $a_2$  are the first two perturbation terms associated with the attractive energy.

#### PC-SAFT dispersion term

Figure 6 shows the pair potential used. The dispersion is modelled using a second order perturbation theory according to Barker et Henderson (1967), on *chain molecules* rather than *spheres* (the *hc* superscript is used rather than *hs*). As a result, the dispersion terms  $a_1$  and  $a_2$  are functions of the chain length  $m$ . The contributions to the Helmholtz energy,

$a_1$  and  $a_2$ , are given by Gross and Sadowski (2000) using results of Chiew (1991).

Modelling polar non ideal systems with classical equations of state requires the use of additional parameters that depends generally on the system conditions such as temperature. The alternative approach proposed here is to explicitly take into account the polarity. The commonly used expression for the polar terms is proposed by Twu and Gubbins (1978). It is written as a perturbation development.

$$A^{polar} = A_2 \left[ \frac{1}{1 - \frac{A_3}{A_2}} \right]$$

The second and third perturbation terms are explicitly calculated. The first term vanishes in the development and the other terms are determined in the spirit of a Padé approximation by Stell *et al.* (1974). The expressions of  $A_2$  and  $A_3$  of the dipole - dipole and quadrupole - quadrupole terms for pure and non spherical compounds can be found in the papers of Gubbins and Twu (1978) and Kraska and Gubbins (1996). The use of these terms implies one additional parameter for each contribution: the dipole moment for the dipole-dipole interaction, and the quadrupole moment for the quadrupole - quadrupole interaction.

## 2.2 The Parameters

As we will later discuss the pure component parameters, it is useful to summarise them as in Table 2. Excluding the association term, three parameters are generally needed for each pure component, except for SAFT-VR that uses four.

The first of these parameters is the *hard sphere size* of the molecules. For cubic equations, this size is equal to the covolume  $b$ , expressed in molar volume units. The SAFT equations tend to use molecular parameters, and use therefore:

$$\frac{\pi N_{Av}}{6} d^3 m$$

where  $d$  is expressed in Angstrom, and  $m$  is the number of segments in the molecule. This volume is independent of temperature for both SAFT-VR and CPA. It is calculated by two different temperature-dependent expressions in the SAFT-0 and the PC-SAFT EOS (see the last line of Table 1).

SAFT-0:

$$d = \sigma f_1(T) = \sigma \left( \frac{1 + 0.2977(kT / \epsilon)}{1 + 0.33163(kT / \epsilon) + 0.0010477(kT / \epsilon)^2} \right)$$

PC-SAFT:

$$d = \sigma f_2(T) = \sigma \left[ 1 - 0.12 \exp\left(-\frac{3\epsilon}{kT}\right) \right]$$

The number of segments is a measure of the *molecular shape*. In cubic equations, it is usually expressed using the acentric factor, that appears in the equation in the Soave function of the energy parameter  $a(T)$ . CPA uses exactly the same expression as that of Soave (1972) for non-associating components. However, while the temperature dependence of the  $a$  parameter is kept for non-associating components, the Soave function of the acentric factor can no longer be used. The parameter  $c_j$  is then considered as an adjustable parameter.

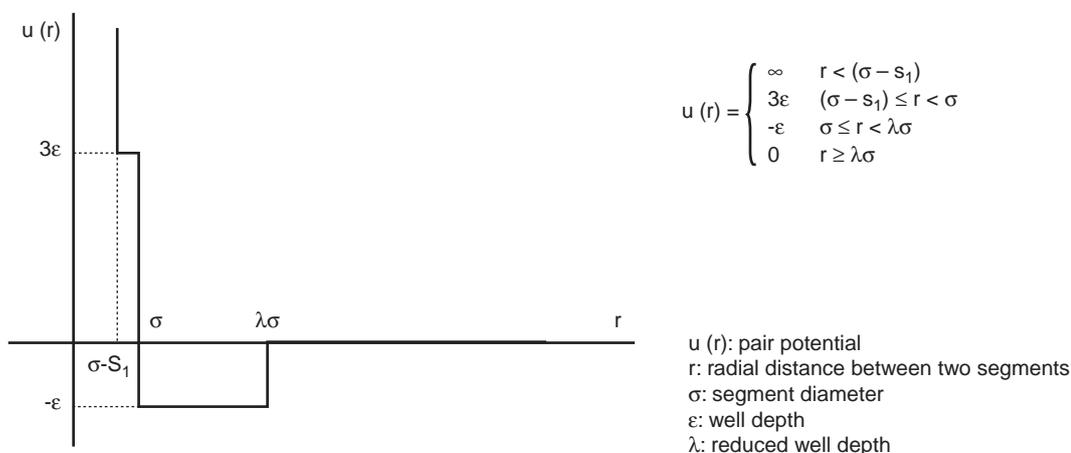


Figure 6

Potential proposed by Chen and Kreglewski 1997 and used by PC-SAFT;  $s_1/\sigma = 0.12$ .

Two parameters are required for describing each pair of associating sites. Although the number of sites on each molecule may vary from 1 to 4, only two types of sites are considered: electropositive or electronegative. Sites may only associate when they are of opposite sign. As only self-associating molecules are considered, at least one electropositive and one electronegative site is found on each molecule (in the case a molecule contains one single site, no electrostatic sign is given to the site, and it can associate with any other). Two parameters describes each pair of sites (they have a double superscript, *AB*): one energy parameter and one volume parameter. The *energy parameter* is expressed in an identical fashion for all equations considered. The *association volume* is a proportion of the average segment volumes of the two associating molecules. This is why a double index is required for *d* in the case of SAFT, and for *b* in the case of CPA. These parameters are determined for self-associating molecules, and as a result they are considered as molecular parameters. When considering cross-association, as in the case of methanol and water, a combination rule is required. It is given in the next section.

Each polar interaction comes with one additional pure component parameter. To our knowledge, the use of these additional terms has only been applied to SAFT-type equations.

### 2.3 Extension to Mixtures

The usual approach for mixture is the so-called “one-fluid” approach that states that the equation of state for a mixture

has exactly the same shape as that for a pure component. The mixture composition then appears in the mixing rules applied to the pure component parameters. This can also be applied to the SAFT equations, except for SAFT-VR. In Table 3, the mixing rules for a number of parameters are shown.

Note that in the combination rules, an adjustable *k<sub>ij</sub>* parameter is employed for the energy parameter ( $\epsilon$  or *a*), but not for the size parameter ( $\sigma$  or *b*).

The one-fluid mixing rule can be used in SAFT-VR also, but in this work, we use the MX3B mixing rule (Galindo *et al.*, 1998), which introduces the mixture explicitly in the SAFT-VR equation. However, cross-parameters (double index) are defined in a similar way as for SAFT-0 and PC-SAFT. The same is true for the association term and the terms describing the polar contributions. Combination rules for the association parameters are needed when two associating species are considered in the same mixture. These are different for SAFT and CPA. None of the combination rules considered here use a binary interaction parameter.

For SAFT, we take:

$$\kappa_{ij}^{AB} = \left( \frac{(\kappa_{ii}^{AB})^{1/3} + (\kappa_{jj}^{AB})^{1/3}}{2} \right)^3$$

and

$$\epsilon_{ij}^{AB} = \sqrt{\epsilon_{ii}^{AB} \epsilon_{jj}^{AB}}$$

TABLE 3  
Mixing rules for the one-fluid approach

Parameter	mixing rules		Combination rules (cross parameters)
	SAFT-0 & PC-SAFT	CPA	
<i>m</i>	$m_x = \sum_{i=1}^n x_i m_i$	–	–
$\epsilon$ or <i>a</i>	$\epsilon_x \sigma_x^3 = \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j m_i m_j \epsilon_{ij} \sigma_{ij}^3}{\left( \sum_{i=1}^n x_i m_i \right)^2}$	$a = \sum_i \sum_j x_i x_j a_{ij}$	$\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} (1 - k_{ij})$ $a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$
$\sigma$ or <i>b</i>	$\sigma_x^3 = \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j m_i m_j \sigma_{ij}^3}{\left( \sum_{i=1}^n x_i m_i \right)^2}$	$b = \sum_i \sum_j x_i x_j b_{ij}$	$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ $b_{ij} = (b_i + b_j)/2$
$\lambda$	–	–	$\lambda_{ij} = \frac{\lambda_{ii} \sigma_{ii} + \lambda_{jj} \sigma_{jj}}{\sigma_{ii} + \sigma_{jj}}$

For CPA, several mixing rules (Derawi, 2002) can be used. Some of them are applied on the cross energy and volume association ( $\epsilon$  and  $\beta$ ) and others are directly applied to the cross association strength ( $\Delta$ ) as proposed by Suresh and Elliot (1991). In this work, we have used the following mixing rules:

$$\beta_{ij} = \sqrt{\beta_{ii}\beta_{jj}} \quad \text{and} \quad \epsilon = \frac{\epsilon_{ii} + \epsilon_{jj}}{2}$$

### 3 APPLICATIONS

The applications of this type of equation in the petroleum industry are potentially numerous. Depending on the type of application, different features may be of interest. We will discuss some of these applications in some more detail:

- for mixtures containing small associating molecules such as water and alcohols, the association term makes a significant difference, even combined with a simple cubic equation. This will be discussed below;
- when considering long chain molecules (polymers, long chain esters, heavy oils, paraffinic mixtures as in the case of Fischer-Tropsch synthesis), the SAFT approach allows the use of group contribution methods for the calculation of pure component parameters (Tamouza *et al.*, 2004). As we will see, it is even possible to differentiate between isomers, which is usually one of the limitations of group contribution methods;
- the possibility to add terms that represent specific polar interactions opens up the possibility to use the SAFT EOS in a predictive manner for a number of applications that previously required a large amount of data in order to fit empirical parameters ( $k_{ij}$ ). We will illustrate this by two examples. In the first example, two isomers are differentiated by a dipolar contribution. In the second example, the use of a quadrupolar term is shown to be sufficient to describe non-idealities in mixtures containing aromatic molecules;
- obviously, when the above difficulties are combined, the new type of equations is expected to provide a significant improvement with respect to the classical methods.

Beyond this list that describes the applications where it seems to us that the statistical mechanic EOS bring a significant improvement, the SAFT equation has also been used on more exotic cases such as asphaltene precipitation (Ting *et al.*, 2003) or hydrogen solubility (Florusse *et al.*, 2003; Gosh *et al.*, 2003).

#### 3.1 Phase Equilibria of Water and Alcohol-Containing Mixtures

Small molecules such as water and methanol have a strong hydrogen bonding faculty. As a result, they exhibit a strongly

non-ideal behaviour. Three types of phase behaviour can be found:

- the binary systems which have a type I phase behaviour do not show liquid-liquid equilibria. Examples are binary hydrocarbon systems containing methane ;
- those of type II are those where liquid-liquid equilibria do exist, but are unconnected to the liquid-vapour equilibria. An example is the propane-methanol system;
- finally, the type III such as the ethane-methanol binary and almost all water-hydrocarbon systems give a liquid-liquid-vapour equilibrium.

Each of these systems will be investigated in turn, and the use of the CPA equation will be illustrated. In all cases, methanol is considered as a component with two association sites (Voutsas *et al.*, 1997) and it is described with a 2B model. Water is considered as a 4C associating component. The pure component parameters are taken from Kontogeorgis *et al.* (1999) and are reported in Table 4. The parameters of the non-associating components are calculated using the critical constraints (Soave, 1972). Their critical parameters are provided in Table 5.

##### 3.1.1 Binary Systems Containing Methanol and a Light Hydrocarbon

We present here two binary systems, ethane-methanol and pentane-methanol. We choose them because they summarise the principal difficulties that may be found in fluid phase equilibrium modelling, *i.e.* phenomena such as liquid- liquid-vapour equilibrium, azeotropic point and critical point of liquid- liquid equilibrium.

###### *Methanol-ethane system*

The investigation of the ethane-methanol system permits us to emphasise the contribution of the association term by comparing the results of the CPA and the SRK equations of state without binary interaction parameter. Figure 7 shows the phase diagram of the binary system at 298.15 K. Although SRK correctly shows a liquid - liquid phase equilibrium split, the three - phase pressure and the composition of the liquid phases are underestimated. On the contrary, CPA yields good results particularly with regard to the three phase liquid- liquid-vapour condition. Comparing the CPA results with the experimental data provided, we observe a good modelling of the VLE especially in vicinity of the liquid- liquid- vapour equilibrium. The comparative performance between CPA and SRK, based on the experimental results of Ishihara *et al.* (1998) at the three phase equilibrium is summarised in Table 6.

Table 7 provides some information concerning the average relative deviation between the two equations and the experimental data. This additional piece of information will help evaluating the capacity of these equations using other binary systems. The compositions of the alcohol and of the organic liquid phases are differentiated using respectively  $x$

TABLE 4  
CPA parameters for the associating components (from Derawi, 2002)

	$a_0$ (Pa.m <sup>3</sup> /mol)	$c_1$	$b$ ( $\times 10^5$ ) (m <sup>3</sup> /mol)	$\varepsilon^{OH/R}$ (Pa.m <sup>3</sup> /mol)	$\beta^{OH}$
Methanol	0.40521	0.431	3.0978	2957	0.0161
Water	0.12274	0.67359	1.4515	2002.73	0.0692

TABLE 5  
Critical parameters for the hydrocarbons

	$T_C$ (K)	$P_C$ (MPa)	$\omega$
Methane	190.55	4.6	0.0111
Ethane	305.43	4.884	0.097
Propane	369.82	4.25	0.1536
<i>n</i> -butane	425.13	3.8	0.2008
<i>n</i> -pentane	469.65	3.369	0.2506

TABLE 6  
Three phase equilibrium pressure and composition for the ethane - methanol mixture at 298.15K experimental and predicted

	$P$ (MPa)	$x$ (ethane)	$x'$ (ethane)	$y$ (ethane)
Ishihara <i>et al.</i> (1998)	4.091	0.40	0.962	0.9950
CPA	4.223	0.39	0.9768	0.9936
SRK	3.525	0.30	0.8205	0.9902

TABLE 7  
Correlation performance of the CPA and SRK EOS for the ethane (1) methanol (2) system: analysis in terms of the average relative deviation (%).

	$\Delta P/P$	$\Delta x/x_1$	$\Delta x/x_2$	$\Delta x'/x_1$	$\Delta x'/x_2$	$\Delta y/y_1$	$\Delta y/y_2$
CPA	-3.13	2.56	1.64	-1.52	-63.79	0.14	21.87
SRK	16.06	33.33	1.43	17.25	78.83	0.48	48.98

and  $x'$ , and ethane is component 1. We can see that a weak deviation as shown in Figure 7 can yield an important relative deviation. When we compare both equations of state, the deviations obtained for each confirm the important contribution of the association term. The use of this term improves significantly the phase equilibrium calculation.

#### Methanol-pentane system

The experimental data available for the binary pentane-methanol system allows us to study simultaneously liquid-vapour and liquid-liquid equilibrium at atmospheric pressure. In Figure 8 the predictions for both equilibrium lenses by CPA is compared with experimental data of Bernabe *et al.* (1988) for the liquid-liquid equilibrium and Budantseva *et al.* (1975) for the vapour-liquid equilibrium. CPA has been used with no binary interaction parameter. This binary system confirms the observations made previously, namely that the association term improves the modelling of the methanol-hydrocarbon system. We can predict correctly liquid- vapour

equilibrium as well as liquid-liquid equilibrium. The azeotropic point and the upper critical end point (UCEP) are reproduced with errors on the pentane composition of between 3% and 9%.

Although a zero binary interaction parameter provides reasonable results, it appears that a small non-zero value may improve significantly the liquid-liquid equilibrium predictions. Table 8 shows the average relative deviations on the mole fraction of each component in each phase and on the equilibrium pressure, with and without  $k_{ij}$ . No real trend can be observed in the value of this parameter with molecular weight of the hydrocarbon.

In Table 8, number 1 refers to the hydrocarbon and  $x$  and  $x'$  are respectively the alcohol and organic phase composition. If we compare with the deviations shown in Table 7, we notice that the CPA model can provide reasonable results despite the important deviations. Generally speaking, with a binary interaction parameter, CPA provides better results for

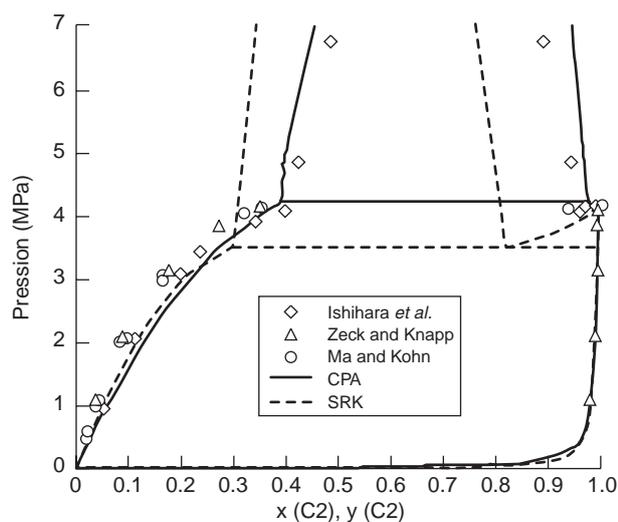


Figure 7  
Comparison of the SRK and CPA performance compared to the literature data for the ethane-methanol system at 298.15 K.

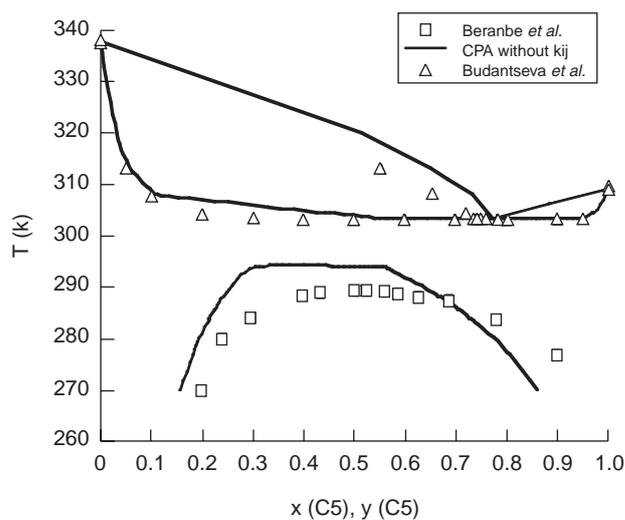


Figure 8  
Phase diagram of pentane-methanol system at the atmospheric pressure. The points represent data; the line is the prediction from CPA ( $k_{ij}=0$ ).

TABLE 8  
Correlation performance of the CPA model (deviations in %)

Vapour-Liquid-Equilibrium ( <i>1 is the hydrocarbon</i> )										
Systems	T range (K)	NP	CPA without $k_{ij}$			CPA with $k_{ij}$ from Table 9				
			$\Delta P/P$	$\Delta y/y_1$	$\Delta y/y_2$	$\Delta P/P$	$\Delta y/y_1$	$\Delta y/y_2$		
C <sub>1</sub> - methanol	220-340	56	-11.8	0.1	9.3	-6.5	0.19	0.19		
C <sub>2</sub> - methanol	298-323	30	-17.0	-1.7	-14.9	-19.4	-1.3	-1.3		
C <sub>3</sub> - methanol	213-474	46	-11.3	-7.9	-1.69	-14.3	-9.6	-9.0		
nC <sub>4</sub> - methanol	273-373	33	-4.1	0.7	-9.2	-2.9	0.3	0.3		
nC <sub>5</sub> - methanol	303-422	90	-4.5	2.7	2.6	-8.7	0.7	0.7		
Liquid-Liquid-Equilibrium										
Systems	T range (K)	NP	CPA without $k_{ij}$				CPA with $k_{ij}$ from Table 9			
			$\Delta x/x_1$	$\Delta x/x_2$	$\Delta x'/x_1$	$\Delta x'/x_2$	$\Delta x/x_1$	$\Delta x/x_2$	$\Delta x'/x_1$	$\Delta x'/x_2$
C <sub>2</sub> - methanol	233-300	10	17.1	10.1	-3.6	-49.8	-6.6	-4.8	-4.5	-62.7
C <sub>3</sub> - methanol	323-250	10	52.3	36.2	2.8	32.4	-40.1	-28.7	-10.7	-72.6
nC <sub>4</sub> - methanol	263-272	31	23.8	22.1	8.9	39.8	1.8	10.0	-16.9	22.9
nC <sub>5</sub> - methanol	269-277	15	-6.8	-18.0	-6.3	-4.3	-5.0	9.8	6.5	6.4

all systems and it remains difficult to calculate the composition of the minority component in each phase. Although we use  $k_{ij}$  fitted on liquid-liquid equilibrium data, the results are also improved for vapour-liquid equilibrium.

For each binary system, the vapour-liquid and liquid-liquid equilibrium have been calculated with the same binary interaction parameter ( $k_{ij}$ ). These parameters have been fitted only on liquid-liquid equilibrium data by minimising the following objective function:

$$OF = \sum_{n=1}^{NP} \left( \sum_{i=1}^2 \left( \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{x_i^{\text{exp}}} \right)^2 + \left( \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{x_i^{\text{exp}}} \right)^2 \right)$$

where  $x_1$  is the mole fraction of methanol and  $x_2$  that of the hydrocarbon.

TABLE 9  
Alcohol- hydrocarbon binary parameters used,  
with  $k_{ij} = k_{ij}^{(1)} \cdot T + k_{ij}^{(2)}$

Binaries systems methanol +	$k_{ij}^{(1)}$	$k_{ij}^{(2)}$
Methane	0.00	1.00E-02
Ethane	-2.77E-04	8.31E-02
Propane	-2.86E-04	8.03E-02
<i>n</i> -butane	-1.36E-05	8.71E-03
<i>n</i> -pentane	-1.52E-05	5.73E-03

The vapour-liquid equilibrium is almost insensitive to the value of the  $k_{ij}$ , while a small  $k_{ij}$  may significantly affect the

liquid-liquid equilibrium calculation. We observe that the best results are obtained with a temperature-dependent  $k_{ij}$ . The parameters are listed on Table 9, when the  $k_{ij}$  is obtained from the linear equation:

$$k_{ij} = k_{ij}^{(1)} \cdot T + k_{ij}^{(2)}$$

### 3.1.2 Binary water - light hydrocarbon systems

Water-hydrocarbon mixtures are frequently encountered in the petroleum industry. Due to the strong polarity of water, the mutual solubilities are very small. This is the reason why the relative uncertainties on the experimental data are significant and large scatter is observed.

Several authors have attempted to model these systems (Soreide and Whitson, 1992; Dhima, 1998; Daridon *et al.*, 1993) but all came to the conclusion that a different model (or different parameters) is required for a correct description of the solubilities.

Figures 9 to 12 show how the CPA model is able to predict the hydrocarbon solubility in water. The figures show both the predictions in the absence of a  $k_{ij}$ , and with a  $k_{ij}$  that has been fitted on the data. The optimal  $k_{ij}$  parameters are generally temperature-dependent.

The pressure and temperature range of the water-hydrocarbon experimental data are summarised in Table 10. The values of the binary parameters in function of temperature are provided in Table 11.

The water- methanol mixture has similarly been tested, and a single binary interaction parameter of -0.03 has been found to best reproduce the data.

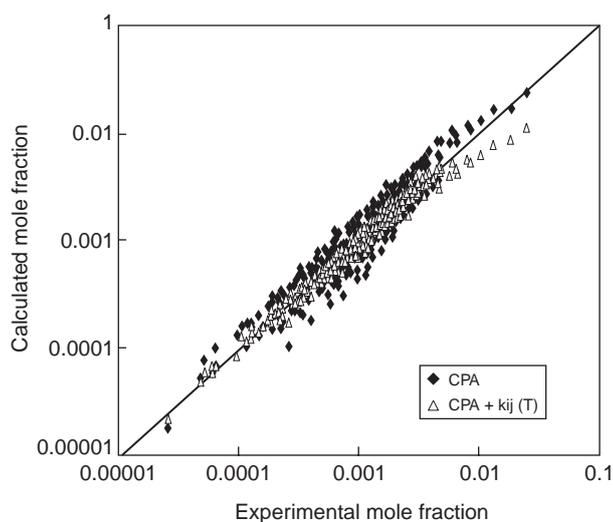


Figure 9  
Experimental vs calculated methane solubility in water.

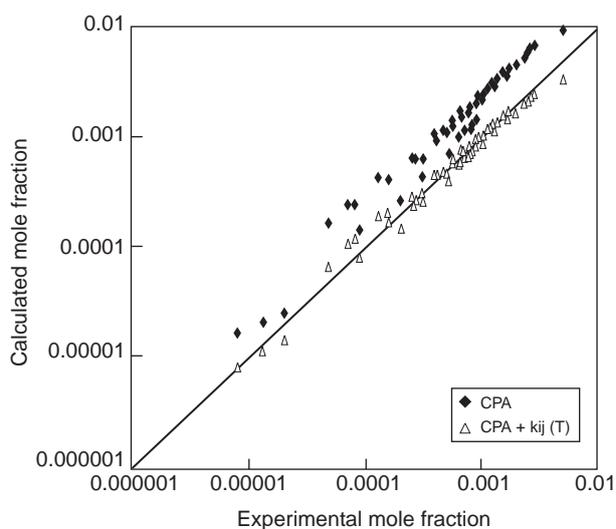


Figure 10  
Experimental vs calculated ethane solubility in water.

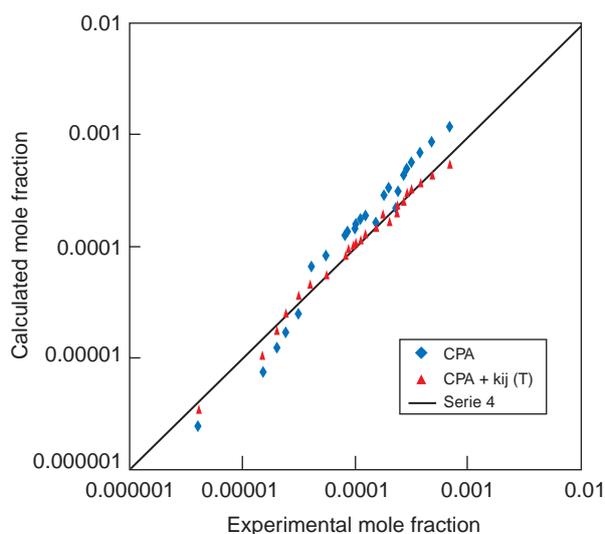


Figure 11  
Experimental vs calculated propane solubility in water.

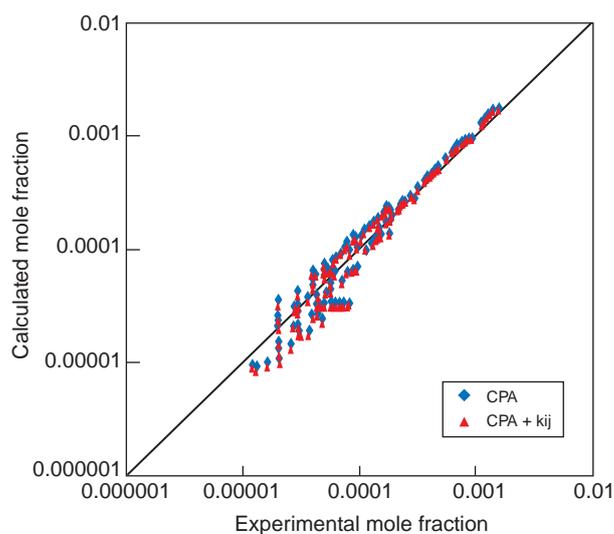


Figure 12  
Experimental vs calculated n-Butane solubility in water.

### 3.1.3 Multicomponent Systems Hydrocarbons-Methanol and Water

In conclusion of our CPA study, we examine a quaternary system containing methane, propane, water and methanol. A study of this system has been published by Rossilhol (1995). The purpose is here to test the predictive capacities of CPA for multicomponent mixtures when we use the defined binary parameters.

TABLE 10  
The data sets used to evaluate CPA

Binary	T(K)	P(MPa)	Points number
Water - methane	283.15-573.15	0.097-75	448
Water - ethane	298.15-510.93	0.06-50	115
Water - propane	273.15-422	0.01-19.32	46
Water - <i>n</i> -butane	298.15-477.59	0.1-48.26	230

TABLE 11  
Water - hydrocarbon binary parameters used,  
with  $k_{ij} = k_{ij}^{(1)}.T + k_{ij}^{(2)}$

Binaries systems water +	$k_{ij}^{(1)}$	$k_{ij}^{(2)}$
Methane	1.76E-03	-0.539
Ethane	9.22E-04	-0.230
Propane	7.65E-04	-0.229
<i>n</i> -butane	0	0.0057

Tables 12 and 13 show both the CPA calculation results and the experimental values for the three phase VLE of a four component mixture at 6.7 MPa, for two temperatures (253.15 K and 263.15 K). CPA correctly predicts a three phase equilibrium. The mole fraction prediction of the minority components (the hydrocarbons) in the aqueous phase, where the association phenomena are most important, is very accurate. The vapour phase also is accurately reproduced. In the organic phase, CPA reproduces well the molar fraction of the majority components, but there are significant deviations from experiment concerning methanol and water. Nevertheless, we notice that the order of magnitude is correct. The results on this quaternary system show that CPA is able to model in a very satisfactory way the complex systems containing hydrocarbons and associating components. We can notice that these good results are obtained with the same equation of state for each phase and that the same binary parameters are used for each compound. To perform the same kind of results with classical EOS, we would need to use more complicated mixing rules such as Huron-Vidal or MHV2.

### 3.2 Vapour Pressure of Heavy Molecules

In this second section, we illustrate the use of the SAFT equation of state coupled with a group contribution method.

Heavy hydrocarbon molecules are often present in petroleum fluids, and their properties must also be adequately described. When cubic equations are used, their properties are predicted through a double assumption. First, the cubic equation parameters are calculated using the corresponding

TABLE 12  
Three phase equilibrium for quaternary systems at 253.15 K and 6.7 MPA

Component	Feed	Experimental data			CPA predictions		
		Aqueous phase	Organic liquid phase	Vapour phase	Aqueous phase	Organic liquid phase	Vapour phase
Methanol	0.153	0.536	0.0007		0.528	0.00165	0.000219
Water	0.128	0.447			0.444	0.000039	0.000017
Methane	0.532	0.0105	0.540	0.874	0.0201	0.522	0.908
Propane	0.187	0.0071	0.459	0.126	0.0078	0.477	0.092
Mole fractions	1	0.286	0.286	0.429	0.288	0.310	0.401

TABLE 13  
Three phase equilibrium for quaternary systems at 263.15 K and 6.7 MPA

Component	Feed	Experimental data			CPA predictions		
		Aqueous phase	Organic liquid phase	Vapour phase	Aqueous phase	Organic liquid phase	Vapour phase
Methanol	0.156	0.545	0.001		0.539	0.0030	0.00042
Water	0.124	0.435			0.432	0.000081	0.000034
Methane	0.520	0.0105	0.516	0.861	0.0190	0.474	0.880
Propane	0.200	0.0098	0.483	0.139	0.0095	0.523	0.119
Mole fractions	1	0.28557	0.286	0.429	0.287	0.279	0.434

states principle. Here, it is assumed that if the critical point is correctly represented, all properties, including at very low reduced temperatures, are correctly represented. The second assumption lies in the prediction method of these critical properties that is impossible to verify with physical experiments, since the molecules are unstable at high temperature. Many methods exist, but their extrapolations to very long chains differ significantly. Probably the best of them is based on theoretical concepts that provide a limit for these properties for infinite chain length (Elliott *et al.*, 1990).

The industrial need, however, concerns a moderate temperature range, that usually corresponds to very low reduced temperatures, and very low vapour pressures. Some data exist, which will allow us to validate the proposed method, but much more data would be necessary considering the number of isomers and the large experimental errors that are observed in these extremely low pressure ranges. Hence, there is a need for predictive calculation methods.

In their work, Tamouza *et al.* (2004) propose a group contribution method for calculating SAFT pure component parameters. It is believed that because the SAFT equation is based on physical concepts, the use of group contributions for determining its parameters is justified. However, they remain adjustable parameters, and the use of experimental data is needed for regressing the group parameters.

The three SAFT parameters are then calculated as follows (four parameters if we include  $\lambda$  for SAFT -VR):

$$\varepsilon_{\text{molécule}} = \sum_{i=1}^{n_{\text{groupes}}} n_i \sqrt{\left( \prod_{i=1}^{n_{\text{groupes}}} \varepsilon_i^{n_i} \right)}$$

$$\sigma_{\text{molécule}} = \frac{\sum_{i=1}^{n_{\text{groupes}}} n_i \sigma_i}{\sum_{i=1}^{n_{\text{groupes}}} n_i}$$

$$\lambda_{\text{molécule}} = \frac{\sum_{i=1}^{n_{\text{groupes}}} n_i \lambda_i}{\sum_{i=1}^{n_{\text{groupes}}} n_i}$$

$$m_{\text{molécule}} = \sum_{i=1}^{n_{\text{groupes}}} n_i R_i$$

where  $n_i$ , is the number of groups of type  $i$  in the molecule. Figure 13 shows an example of how a molecule is split into groups.

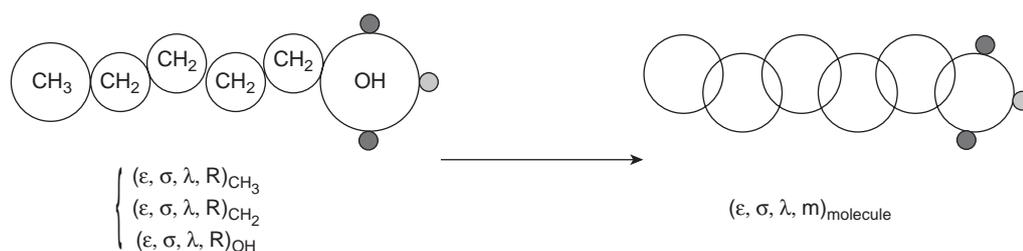


Figure 13

Group contribution and SAFT models for 1-pentanol, with three associating sites.

 TABLE 14  
 Group contribution parameters for SAFT-0, SAFT-VR and PC-SAFT EOS

Equation	Group	$\varepsilon/k \cdot K$	$\sigma \cdot \text{Å}$	$\lambda$	R	$\varepsilon^{AB}/k \cdot K^{(1)}$	$k^{AB(1)}$
SAFT-0	-CH <sub>2</sub> -	208.1	3.42		0.51	2212.0	0.01382
	-CH <sub>3</sub>	167.9	3.51		0.86		
	-OH	279.9	2.87		0.93		
	(C) <sub>α-oléf.</sub>	186.6	3.41		0.64		
	(C) <sub>Bz</sub>	243.5	3.45		0.42		
	(C) <sub>Ch</sub>	239.9	3.69		0.41		
SAFT-VR	-CH <sub>2</sub> -	136.4	3.42	1.90	0.47	2170.0	0.01122
	-CH <sub>3</sub>	202.9	3.54	1.47	0.80		
	-OH	328.2	2.97	1.55	0.82		
	(C) <sub>α-oléf.</sub>	280.7	3.95	1.47	0.41		
	(C) <sub>Bz</sub>	165.6	3.43	1.88	0.39		
	(C) <sub>Ch</sub>	233.2	3.96	1.70	0.30		
PC-SAFT	-CH <sub>2</sub> -	261.1	3.93		0.38	2281.6	0.00554
	-CH <sub>3</sub>	190.0	3.49		0.79		
	-OH	391.8	3.15		0.67		
	(C) <sub>α-oléf.</sub>	226.1	3.63		0.54		
	(C) <sub>Bz</sub>	306.7	3.83		0.32		
	(C) <sub>Ch</sub>	305.3	4.09		0.31		

(1) Here, the association is considered with a three sites (3B) model.

The parameters that have been proposed for the equations SAFT-0 and SAFT-VR (Tamouza *et al.*, 2004) have been extended here with those more recently determined for PC-SAFT and they are reported in Table 14.

In Tables 15 and 16, and Figures 14 and 15, the method is used in a predictive mode, *i.e.* no additional regression was performed. The vapour pressures and liquid molar volumes results are shown for several n-alkanes, n-alkanols, an olefin and a heavy alkyl-benzene. None of these compounds belong to the fitting data bank. It can be seen that the deviations between calculations and experimental data increase with chain length. Not surprisingly, the vapour pressure data are the most difficult to predict. Despite this, the VR-SAFT method is clearly superior, probably because of the additional parameter. The results are impressively accurate as the average deviation remains below 15%, which is of the same order of magnitude as the experimental uncertainties. The molar

volumes are predicted with a deviation of less than 5%. The results are compared with another group contribution method, reported by Mattedi *et al.* (1998). Note that no polar term was used in the predictions reported here.

More recently Tamouza *et al.* (2005) have adapted their approach by including methyl-alkanes in their group contribution method. Here, the branched methyl group is considered as an additional group that has the same contribution to the  $\sigma$  and  $\varepsilon/k$  parameters, but that is differentiated from the regular -CH<sub>3</sub> group in its R parameter. The reason for this choice is that it may be considered that the contribution of a branched methyl group does not change the global alkane energy contribution, nor the segment size, but that the chain length is now no longer linear with the number of carbon atoms. Depending on whether the branched methyl group is at position 2, 3 or beyond, the contribution is found to change according to the Table 17, and the graph shown in Figure 16.

TABLE 15

Deviation of the predictions of vapor pressure using different group contribution methods

Component	T (K)	Npt.	SAFT method			Mattedi <i>et al.</i> (1998)
			SAFT-0	SAFT-VR	PC-SAFT	
<i>n</i> -hexadecane	291 – 721	30	7.38	4.46	5.54	2.87
	391 – 581	20	6.83	5.02		
<i>n</i> -docosane	317 – 782	32	16.19	6.12	13.05	9.16
	452 – 572	13	13.16	2.91		
<i>n</i> -tetracosane	324 – 804	33	20.09	8.13	15.97	11.73
	453 – 589	15	13.23	5.58		
<i>n</i> -pentacosane	327 – 804	33	20.72	7.62	16.83	18.49
<i>n</i> -octacosane	334 – 829	34	23.04	7.06	19.30	
	484 – 590	12	20.30	3.97		
<i>n</i> -dotriacontane	342 – 852	35	30.64	12.10	25.84	
1-dodécanol	298 – 619	26	4.86	7.67	6.64	
1-octadécanol	365 – 760	17	11.33	4.84	10.92	
<i>n</i> -octadécyl-benzène <sup>(1)</sup>	484 – 834	9	23.41	7.38	17.17	
1-octadécène	375 – 703	24	6.76	6.93	5.68	

TABLE 16

Deviation of the predictions of liquid molar volumes using different group contribution methods

Component	T (K)	Npt.	SAFT method		
			SAFT-0	SAFT-VR	PC-SAFT
<i>n</i> -hexadecane	291 – 721	30	3.93	3.97	1.78
<i>n</i> -docosane	317 – 782	32	4.39	5.10	1.78
<i>n</i> -tetracosane	324 – 804	33	4.15	4.82	3.26
<i>n</i> -pentacosane	327 – 807	33	4.28	5.25	2.29
<i>n</i> -octacosane	334 – 829	34	4.53	5.66	2.50
<i>n</i> -dotriacontane	342 – 852	35	3.73	4.89	3.83
1-dodécanol	298 – 573	20	3.07	6.92	0.12
1-octadécanol	333 – 573	13	2.67	3.02	1.16
<i>n</i> -octadécyl-benzène(1)	313 – 513	7	3.16	3.31	1.58
1-octadécène	291 – 393	13	5.15	3.65	1.65

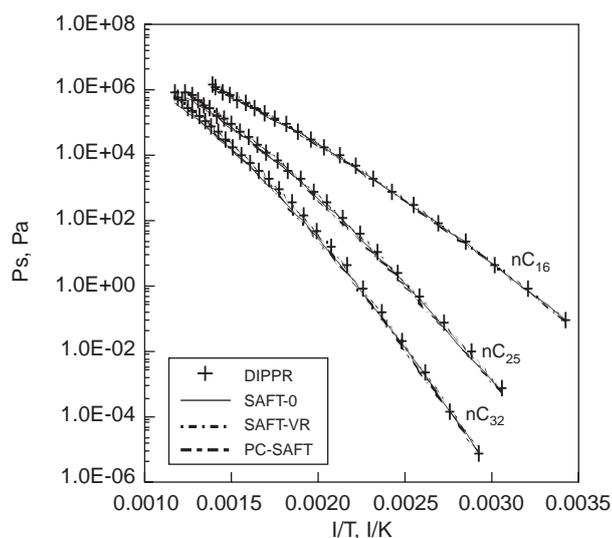


Figure 14

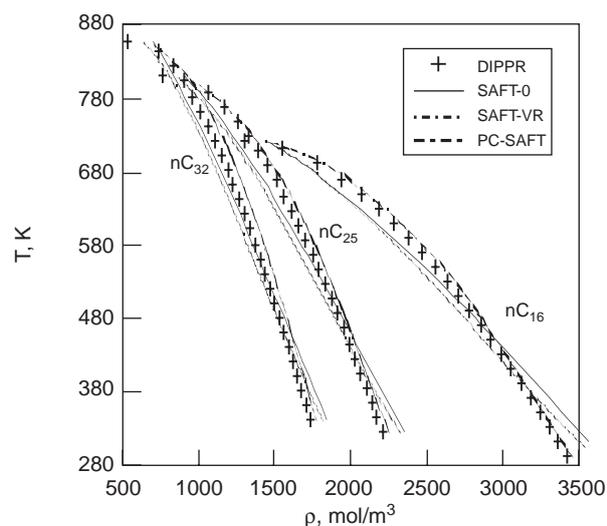
Prediction of vapor pressures for several *n*-alkanes.

Figure 15

Prediction of liquid molar volumes for several *n*-alkanes.

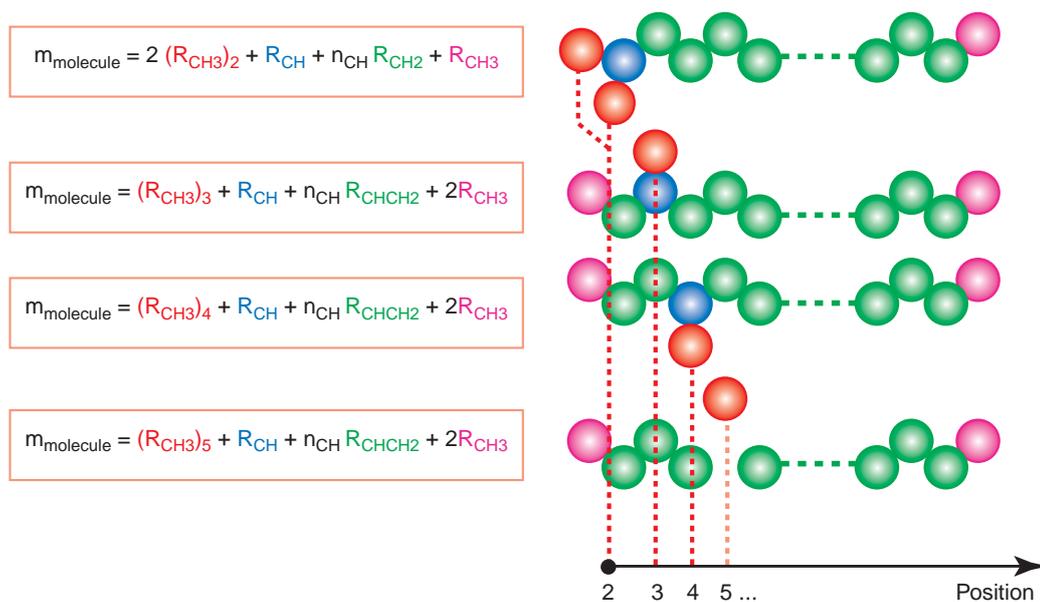


Figure16

Sketch of branched molecules, and the calculation method of the  $m$  parameter. Note that all other parameters remain identical whatever the position of the branched group.

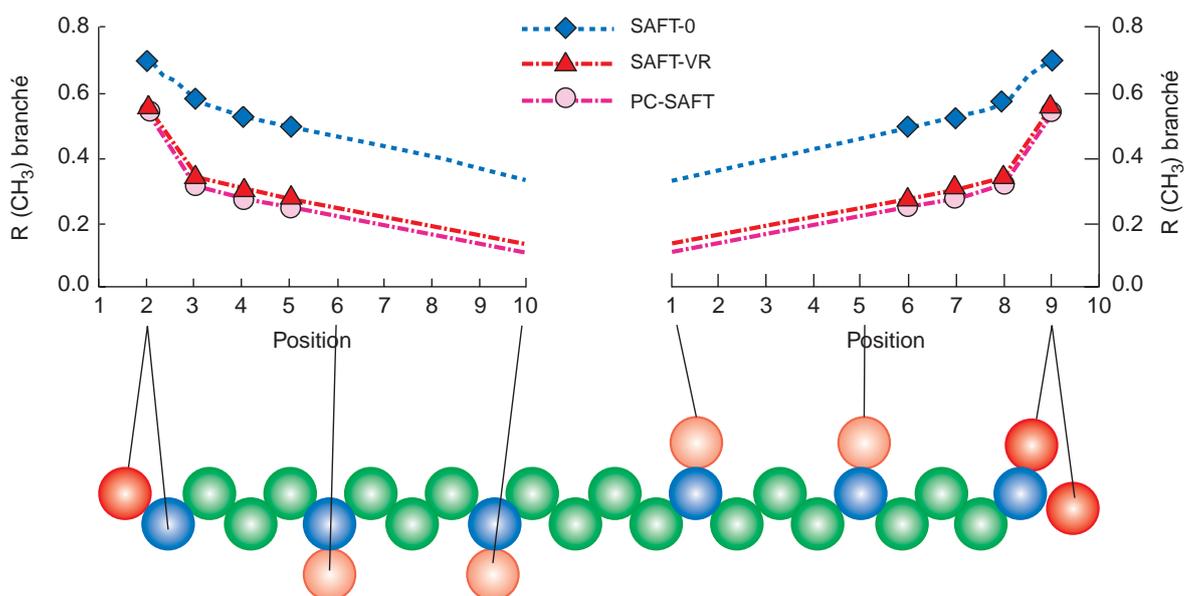


Figure 17

Extrapolation of the contribution of the branched group to the  $m$  parameter.

TABLE 17  
Contribution to the  $m$  parameter of a branched group

Position of the branched methyl	R <sub>i</sub> (SAFT-0)	R <sub>i</sub> (SAFT-VR)	R <sub>i</sub> (PC-SAFT)
2	0.71	0.55	0.55
3	0.58	0.33	0.34
4	0.53	0.28	0.30
5	0.50	0.25	0.27

In order to extend the method to long chain molecules, a linear extrapolation was found to perform best (Fig. 17):

$$R_i = -0.033 p_i + 0.662 \quad \text{for the SAFT-0 equation, and}$$

$$R_i = -0.028 p_i + 0.392 \quad \text{for the SAFT-VR equation, and}$$

$$R_i = -0.029 p_i + 0.418 \quad \text{for the PC-SAFT equation}$$

Where  $p_i$  is the position of the branched methyl group in the molecule.

By doing so, it is now possible to predict the properties of long chain isoalkanes. As an example, the vapour pressure of squalane (2-6-10-15-19-23 hexamethyl tetracosane) is predicted with an average error of 30% for SAFT-0 and 10% for SAFT-VR, while the liquid molar volume is predicted with both equations with a 10% error. Note that the experimental uncertainty on the vapour pressure of squalane is of the order of 20%.

### 3.3 Non Ideality in Hydrocarbon Mixtures Due to Polar Interactions

#### 3.3.1 Quadrupole-Quadrupole Interaction Term

One important goal in the refining industry is to eliminate traces of selected components in a petroleum product. A

distillation is performed on the feed, and at some position on the distillation column, where the concentration of the trace element is highest, a side stream is removed and injected in a reactor where this component is converted. The location of the side stream is computed within the column, and is very sensitive to the thermodynamic model used. The volatility of this component at very low dilution in a stream of varying composition must be correctly modelled.

In order to tune the model (usually a cubic equation) for this purpose, all binary mixtures containing the trace component are investigated within the temperature range of the column, and a binary interaction parameter is fitted to each of these mixtures. Note that, even if all these data existed, they most often deal with medium dilution. The fit may thus be mathematically adequate in the medium dilution range, but is not necessarily correct in the high dilution range.

Let us take the example of a process where benzene must be extracted from a gasoline feed. Two azeotropic binaries exist (benzene - 2,4 dimethyl pentane, and benzene - *n*-hexane). No liquid - vapour equilibrium data exist for the benzene - dimethylpentane binary. The only solution for the process engineer is therefore to use a zero binary interaction parameter. It is therefore almost impossible to determine the optimum binary interaction parameter for this set of components.

For the benzene - *n*-hexane binary mixture, where data exist, it is possible to determine parameters, but it is also possible to evaluate the risk of using no binary parameter. Figure 18 shows the result of both a PC-SAFT and a SAFT-VR equation that incorporates a quadrupole-quadrupole interaction term. It is evident that the use of an interaction parameter is the best solution, but in the absence of any information, the use of a predictive equation such as the PC-SAFT

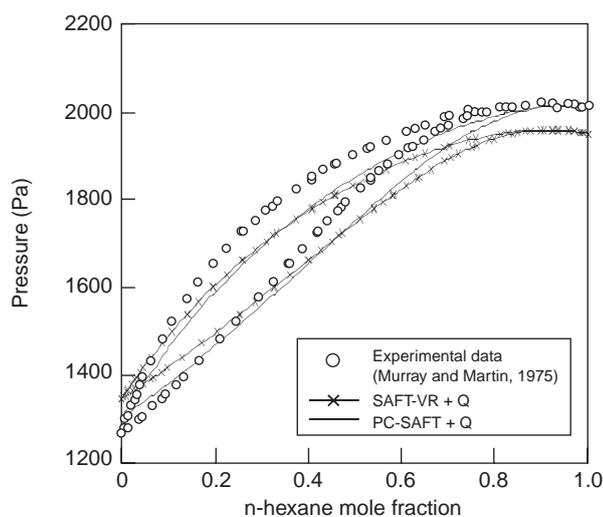


Figure 18

*n*-hexane – benzene binary mixture at 298.15 K

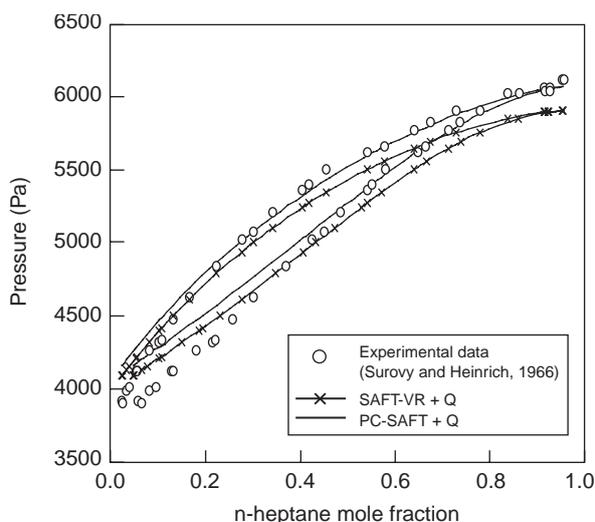


Figure 19

*n*-heptane – toluene binary mixture at 298.15 K

TABLE 18  
Parameters for the aromatic component, including a quadrupole-quadrupole interaction term

Equation	Group	$\epsilon/k$ (K)	$\sigma$ (Å°)	$\lambda$	R	Q (B)
SAFT-VR	(C) <sub>Bz</sub>	72.9	3.0833	2.4925	0.1689	9.36
	(CH) <sub>Bz</sub>	252.0	3.6569	1.6164	0.3799	
PC-SAFT	(C) <sub>Bz</sub>	400.0	4.2637		0.0000	9.16
	(CH) <sub>Bz</sub>	287.3	3.7056		0.3916	

TABLE 19  
Parameters for the aromatic component, including a dipole-dipole interaction term.

Equation	Group	$\epsilon/k$ (K)	$\sigma$ (Å°)	$\lambda$	R2	R3
SAFT-VR	(CH=) <sub>olef</sub>	172.3	3.4779	1.8250	0.3633	0.3432
PC-SAFT	(CH=) <sub>olef</sub>	287.4	3.8614		0.3134	0.2966

is the best choice. The same conclusion can be drawn for the *n*-heptane – toluene system, illustrated in Figure 19.

In these calculations, the alkane is described using the group contribution presented in the previous section. The parameters of the aromatic molecule have been regressed again, this time including a quadrupole term. The parameters are shown in Table 18. Note the unit of the quadrupole moment Buckingham, ( $1B = 3.3357 \cdot 10^{-40} C \cdot m^2$ ).

### 3.3.2 Dipole-Dipole Term

Even though dipolar molecules are less abundant in the petrochemical industry, the same improvements as mentioned above for quadrupoles can be found for dipolar molecules. Below, we illustrate the case where we now can differentiate between the *cis*- and *trans*- isomers of 2-butene. To date, no real differentiation had been possible. However, it is known from experimental data that *cis*-2butene has a dipole moment, while *trans*-2 butene has none. Figure 20 illustrates the results of the prediction of various versions of the SAFT EOS, including a dipole term, on the bubble curve of the binary mixture of butane with *cis*-2butene. *Trans*-2butene has no dipole moment, hence, no difference is observed between the two approaches. In Figure 20, the pressure scale is strongly enlarged in order to visualise the trends.

In these calculations, the alkane is described using the group contribution presented in the previous section. The parameters of the olefinic molecule have been regressed again, this time including a dipole term. The dipole moment used is given in Fig. 20. The other parameters are shown in Table 19. The dipole that is found here (1.55 D) is approximately three times larger than the experimental value (0.5D). It has been shown (Tamouza, 2004) that below a dipole moment of 1 Debye, the equation is insensitive to its presence. If the approach is truly promising, the equation remains an approximation and its parameters can therefore not be considered as experimental values.

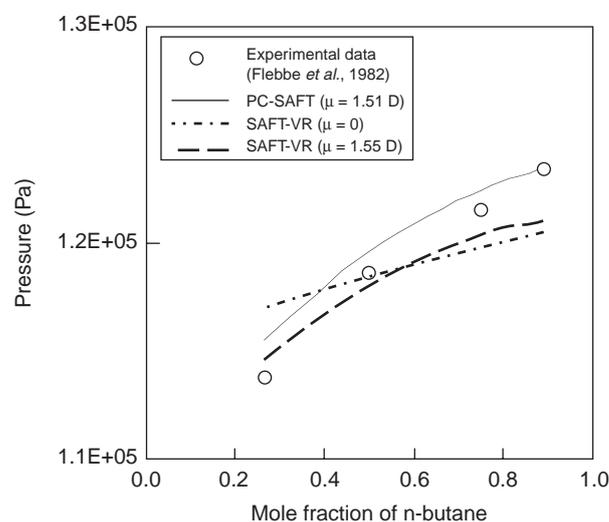


Figure 20  
Prediction of the bubble curve of the *cis*-2butene – *n*-butane binary mixtures at 278.15 K.

## CONCLUSIONS

This paper investigates a number of potential applications for the new generation equations of state that are developed using the statistical thermodynamic perturbation theory approach. It is constructed in two main sections.

In a first section, the equations that are issued from the TPT are described and put into a common perspective. The full theory is developed with the SAFT equations. It is based on two concepts. The first is the expression for the association among molecules. This term is now widely accepted. The second is the description of molecules as a chain of segments.

Several authors, however, use with success the observation that the equation may be constructed from a sum of energetic terms, each originating from a different theory. Thus, the equation CPA was developed. We start with the association term, which is the most significant breakthrough that the TPT has brought about, rapidly summarize the various SAFT equations, issued from this approach, and end by mentioning that other contributions can be included for polar molecules.

The second section of this paper presents some industrial applications of these equations of state. Three examples are shown, the most illustrative examples of the use of the association term coming from the gas processing industry, where liquid – liquid – vapour equilibria between water, alcohol and light hydrocarbons must be described accurately. Here, the CPA equation brings a clear advantage while keeping in the limit of no association the simple structure provided by the cubic equations of state.

The hydrocarbon-methanol binaries show that the association term improves significantly the phase equilibria prediction because it takes explicitly into account the hydrogen bonding which is at the origin of non-ideal behaviour. In pure prediction (without interaction parameter), CPA can describe vapour-liquid equilibria, liquid - liquid equilibria and the azeotropic point. In order to improve the accuracy, the liquid-liquid equilibrium may need an appropriate interaction parameter. It is fitted with liquid- liquid equilibrium data in this case.

For the prediction of water-hydrocarbon equilibria, a qualitatively good description is provided (*i.e.* the same model is used in both hydrocarbon and aqueous phase!), but a binary interaction parameter is necessary to obtain accurate results. In fact, better results are obtained with hydrocarbon-methanol systems than with hydrocarbon-water systems.

In conclusion, CPA can be a reliable tool for calculating fluid phase equilibria of complex systems containing small associating components such as water and methanol. The difficulty of this equation is the determination of the pure component parameters for the associating compounds (where 5 pure component parameters are needed).

The SAFT equation is designed for long chain molecules. The group contribution method developed by Tamouza has been extended to isomers, and allows to describe with reasonable accuracy the most important thermodynamic properties of long chain molecules from various families.

The application of the SAFT equation including a polar or a quadrupolar contribution to industrial problems is illustrated using a reactive distillation example. This is a case where the predictive capacity of the equation of state in the low concentration range is put to the test. We believe that SAFT can bring some new answers in this field:

- SAFT-0 is probably the simplest version of SAFT; it is relatively accurate. However, the more recent versions have improved the predictive power of this equation;

- More accurate representation of vapour pressure is provided by PC-SAFT, especially for alkanes, and close to the critical point;
- The prediction of properties of heavy molecules is more accurate with SAFT-VR.

The equations based on the TPT theory are rather recent in the physical properties world. Thanks to their physical basis, we believe that their predictive potential is large. A major threshold that limits their widespread use is their computational complexity and the reticence of many engineers who have long been trained in the tuning of the cubic equations to their particular need. However, thanks to the advances proposed for facilitating the programming of the association term (which is truly the most complex), the advances in computational power, and the widening evidence of the predictive power of these equations, their availability and their use will increase steadfastly in the coming decade.

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