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Thermodynamic Models for the Prediction of Petroleum-Fluid Phase Behaviour

Romain Privat and Jean-Noël Jaubert

Ecole Nationale Supérieure des Industries Chimiques, Université de Lorraine
France

1. Introduction

Petroleum fluids, which include natural gases, gas condensates, crude oils and heavy oils are in the category of complex mixtures. A complex mixture is defined as one in which various families of compounds with diverse molecular properties are present. In petroleum fluids, various families of hydrocarbons such as paraffins, naphthenes and aromatics exist. Such mixtures also contain some heavy organic compounds such as resins and asphalthenes and some impurities such as mercaptans or other sulphur compounds. Non hydrocarbons are typically nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulphide (H_2S), hydrogen (H_2) among few others. Water is another fluid that is typically found co-existing with naturally occurring hydrocarbon mixtures.

Not only do oil and gas engineering systems handle very complex mixtures, but they also operate within exceptionally wide ranges of pressure and temperature conditions. Extremely low temperatures are required in liquefied natural gas (LNG) applications, while very high temperatures are needed for thermal cracking of heavy hydrocarbon molecules. Between these two extremes, hydrocarbon fluids are found underground at temperatures that can reach 90 °C or more, while surface conditions can hover around 20 °C. Pressure can vary from its atmospheric value (or lower in the case of vacuum distillation) to a number in the hundreds of MPa. Due to their complexity, multi-family nature and ample range of conditions, petroleum fluids undergo severe transformations and various phase transitions which include, but not limited to, liquid–vapour, liquid–liquid and liquid–liquid–vapour.

The major obstacle in the efficient design of processes dealing with hydrocarbon mixtures, e.g. primary production, enhanced oil recovery, pipeline transportation or petroleum processing and refining is the difficulty in the accurate and efficient prediction of their phase behaviour and other properties such as mixing enthalpies, heat capacities and volumetric properties. There is thus a great deal of interest to develop accurate models and computational packages to predict the phase behaviour and thermodynamic properties of such mixtures with the least amount of input data necessary. To reach this objective, equations of state have been widely used during the last decades.

The goal of this chapter is to present and analyse the development of Van der Waals-type cubic equations of state (EoS) and their application to the correlation and prediction of phase equilibrium and volumetric properties. A chronological critical walk through the most

important contributions during the first part of the 1900s is made, to arrive at the equation proposed by Redlich and Kwong in 1949. The contributions after Redlich and Kwong to the modern development of equations of state and the most recent equations proposed in the literature like the PPR78 and PR2SRK models are analyzed. The application of cubic equations of state to petroleum fluids and the development of mixing rules is put in a proper perspective. The main applications of cubic equations of state to petroleum mixtures including high-pressure phase equilibria and supercritical fluids are summarized. Finally, recommendations on which equations of state and which mixing rules to use for given applications in the petroleum industry are presented.

2. Some words about cubic equations of state History

Our current industrialized world transports and produces chemicals on an unprecedented scale. Natural gas and oil are today key-raw materials from which are derived the gaseous and liquid fuels energizing factories, electric power plants and most modes of transportation as well. Processes of evaporation and condensation, of mixing and separation, underlie almost any production method in the chemical industry. These processes can be grandly complex, especially when they occur at high pressures. Interest for them has mainly started during the industrial revolution in the 19th century and has unceasingly grown up since then. A huge leap in understanding of the phase behaviour of fluids was accomplished during the second half of this century by the scientists Van der Waals and Kamerlingh Onnes - and more generally by the Dutch School. It is undisputable that their discoveries were built on many talented anterior works as for instance:

- the successive attempts by Boyle (in 1662), Mariotte (more or less in the same time) and Gay-Lussac (in 1801) to derive the perfect-gas equation,
- the first observation of critical points by Cagniard de la Tour in 1822,
- the experimental determination of critical points of many substances by Faraday and Mendeleev throughout the 19th century,
- the measurement of experimental isotherms by Thomas Andrews (1869) showing the behaviour of a pure fluid around its critical point.

As the major result of the Dutch School, the Van der Waals equation of state (1873) - connecting variables P (pressure), v (molar volume) and T (temperature) of a fluid - was the first mathematical model incorporating both the gas-liquid transition and fluid criticality. In addition, its foundation on – more or less rigorous – molecular concepts (Van der Waals' theory assumes that molecules are subject to attractive and repulsive forces) affirmed the reality of molecules at a crucial time in history. Before Van der Waals, some attempts to model the real behaviour of gases were made. The main drawback of the P-v-T relationships presented before was that they did not consider the finite volume occupied by the molecules, similarly to the perfect-gas equation. Yet, the idea of including the volume of the molecules into the repulsive term was suggested by Bernoulli at the end of the 18th century and was then ignored for a long time. Following this idea, Dupré and Hirn (in 1863 - 1864) proposed to replace the molar volume v by ($v - b$), where b is the molar volume that molecules exclude by their mutual repulsions. This quantity is proportional to the temperature-independent molecular volume v_0, and named *covolume* by Dupré (sometimes also called *excluded volume*). However, none of these contributions were of general use and

none was able to answer the many questions related to fluid behaviour remaining at that time. It was Van der Waals with his celebrated doctoral thesis on "*The Continuity of the Liquid and Gaseous States*" (1873) and his famous equation of state who proposed for the first time a physically-coherent description of fluid behaviour from low to high pressures. To derive his equation, he considered the perfect-gas law (i.e. $Pv = RT$) and took into account the fact that molecules occupy space by replacing v by $(v-b)$, and the fact that they exert an attraction on each other by replacing P by $P + a/v^2$ (cohesion effect). Therefore, due to mutual repulsion of molecules the actual molar volume v has to be greater than b while molecular attraction forces are incorporated in the model by the coefficient a. Note also that in Van der Waals' theory, the molecules are assumed to have a core in the form of an impenetrable sphere. Physicists and more particularly thermodynamicists rapidly understood that Van der Waals' theory was a revolution upsetting classical conceptions and modernizing approaches used until then to describe fluids. As a consecration, Van der Waals was awarded the Nobel Prize of physics the 12th December 1910; he can be seen as the father of modern fluid thermodynamics. The equation that Van der Waals proposed in his thesis (Van der Waals, 1873) writes:

$$\left(P + \frac{a}{v^2} \right)(v - b) = R(1 + \alpha t) \tag{1}$$

where P and v are the externally measured pressure and molar volume. $R = 8.314472 \; J \cdot mol^{-1} \cdot K^{-1}$ is the gas constant and α is a measure of the kinetic energy of the molecule. This equation was rewritten later as follows (see for example the lecture given by Van der Waals when he received the Nobel Prize):

$$P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2} \tag{2}$$

It appears that the pressure results from the addition of a repulsive term $P_{\text{rep}} = RT / (v - b)$ and an attractive term $P_{\text{att}} = -a / v^2$. Writing the critical constraints (i.e. that the critical isotherm has a horizontal inflection point at the critical point in the *P-v* plane), it becomes possible to express the *a* and *b* parameters with respect to the experimental values of T_c and P_c, resp. the critical temperature and pressure:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \quad \text{and} \quad b = \Omega_b \frac{RT_c}{P_c} \quad \text{with:} \begin{cases} \Omega_a = 27/64 \\ \Omega_b = 1/8 \end{cases} \tag{3}$$

The Van der Waals equation is an example of *cubic equation*. It can be written as a third-degree polynomial in the volume, with coefficients depending on temperature and pressure:

$$v^3 - v^2 \left(b + \frac{RT}{P} \right) + \frac{a}{P} v - \frac{ab}{P} = 0 \tag{4}$$

The cubic form of the Van der Waals equation has the advantage that three real roots are found at the most for the volume at a given temperature and pressure. EoS including higher powers of the volume comes at the expense of the appearance of multiple roots, thus

complicating numerical calculations or leading to non-physical phenomena. In the numerical calculation of phase equilibrium with cubic equations, one simply discards the middle root, for which the compressibility is negative (this root is associated to an unstable state). Van der Waals' EoS and his ideas on intermolecular forces have been the subjects of many studies and development all through the years. (Clausius, 1880) proposed an EoS closely similar to the Van der Waals equation in which (i) an additional constant parameter (noted c) was added to the volume in the attractive term, (ii) the attractive term is made temperature-dependent. Containing one more adjustable parameter than Van der Waals' equation, Clausius' equation showed a possible way for increasing the model accuracy.

$$\text{Clausius: } P(T,v) = \frac{RT}{v-b} - \frac{a/T}{(v+c)^2} \tag{5}$$

In the middle of the 20th century, (Redlich & Kwong, 1949) published a new model derived from Van der Waals' equation, in which the attractive term was modified in order to obtain better fluid phase behaviour at low and high densities:

$$\text{Redlich-Kwong: } P(T,v) = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad \text{with: } \begin{cases} a(T) = a_c \cdot \alpha(T) \; ; \; b = \Omega_b RT_c / P_c \\ a_c = \Omega_a R^2 T_c^2 / P_c \text{ and } \alpha(T) = \sqrt{T_c/T} \\ \Omega_a = 1/\left[9\left(\sqrt[3]{2}-1\right)\right] \approx 0.4274 \\ \Omega_b = \left(\sqrt[3]{2}-1\right)/3 \approx 0.08664 \end{cases} \tag{6}$$

Similarly to Clausius' equation, a temperature dependency is introduced in the attractive term. The a parameter is expressed as the product of the constant coefficient $a_c = a(T_c)$ and $\alpha(T)$ (named alpha function) which is unity at the critical point. Note that only the two pure-component critical parameters T_c and P_c are required to evaluate a and b. The modifications of the attractive term proposed by Redlich and Kwong - although not based on strong theoretical background – showed the way to many contributors on how to improve Van der Waals' equation. For a long time, this model remained one of the most popular cubic equations, performing relatively well for simple fluids with acentric factors close to zero (like Ar, Kr or Xe) but representing with much less accuracy complex fluids with nonzero acentric factors. Let us recall that the acentric factor ω_i, defined by Pitzer as:

$$\omega_i = -\log\left[P_i^{sat}(T = 0.7T_{c,i}) / P_{c,i}\right] - 1 \tag{7}$$

where P_i^{sat} is the vaporization pressure of pure component i, is a measure of the acentricity (i.e. the non-central nature of the intermolecular forces) of molecule i. The success of the Redlich-Kwong equation has been the impetus for many further empirical improvements. In 1972, the Italian engineer Soave suggested to replace in Eq. (6) the α function by a more general temperature-dependent term. Considering the variation in behaviour of different fluids at the same reduced pressure (P/P_c) and temperature (T/T_c), he proposed to turn from a two-parameter EoS (the two parameters are T_c and P_c) to a three-parameter EoS by introducing the acentric factor as a third parameter in the definition of $\alpha(T)$. The acentric factor is used to take into account molecular size and shape effects since it varies with the

chain length and the spatial arrangement of the molecules (small globular molecules have a nearly zero acentric factor). The resulting model was named the Soave-Redlich-Kwong equation or the SRK equation (Soave, 1972), and writes:

$$\text{SRK: } P(T,v) = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad \text{with:} \begin{cases} a(T) = a_c \cdot \alpha(T) \ ; \ b = \Omega_b RT_c / P_c \\ a_c = \Omega_a R^2 T_c^2 / P_c \text{ and } \alpha(T) = \left[1 + m\left(1 - \sqrt{T/T_c}\right)\right]^2 \\ m = 0.480 + 1.574\omega - 0.176\omega^2 \\ \Omega_a = 1 / \left[9\left(\sqrt[3]{2} - 1\right)\right] \approx 0.4274 \\ \Omega_b = \left(\sqrt[3]{2} - 1\right) / 3 \approx 0.08664 \end{cases} \tag{8}$$

The alpha function $\alpha(T)$ used in the SRK equation is often named *Soave's alpha function*. The accuracy of this model was tested by comparing vapour pressures of a number of hydrocarbons calculated with the SRK equation to experimental data. Contrary to the Redlich-Kwong equation, the SRK equation was able to fit well the experimental trend. After Soave's proposal, many modifications were presented in the literature for improving the prediction of one or another property. One of the most popular ones is certainly the modification proposed by (Peng & Robinson, 1976) (their equation is named PR76 in this chapter). They considered the same alpha function as Soave but coefficients of the m function were recalculated. In addition, they also modified the volume dependency of the attractive term:

$$\text{PR76: } P(T,v) = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \quad \text{with:} \begin{cases} a(T) = a_c \cdot \alpha(T) \ ; \ b = \Omega_b RT_c / P_c \\ a_c = \Omega_a R^2 T_c^2 / P_c \text{ and } \alpha(T) = \left[1 + m\left(1 - \sqrt{T/T_c}\right)\right]^2 \\ m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \\ X = \frac{1}{3}\left(-1 + \sqrt[3]{6\sqrt{2} + 8} - \sqrt[3]{6\sqrt{2} - 8}\right) \approx 0.2531 \\ \Omega_a = 8(5X + 1) / (49 - 37X) \approx 0.45723 \\ \Omega_b = X / (X + 3) \approx 0.077796 \end{cases} \tag{9}$$

The accuracy of the PR76 equation is comparable to the one of the SRK equation. Both these models are quite popular in the hydrocarbon industry and offer generally a good representation of the fluid phase behaviour of few polar and few associated molecules (paraffins, naphthenes, aromatics, permanent gases and so on). (Robinson & Peng, 1978) proposed to slightly modify the expression of the m function in order to improve the representation of heavy molecules i such that $\omega_i > \omega_{n-decane} = 0.491$. This model is named PR78 in this chapter.

$$\text{PR78: } \begin{cases} m = 0.37464 + 1.54226\omega - 0.26992\omega^2 & \text{if } \omega \leq 0.491 \\ m = 0.379642 + 1.487503\omega - 0.164423\omega^2 + 0.016666\omega^3 & \text{if } \omega > 0.491 \end{cases} \tag{10}$$

In order to improve volume predictions (Péneloux et al., 1982) proposed a consistent correction for cubic EoS which does not change the vapour-liquid equilibrium conditions. Their method consists in translating the EoS by replacing v by $v+c$ and b by $b+c$. The

volume translation c can be estimated from the following correlation which involves the Rackett compressibility factor, z_{RA}:

$$\text{Volume-translated equations: }\begin{cases} c = \dfrac{RT_c}{P_c}\left[0.1156 - 0.4077\,z_{RA}\right], \text{ for the SRK equation} \\[2mm] c = \dfrac{RT_c}{P_c}\left[0.1154 - 0.4406\,z_{RA}\right], \text{ for the PR76 equation} \end{cases} \tag{11}$$

3. General presentation of cubic equations of state

All the cubic equations can be written under the general following form:

$$P(T,v) = \frac{RT}{v-b} - \frac{a(T)}{(v-r_1 b)(v-r_2 b)} \tag{12}$$

wherein r_1 and r_2 are two universal constants (i.e. they keep the same value whatever the pure component). As shown with Van der Waals' equation (see Eq. (4)), cubic EoS can be written as third-degree polynomials in v at a fixed temperature T and pressure P:

$$v^3 - v^2\left[b(r_1+r_2+1)+RT/P\right] + v\left[b^2\left(r_1 r_2 + r_1 + r_2\right) + RTb(r_1+r_2)/P + a/P\right] - b\left(r_1 r_2 b^2 + r_1 r_2 bRT/P + a/P\right) = 0 \tag{13}$$

As a drawback of cubic equations, the predicted critical molar compressibility factor, $z_c = P_c v_c / (RT_c)$, is found to be a universal constant whereas experimentally, it is specific to each pure substance. In a homologous chemical series, the z_c coefficient diminishes as the molecular size increases. For normal substances, z_c is found around 0.27. Table 1 here below provides values of r_1, r_2 and z_c for all the equations presented above:

Equation of state	r_1	r_2	z_c
Van der Waals or Clausius	0	0	$3/8 = 0.375$
Redlich-Kwong or SRK	0	-1	$1/3 \approx 0.333$
PR76 or PR78	$-1-\sqrt{2}$	$-1+\sqrt{2}$	≈ 0.3074

Table 1. values of r_1, r_2 and z_c for some popular cubic equations of state.

Experimental values of T_c and P_c can be used to determine the expressions of $a_c = a(T_c)$ and b. Indeed, by applying the critical constraints, one obtains the following results:

$$\begin{cases} X = \left[1 + \sqrt[3]{(1-r_1)(1-r_2)^2} + \sqrt[3]{(1-r_2)(1-r_1)^2}\right]^{-1} \\[2mm] a_c = \Omega_a R^2 T_c^2 / P_c \quad \text{and} \quad b = \Omega_b RT_c / P_c \\[2mm] \Omega_a = (1-r_1 X)(1-r_2 X)\left[2-(r_1+r_2)X\right] / \left[(1-X)\left[3-X(1+r_1+r_2)\right]\right]^2 \\[2mm] \Omega_b = X / \left[3 - X\left(1+r_1+r_2\right)\right] \end{cases} \tag{14}$$

Note that a cubic equation of state applied to a given pure component is completely defined by the universal-constant values r_1 and r_2, by the critical temperature and pressure of the

substance (allowing to calculate b and a_c) but also by the considered alpha function (allowing to evaluate the attractive parameter $a(T) = a_c \cdot \alpha(T)$). The next subsection is dedicated to present some $\alpha(T)$ functions frequently used with cubic equations.

4. Presentation of some alpha functions usable with cubic equations of state

Modifications of the temperature-dependent function $\alpha(T)$ in the attractive term of the SRK and PR equations have been mainly proposed to improve correlations and predictions of vapour pressure for polar fluids. Some of the most used are presented in this section.

- The most popular alpha function is certainly that of (Soave, 1972):

$$\alpha(T) = \left[1 + m\left(1 - \sqrt{T / T_c} \right) \right]^2 \tag{15}$$

wherein the m parameter is a function of the acentric factor (expressions of m for the SRK, PR76 and PR78 models are resp. given in Eqs. (8), (9) and (10)).

- (Mathias & Copeman, 1983) developed an expression for the alpha function aimed at extending the application range of the PR equation to highly polar components:

$$\begin{cases} \alpha(T) = \left[1 + C_1\left(1 - \sqrt{T / T_c} \right) + C_2\left(1 - \sqrt{T / T_c} \right)^2 + C_3\left(1 - \sqrt{T / T_c} \right)^3 \right]^2 & if \ T \leq T_c \\ \alpha(T) = \left[1 + C_1\left(1 - \sqrt{T / T_c} \right) \right]^2 & if \ T > T_c \end{cases} \tag{16}$$

Parameters C_1, C_2 and C_3 are specific to each component. They have to be fitted on vapour-pressure data.

- (Stryjek & Vera, 1986) proposed an alpha function for improving the modelling capacity of the PR equation at low reduced temperatures:

$$\begin{cases} \alpha(T) = \left[1 + m\left(1 - \sqrt{T / T_c} \right) \right]^2 \\ with \ m = m_0 + m_1\left(1 + \sqrt{T / T_c} \right)\left(0.7 - T / T_c \right) \\ and \ m_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \end{cases} \tag{17}$$

m_1 has to be fitted on experimental vapour-pressure data. Compared to the original PR EoS, this alpha function uses a higher order polynomial function in the acentric factor for the m parameter that allows a better modelling of heavy-hydrocarbon phase behaviour.

- (Twu et al., 1991, 1995a, 1995b) proposed two different alpha functions. The first one requires - for each pure component - to fit the model parameters (N, M and L) on experimental pure-component VLE data:

$$\alpha(T) = \left(T / T_c \right)^{N(M-1)} \exp\left[L\left[1 - \left(T / T_c \right)^{NM} \right] \right] \tag{18}$$

The second one is a predictive version of the first one, only requiring the knowledge of the acentric factor. Following Pitzer's corresponding-states principle, Twu et al. proposed:

$$\alpha(T) = \alpha^0(T) + \omega \left[\alpha^1(T) - \alpha^0(T) \right] \tag{19}$$

wherein the expressions of α^0 and α^1 are given by Eq. (18). Parameters *L*, *M* and *N* involved in these two functions are provided in Table 2.

alpha function parameters	$T \leq T_c$		$T > T_c$	
	α^0	α^1	α^0	α^1
PR:				
L	0.125283	0.511614	0.401219	0.024955
M	0.911807	0.784054	4.963070	1.248089
N	1.948150	2.812520	–0.200000	–8.000000
SRK:				
L	0.141599	0.500315	0.441411	0.032580
M	0.919422	0.799457	6.500018	1.289098
N	2.496441	3.291790	–0.200000	–8.000000

Table 2. Generalized parameters of the predictive version of the Twu et al. alpha function.

5. Petroleum-fluid phase behaviour modelling with cubic equations of state

The SRK and the PR EoS are the primary choice of models in the petroleum and gas processing industries where *high-pressure* models are required. For a pure component, the three required parameters (T_c, P_c and ω) were determined from experiments for thousands of pure components. When no experimental data are available, various estimation methods, applicable to any kind of molecule, can be used. Extension to mixtures requires mixing rules for the energy parameter and the covolume. A widely employed way to extend the cubic EoS to a mixture containing *p* components, the mole fractions of which are x_i, is via the so-called Van der Waals one-fluid mixing rules [quadratic composition dependency for both parameters – see Eqs. (20)and (21)] and the classical combining rules, i.e. the geometric mean rule for the cross-energy [Eq. (22)] and the arithmetic mean rule for the cross covolume parameter [Eq. (23)]:

$$a = \sum_{i=1}^{p} \sum_{j=1}^{p} x_i x_j a_{ij} \tag{20}$$

$$b = \sum_{i=1}^{p} \sum_{j=1}^{p} x_i x_j b_{ij} \tag{21}$$

$$a_{ij} = \sqrt{a_i a_j} \left(1 - k_{ij}\right) \tag{22}$$

$$b_{ij} = \tfrac{1}{2} \left(b_i + b_j\right)\left(1 - l_{ij}\right) \tag{23}$$

Doing so, two new parameters, the so-called *binary interaction parameters* (k_{ij} and l_{ij}) appear in the combining rules. One of them, namely k_{ij} is by far the most important one. Indeed, a non null l_{ij} is only necessary for complex polar systems and special cases. This is the reason why, dealing with petroleum fluids, phase equilibrium calculations are generally performed with $l_{ij} = 0$ and the mixing rule for the co-volume parameter simplifies to:

$$b = \sum_{i=1}^{p} x_i b_i \qquad (24)$$

We know by experience that the k_{ij} value has a huge influence on fluid-phase equilibrium calculation. To illustrate this point, it was decided to plot – using the PR EoS - the isothermal phase diagram for the system 2,2,4 trimethyl pentane (1) + toluene (2) at $T = 333.15\ K$ giving to k_{12} different values (see Figure 1). The obtained curves speak for themselves:
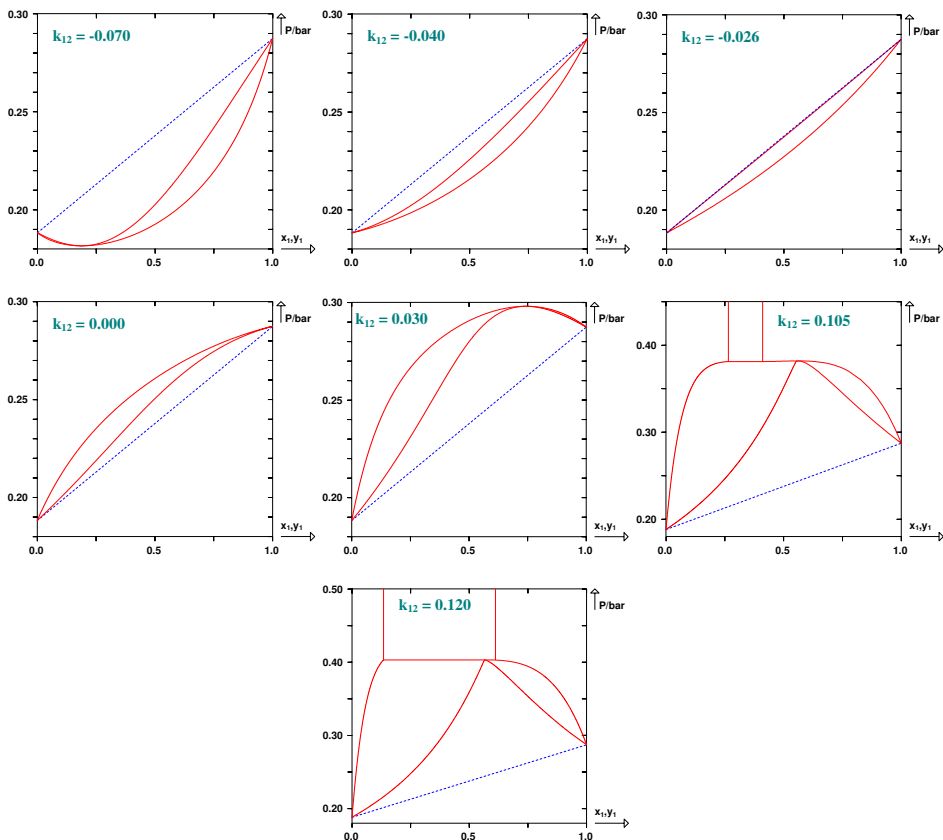

Fig. 1. Influence of k_{12} on the calculated isothermal phase diagram using the PR EoS for the system 2,2,4 trimethyl pentane (1) + toluene (2) at $T/K = 333.15$. The dashed line is Raoult's line.

- for $k_{12} = -0.07$, the system holds a negative homogeneous azeotrope
- for $k_{12} = -0.04$, the system still shows negative deviations from ideality but the azeotrope does not exist anymore
- for $k_{12} = -0.026$, the bubble curve is a straight line and the liquid phase behaves as an ideal solution
- for $k_{12} = 0.0$, the system shows positive deviations from ideality
- for $k_{12} = 0.03$, the system holds a positive homogeneous azeotrope
- for $k_{12} = 0.105$, the system simultaneously holds a positive homogeneous azeotrope and a three-phase line
- for $k_{12} = 0.12$, the system holds a heterogeneous azeotrope.

In front of such a big influence, the safest practice is to fit the k_{ij} value to phase equilibrium data. Such an approach however requires the knowledge of experimental data for all the binary systems it is possible to define in a multi-component system. Unfortunately such data are not always available inciting many researchers to develop correlations or group-contribution methods to estimate the k_{ij}.

5.1 Correlations to estimate the binary interaction parameters

Most of the proposed correlations are purely empirical and thus often unsuitable for extrapolation. Moreover, they often use additional properties besides those (the critical properties and the acentric factor) required by the cubic EoS itself. They are however very useful to help solve a phase equilibrium calculation problem.

Following London's theory, (Chueh & Prausnitz, 1967) proposed a correlation suitable for mixtures of paraffins which only requires knowledge of the critical volume of the two pure substances i and j (see Eq. (25) in Table 3). In 1990, a correlation allowing the estimation of the binary interaction parameters for a modified version of the SRK equation of state was developed by (Stryjek, 1990). It is applicable to mixtures of n-alkanes and is temperature dependent. The author pointed out that although the temperature dependence of the k_{ij} is moderate for mixtures of paraffins, the use of a temperature-dependent k_{ij} significantly improves the modelling of such systems. The proposed correlation has the form given by Eq. (26) in Table 3. (Gao et al., 1992) proposed a correlation suitable for mixtures containing various light hydrocarbons (paraffins, naphthenes, aromatics, alkynes). The theoretical approach adopted by these authors is a continuation of that of Chueh and Prausnitz previously mentioned. Their correlation requires the knowledge of the critical temperature and the critical compressibility factor. Such a parameter is unfortunately not well-known for many hydrocarbons, especially heavy ones. They proposed Eq. (27) shown in Table 3. (Kordas et al., 1995) developed two mathematical expressions to estimate the k_{ij} in mixtures containing methane and alkanes. The first one is suitable for alkanes lighter than the n-eicosane and the second one for heavy alkanes. In such an equation (see Eq. (28) in Table 3), ω is the acentric factor of the molecule mixed with methane. Unfortunately, Kordas et al. failed to generalize their correlations to mixtures containing methane and aromatic molecules. In the open literature, we also can find many correlations to estimate the k_{ij} for systems containing CO_2 and various hydrocarbons. Such equations are of the highest

importance because we know by experience that for such systems the k_{ij} is far from zero. As an example, (Graboski & Daubert, 1978) proposed a correlation suitable for mixtures containing CO_2 and paraffins. The use of this correlation (see Eq. (29) in Table 3), developed for a modified version of the SRK EoS, needs the knowledge of the solubility parameters δ. In Eq. (29), subscript i stands for the hydrocarbon and subscript j for CO_2 (or N_2 or H_2S). Another well-known correlation is the one developed by (Kato et al., 1981) which has the great advantage to be temperature-dependent. It can be applied to the PR EoS and to mixtures containing CO_2 and n-alkanes. It is given in Table 3 (see Eq. (30)). The three coefficients (*a*, *b* and *c*) only depend on the acentric factor of the n-alkane. A similar approach was followed by (Moysan et al., 1986) who developed a correlation in which the temperature-dependent k_{ij} can be estimated knowing the acentric factor of the hydrocarbon mixed with CO_2. A key point of Moysan's work is its applicability to systems containing H_2, N_2 and CO. Another temperature-dependent correlation for systems containing CO_2 and n-alkanes was developed by (Kordas et al., 1994). In their approach, the k_{ij} depends on the CO_2 reduced temperature ($T_{r,i} = T / T_{c,i}$) and on the alkane acentric factor (ω_j). It can be found in Table 3, Eq. (31). Kordas et al. explain that their correlation can also be used with other hydrocarbons (branched alkanes, aromatics or naphthenes) under the condition to substitute in Eq. (31) the acentric factor (ω_j) of the studied hydrocarbon by an *effective acentric factor*, the value of which has been correlated to the molar weight and to the density at 15 °C. The paper by (Bartle et al., 1992) also contains a correlation suitable for many systems containing CO_2. Various correlations for nitrogen-containing systems were also developed. Indeed, as shown by (Privat et al., 2008a), the phase behaviour of such systems is particularly difficult to correlate with a cubic EoS even with temperature-dependent k_{ij}. We can cite the work by (Valderrama et al., 1990) who proposed a correlation principally applicable to systems containing nitrogen and light alkanes. The mathematical shape of this correlation was inspired by the previous work of Kordas et al. (Eq. (31)). It is given in Table 3, Eq. (32). Such a correlation can be applied to various cubic EoS and to mixtures not only containing alkanes and N_2 but also CO_2 and H_2S. The same authors (Valderrama et al., 1999) recently improved their previous work. Although only applicable to the PR EoS, a similar work was realized by (Avlonitis et al. 1994). Once again, the k_{ij} depends on temperature and on the acentric factor (see Eq. (33) in Table 3). We cannot close this section before saying a few words about the correlation proposed by (Nishiumi et al., 1988). As shown by Eq. (34) in Table 3, it is probably the most general correlation never developed since it can be used to predict the k_{ij} of the PR EoS for any mixture containing paraffins, naphthenes, aromatics, alkynes, CO_2, N_2 and H_2S. The positive aspect of this correlation is its possible application to many mixtures. Its negative aspect is the required knowledge of the critical volumes.

Although very useful these many correlations only apply to specific mixtures (e.g. mixtures containing hydrocarbons and methane, mixtures containing hydrocarbons and nitrogen, mixtures containing hydrocarbons and carbon dioxide, mixtures containing light hydrocarbons, etc.) and to a specific cubic EoS. Moreover, they are often empirical and thus unsuitable for extrapolation. In addition, they may need additional properties besides those (the critical properties and the acentric factor) required by the cubic EoS itself. Finally, they do not always lead to temperature-dependent k_{ij} whereas we know by experience that the temperature has a huge influence on these interaction parameters.

Mathematical expression of the correlation	
$$k_{ij} = 1 - \left(\frac{2\sqrt{V_{c,i}^{1/3} V_{c,j}^{1/3}}}{V_{c,i}^{1/3} + V_{c,j}^{1/3}} \right)^n$$	(25)
$$k_{ij} = k_{ij}^0 + k_{ij}^T \left[(T/K) - 273.15 \right]$$	(26)
$$1 - k_{ij} = \left(\frac{2\sqrt{T_{c,i} T_{c,j}}}{T_{c,i} + T_{c,j}} \right)^{Z_{c,ij}} \quad \text{with} \quad Z_{c,ij} = \frac{Z_{c,i} + Z_{c,j}}{2}$$	(27)
$$\begin{cases} k_{ij} = -0,13409\omega + 2,28543\omega^2 - 7,61455\omega^3 + 10,46565\omega^4 - 5,2351\omega^5 \\ k_{ij} = -0,04633 - 0,04367\ln\omega \end{cases}$$	(28)
$$k_{ij} = A + B\left|\delta_i - \delta_j\right| + C\left|\delta_i - \delta_j\right|^2$$	(29)
$$k_{ij} = a(T - b)^2 + c$$	(30)
$$k_{ij} = a(\omega_j) + b(\omega_j) \times T_{r,i} + c(\omega_j) \times T_{r,i}^3$$	(31)
$$k_{ij} = A(\omega_j) + B(\omega_j)/T_{r,j}$$	(32)
$$k_{ij} = Q(\omega_j) - \frac{T_{r,i}^2 + A(\omega_j)}{T_{r,i}^3 + C(\omega_j)}$$	(33)
$$1 - k_{ij} = C + D\frac{V_{c,i}}{V_{c,j}} + E\left(\frac{V_{c,i}}{V_{c,j}} \right)^2 \quad with \quad \begin{cases} C = c_1 + c_2\left|\omega_i - \omega_j\right| \\ D = d_1 + d_2\left|\omega_i - \omega_j\right| \end{cases}$$	(34)

Table 3. Correlations to estimate the binary interaction parameters.

A way to avoid all these drawbacks would be (i) to develop a group-contribution method capable of estimating temperature-dependent k_{ij} and (ii) to develop a method allowing switching from a cubic EoS to another one. These issues are developed in the next subsections.

5.2 Group contribution methods to estimate the binary interaction parameters

In any group-contribution (GC) method, the basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups that constitute these compounds is much smaller. Assuming that a physical property of a fluid is the sum of contributions made by the molecule's functional groups, GC methods

allow for correlating the properties of a very large number of fluids using a much smaller number of parameters. These GC parameters characterize the contributions of individual groups in the properties.

5.2.1 The ARP model

The first GC method designed for estimating the k_{ij} of a cubic EoS was developed by (Abdoul et al., 1991) and is often called the ARP model (ARP for Abdoul-Rauzy-Péneloux, the names of the three creators of the model). Even though accurate, such a model has some disadvantages. Indeed, Abdoul et al. did not use the original PR EoS but instead a non-conventional *translated PR type EoS*. Moreover, in order to estimate the attractive parameter *a(T)* of their EoS, these authors defined two classes of pure compounds. For components which are likely to be encountered at very low pressure, the Carrier-Rogalski-Péneloux (CRP) *a(T)* correlation (Carrier et al., 1988) which requires the knowledge of the normal boiling point was used. For other compounds, they used a Soave-like expression (Rauzy, 1982) which is different from the one developed by Soave for the SRK EoS and different from the one developed by Peng and Robinson for their own equation. Moreover, the decomposition into groups of the molecules is not straightforward and is sometimes difficult to understand. For example, propane is classically decomposed into two CH$_3$ groups and one CH$_2$ group but 2-methyl propane {CH$_3$-CH(CH$_3$)-CH$_3$} is decomposed into four CH groups and not into three CH$_3$ groups and one CH group. Isopentane is formed by one CH$_3$ group, half a CH$_2$ group and three and a half CH groups. Lastly, because this model was developed more than twenty years ago, the experimental database used by Abdoul et al. to fit the parameters of their model (roughly 40,000 experimental data points) is small in comparison to databases today available. The group parameters obtained from this too small data base may lead to unrealistic phase equilibrium calculations at low or at high temperatures. For all these reasons, this model has never been extensively used and never appeared in commercial process simulators.

5.2.2 The PPR78 model

Being aware of the drawbacks of the ARP model, Jaubert, Privat and co-workers decided to develop the PPR78 model which is a GC model designed for estimating, as a function of temperature, the k_{ij} for the widely used PR78 EoS (Jaubert & Mutelet, 2004; Jaubert et al., 2005, 2010; Vitu et al. 2006, 2008; Privat et al. 2008a, 2008b, 2008c, 2008d). Such an equation of sate was selected because it is used in most of the petroleum companies but above all because it is available in any computational package.

5.2.2.1 Presentation

Following the previous work of Abdoul et al., $k_{ij}(T)$ is expressed in terms of group contributions, through the following expression:

$$k_{ij}(T) = \frac{-\dfrac{1}{2}\sum_{k=1}^{N_g}\sum_{l=1}^{N_g}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}\cdot\left(\dfrac{298.15}{T}\right)^{\left(\frac{B_{kl}}{A_{kl}}-1\right)} - \left(\dfrac{\sqrt{a_i(T)}}{b_i}-\dfrac{\sqrt{a_j(T)}}{b_j}\right)^2}{2\dfrac{\sqrt{a_i(T)\cdot a_j(T)}}{b_i\cdot b_j}} \qquad (35)$$

In Eq. (35), T is the temperature. a_i and b_i are the attractive parameter and the covolume of pure i. N_g is the number of different groups defined by the method (for the time being, twenty-one groups are defined and $N_g = 21$). α_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i). $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups) are constant parameters determined during the development of the model ($A_{kk} = B_{kk} = 0$). As can be seen, to calculate the k_{ij} parameter between two molecules i and j at a selected temperature, it is only necessary to know: the critical temperature of both components ($T_{c,i}$, $T_{c,j}$), the critical pressure of both components ($P_{c,i}$, $P_{c,j}$), the acentric factor of each component (ω_i, ω_j) and the decomposition of each molecule into elementary groups (α_{ik}, α_{jk}). It means that no additional input data besides those required by the EoS itself is necessary. Such a model relies on the Peng-Robinson EoS as published by Peng and Robinson in 1978 (Eq. (10)). The addition of a GC method to estimate the temperature-dependent k_{ij} makes it predictive; it was thus decided to call it PPR78 (predictive 1978, Peng Robinson EoS). The twenty-one groups which are defined until now are summarized below.

For alkanes: group1 = CH_3, group2 = CH_2, group3 = CH, group4 = C, group5 = CH_4 i.e. methane, group6 = C_2H_6 i.e. ethane

For aromatic compounds: group7 = CH_{aro}, group8 = C_{aro}, group9 = $C_{fused\ aromatic\ rings}$

For naphthenic compounds: group10 = $CH_{2,cyclic}$, group11 = CH_{cyclic} = C_{cyclic}

For permanent gases: group12 = CO_2, group13 = N_2, group14 = H_2S, group21 = H_2.

For water-containing systems : group16 = H_2O

For mercaptans: group15 = -SH,

For alkenes: group17 = $CH_2=CH_2$ i.e. ethylene, group18 = $CH_{2,alkenic}$ = $CH_{alkenic}$, group19 = $C_{alkenic}$, group20 = $CH_{2,cycloalkenic}$ = $CH_{cycloalkenic}$

The decomposition into groups of the hydrocarbons (linear, branched or cyclic) is very easy, that is as simple as possible. No substitution effects are considered. No exceptions are defined. For these 21 groups, we had to estimate 420 parameters ($210 A_{kl}$ and $210 B_{kl}$ values) the values of which are summarized in Table 4. These parameters have been determined in order to minimize the deviations between calculated and experimental vapour-liquid equilibrium data from an extended data base containing roughly 100,000 experimental data points (56,000 bubble points + 42,000 dew points + 2,000 mixture critical points).

The following objective function was minimized:

$$F_{obj} = \frac{F_{obj,bubble} + F_{obj,dew} + F_{obj,crit.\ comp} + F_{obj,crit.\ pressure}}{n_{bubble} + n_{dew} + n_{crit} + n_{crit}} \tag{36}$$

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18	Group 19	Group 20
Group 1	0																			
Group 2	$A_{12}=74.81$ $B_{12}=165.7$	0																		
Group 3	$A_{13}=261.5$ $B_{13}=388.8$	$A_{23}=51.47$ $B_{23}=79.61$	0																	
Group 4	$A_{14}=396.7$ $B_{14}=804.3$	$A_{24}=88.53$ $B_{24}=315.0$	$A_{34}=-305.7$ $B_{34}=-250.8$	0																
Group 5	$A_{15}=32.94$ $B_{15}=-35.00$	$A_{25}=36.72$ $B_{25}=108.4$	$A_{35}=145.2$ $B_{35}=301.6$	$A_{45}=263.9$ $B_{45}=531.5$	0															
Group 6	$A_{16}=8.579$ $B_{16}=-29.51$	$A_{26}=31.23$ $B_{26}=84.76$	$A_{36}=174.3$ $B_{36}=352.1$	$A_{46}=333.2$ $B_{46}=203.8$	$A_{56}=13.04$ $B_{56}=-6.863$	0														
Group 7	$A_{17}=90.25$ $B_{17}=146.1$	$A_{27}=29.78$ $B_{27}=58.17$	$A_{37}=103.3$ $B_{37}=191.8$	$A_{47}=67.26$ $B_{47}=613.2$	$A_{57}=13.04$ $B_{57}=13.04$	$A_{67}=13.38$ $B_{67}=20.25$	0													
Group 8	$A_{18}=62.80$ $B_{18}=41.86$	$A_{28}=3.775$ $B_{28}=144.8$	$A_{38}=6.177$ $B_{38}=-53.97$	$A_{48}=79.61$ $B_{48}=-326.0$	$A_{58}=139.3$ $B_{58}=464.3$	$A_{68}=-3.088$ $B_{68}=13.04$	$A_{78}=-13.38$ $B_{78}=20.25$	0												
Group 9	$A_{19}=62.80$ $B_{19}=41.86$	$A_{29}=3.775$ $B_{29}=144.8$	$A_{39}=6.177$ $B_{39}=-53.97$	$A_{49}=79.61$ $B_{49}=-326.0$	$A_{59}=139.3$ $B_{59}=464.3$	$A_{69}=-3.088$ $B_{69}=13.04$	$A_{79}=-13.38$ $B_{79}=20.25$	$A_{89}=0.000$ $B_{89}=0.000$	0											
Group 10	$A_{1\text{-}10}=40.38$ $B_{1\text{-}10}=95.90$	$A_{2\text{-}10}=12.78$ $B_{2\text{-}10}=-90.93$	$A_{3\text{-}10}=101.9$ $B_{3\text{-}10}=-90.93$	$A_{4\text{-}10}=177.1$ $B_{4\text{-}10}=601.9$	$A_{5\text{-}10}=36.37$ $B_{5\text{-}10}=26.42$	$A_{6\text{-}10}=8.579$ $B_{6\text{-}10}=76.86$	$A_{7\text{-}10}=29.17$ $B_{7\text{-}10}=69.32$	$A_{8\text{-}10}=34.31$ $B_{8\text{-}10}=95.39$	$A_{9\text{-}10}=34.31$ $B_{9\text{-}10}=95.39$	0										
Group 11	$A_{1\text{-}11}=98.48$ $B_{1\text{-}11}=231.6$	$A_{2\text{-}11}=-54.90$ $B_{2\text{-}11}=-319.5$	$A_{3\text{-}11}=-226.5$ $B_{3\text{-}11}=-51.47$	$A_{4\text{-}11}=117.84$ $B_{4\text{-}11}=-109.5$	$A_{5\text{-}11}=40.15$ $B_{5\text{-}11}=255.3$	$A_{6\text{-}11}=10.29$ $B_{6\text{-}11}=-52.84$	$A_{7\text{-}11}=-26.42$ $B_{7\text{-}11}=-789.2$	$A_{8\text{-}11}=-105.7$ $B_{8\text{-}11}=-286.5$	$A_{9\text{-}11}=-105.7$ $B_{9\text{-}11}=-286.5$	$A_{10\text{-}11}=-90.10$ $B_{10\text{-}11}=-491.1$	0									
Group 12	$A_{1\text{-}12}=164.0$ $B_{1\text{-}12}=269.0$	$A_{2\text{-}12}=136.9$ $B_{2\text{-}12}=254.6$	$A_{3\text{-}12}=287.9$ $B_{3\text{-}12}=762.1$	$A_{4\text{-}12}=359.5$ $B_{4\text{-}12}=346.2$	$A_{5\text{-}12}=137.3$ $B_{5\text{-}12}=194.2$	$A_{6\text{-}12}=135.5$ $B_{6\text{-}12}=239.5$	$A_{7\text{-}12}=102.6$ $B_{7\text{-}12}=163.3$	$A_{8\text{-}12}=110.1$ $B_{8\text{-}12}=637.6$	$A_{9\text{-}12}=102.6$ $B_{9\text{-}12}=444.4$	$A_{10\text{-}12}=130.1$ $B_{10\text{-}12}=225.8$	$A_{11\text{-}12}=91.28$ $B_{11\text{-}12}=82.01$	0								
Group 13	$A_{1\text{-}13}=52.74$ $B_{1\text{-}13}=87.19$	$A_{2\text{-}13}=82.28$ $B_{2\text{-}13}=202.8$	$A_{3\text{-}13}=365.4$ $B_{3\text{-}13}=521.9$	$A_{4\text{-}13}=263.9$ $B_{4\text{-}13}=772.6$	$A_{5\text{-}13}=57.90$ $B_{5\text{-}13}=37.20$	$A_{6\text{-}13}=61.59$ $B_{6\text{-}13}=84.92$	$A_{7\text{-}13}=185.2$ $B_{7\text{-}13}=490.6$	$A_{8\text{-}13}=284.0$ $B_{8\text{-}13}=36.72$	$A_{9\text{-}13}=718.1$ $B_{9\text{-}13}=1892$	$A_{10\text{-}13}=179.5$ $B_{10\text{-}13}=546.6$	$A_{11\text{-}13}=310.9$ $B_{11\text{-}13}=249.8$	$A_{12\text{-}13}=98.42$ $B_{12\text{-}13}=221.4$	0							
Group 14	$A_{1\text{-}14}=158.4$ $B_{1\text{-}14}=241.2$	$A_{2\text{-}14}=134.6$ $B_{2\text{-}14}=138.3$	$A_{3\text{-}14}=393.9$ $B_{3\text{-}14}=307.8$	$A_{4\text{-}14}=305.1$ $B_{4\text{-}14}=-143.1$	$A_{5\text{-}14}=181.2$ $B_{5\text{-}14}=288.9$	$A_{6\text{-}14}=157.2$ $B_{6\text{-}14}=217.1$	$A_{7\text{-}14}=21.96$ $B_{7\text{-}14}=13.04$	$A_{8\text{-}14}=1.029$ $B_{8\text{-}14}=-8.579$	$A_{9\text{-}14}=1.029$ $B_{9\text{-}14}=-8.579$	$A_{10\text{-}14}=120.8$ $B_{10\text{-}14}=163.0$	$A_{11\text{-}14}=-0.13$ $B_{11\text{-}14}=-167.6$	$A_{12\text{-}14}=134.9$ $B_{12\text{-}14}=201.4$	$A_{13\text{-}14}=319.5$ $B_{13\text{-}14}=590.1$	0						
Group 15	$A_{1\text{-}15}=799.9$ $B_{1\text{-}15}=2109$	$A_{2\text{-}15}=459.5$ $B_{2\text{-}15}=627.5$	$A_{3\text{-}15}=423.5$ $B_{3\text{-}15}=514.7$	$A_{4\text{-}15}=1682.9$ $B_{4\text{-}15}=1544$	$A_{5\text{-}15}=706.0$ $B_{5\text{-}15}=1483$	NOT AVAILABLE	$A_{7\text{-}15}=285.5$ $B_{7\text{-}15}=392.0$	$A_{8\text{-}15}=1072$ $B_{8\text{-}15}=1094$	$A_{9\text{-}15}=1072$ $B_{9\text{-}15}=1094$	$A_{10\text{-}15}=446.1$ $B_{10\text{-}15}=549.0$	$A_{11\text{-}15}=411.8$ $B_{11\text{-}15}=-208.5$	NOT AVAILABLE	NOT AVAILABLE	$A_{14\text{-}15}=-77.21$ $B_{14\text{-}15}=156.1$	0					
Group 16	$A_{1\text{-}16}=3357$ $B_{1\text{-}16}=11195$	$A_{2\text{-}16}=4324$ $B_{2\text{-}16}=12126$	$A_{3\text{-}16}=971.4$ $B_{3\text{-}16}=567.6$	$A_{4\text{-}16}=2265$ $B_{4\text{-}16}=4722$	$A_{5\text{-}16}=2333$ $B_{5\text{-}16}=5147$	$A_{6\text{-}16}=7.549$ $B_{6\text{-}16}=19.22$	$A_{7\text{-}16}=20.25$ $B_{7\text{-}16}=62.18$	$A_{8\text{-}16}=543.5$ $B_{8\text{-}16}=411.8$	$A_{9\text{-}16}=1340$ $B_{9\text{-}16}=-6.688$	$A_{10\text{-}16}=4211$ $B_{10\text{-}16}=13031$	$A_{11\text{-}16}=244.0$ $B_{11\text{-}16}=60.39$	$A_{12\text{-}16}=359.3$ $B_{12\text{-}16}=277.9$	$A_{13\text{-}16}=2574$ $B_{13\text{-}16}=5490$	$A_{14\text{-}16}=603.9$ $B_{14\text{-}16}=599.1$	$A_{15\text{-}16}=30.88$ $B_{15\text{-}16}=-113.6$	0				
Group 17	$A_{1\text{-}17}=72.06$ $B_{1\text{-}17}=39.12$	$A_{2\text{-}17}=59.71$ $B_{2\text{-}17}=78.58$	$A_{3\text{-}17}=176.7$ $B_{3\text{-}17}=135.0$	$A_{4\text{-}17}=74.69$ $B_{4\text{-}17}=30.20$	$A_{5\text{-}17}=14.69$ $B_{5\text{-}17}=30.120$	$A_{6\text{-}17}=26.42$ $B_{6\text{-}17}=-7.549$	$A_{7\text{-}17}=20.25$ $B_{7\text{-}17}=94.02$	$A_{8\text{-}17}=65.20$ $B_{8\text{-}17}=125.2$	NOT AVAILABLE	$A_{10\text{-}17}=55.34$ $B_{10\text{-}17}=52.50$	$A_{11\text{-}17}=-38.43$ $B_{11\text{-}17}=-688.4$	$A_{12\text{-}17}=73.09$ $B_{12\text{-}17}=115.3$	$A_{13\text{-}17}=125.2$ $B_{13\text{-}17}=1091$	NOT AVAILABLE	NOT AVAILABLE	$A_{16\text{-}17}=1632$ $B_{16\text{-}17}=1612$	0			
Group 18	$A_{1\text{-}18}=54.22$ $B_{1\text{-}18}=142.4$	$A_{2\text{-}18}=11.67$ $B_{2\text{-}18}=29.51$	$A_{3\text{-}18}=138.4$ $B_{3\text{-}18}=158.9$	$A_{4\text{-}18}=50.79$ $B_{4\text{-}18}=-284.5$	$A_{5\text{-}18}=52.84$ $B_{5\text{-}18}=110.5$	NOT AVAILABLE	$A_{7\text{-}18}=8.579$ $B_{7\text{-}18}=-7.549$	$A_{8\text{-}18}=-70.69$ $B_{8\text{-}18}=36.72$	NOT AVAILABLE	$A_{10\text{-}18}=27.11$ $B_{10\text{-}18}=454.7$	NOT AVAILABLE	$A_{12\text{-}18}=59.71$ $B_{12\text{-}18}=210.3$	$A_{13\text{-}18}=129.2$ $B_{13\text{-}18}=285.5$	NOT AVAILABLE	NOT AVAILABLE	$A_{16\text{-}18}=2243$ $B_{16\text{-}18}=5199$	$A_{17\text{-}18}=117.16$ $B_{17\text{-}18}=36.72$	0		
Group 19	$A_{1\text{-}19}=115.6$ $B_{1\text{-}19}=118.4$	$A_{2\text{-}19}=60.39$ $B_{2\text{-}19}=722.8$	$A_{3\text{-}19}=103.6$ $B_{3\text{-}19}=430.6$	NOT AVAILABLE	NOT AVAILABLE	NOT AVAILABLE	$A_{7\text{-}19}=1.029$ $B_{7\text{-}19}=16.81$	$A_{8\text{-}19}=217.5$ $B_{8\text{-}19}=-170.2$	NOT AVAILABLE	$A_{10\text{-}19}=-3.088$ $B_{10\text{-}19}=-166.5$	NOT AVAILABLE	$A_{12\text{-}19}=22.68$ $B_{12\text{-}19}=-186.0$	$A_{13\text{-}19}=455.7$ $B_{13\text{-}19}=50.54$	NOT AVAILABLE	NOT AVAILABLE	NOT AVAILABLE	$A_{17\text{-}19}=0.137$ $B_{17\text{-}19}=31.23$	$A_{18\text{-}19}=21.62$ $B_{18\text{-}19}=134.9$	0	
Group 20	$A_{1\text{-}20}=717.1$ $B_{1\text{-}20}=358.9$	$A_{2\text{-}20}=1000$ $B_{2\text{-}20}=-7.206$	$A_{3\text{-}20}=39.12$ $B_{3\text{-}20}=1038$	NOT AVAILABLE	NOT AVAILABLE	$A_{6\text{-}20}=137.6$ $B_{6\text{-}20}=190.0$	$A_{7\text{-}20}=6.177$ $B_{7\text{-}20}=5.490$	$A_{8\text{-}20}=3.431$ $B_{8\text{-}20}=-37.75$	$A_{9\text{-}20}=549.0$ $B_{9\text{-}20}=254.6$	$A_{10\text{-}20}=51.47$ $B_{10\text{-}20}=254.6$	$A_{11\text{-}20}=37.75$ $B_{11\text{-}20}=4173$	$A_{12\text{-}20}=265.9$ $B_{12\text{-}20}=94.37$	$A_{13\text{-}20}=65.20$ $B_{13\text{-}20}=70.10$	$A_{14\text{-}20}=145.8$ $B_{14\text{-}20}=823.5$	NOT AVAILABLE	$A_{16\text{-}20}=830.8$ $B_{16\text{-}20}=-137.9$	$A_{17\text{-}20}=-43.24$ $B_{17\text{-}20}=1798$	$A_{18\text{-}20}=119.8$ $B_{18\text{-}20}=-721.6$	$A_{19\text{-}20}=-392.9$ $B_{19\text{-}20}=-397.3$	0
Group 21	$A_{1\text{-}21}=202.8$ $B_{1\text{-}21}=317.4$	$A_{2\text{-}21}=132.5$ $B_{2\text{-}21}=1672$	$A_{3\text{-}21}=415.2$ $B_{3\text{-}21}=726.4$	$A_{4\text{-}21}=226.5$ $B_{4\text{-}21}=1812$	$A_{5\text{-}21}=156.1$ $B_{5\text{-}21}=92.99$	$A_{6\text{-}21}=284.8$ $B_{6\text{-}21}=175.0$	$A_{7\text{-}21}=175.0$ $B_{7\text{-}21}=175.0$	$A_{8\text{-}21}=232.0$ $B_{8\text{-}21}=1201$	$A_{9\text{-}21}=232.0$ $B_{9\text{-}21}=1476$	$A_{10\text{-}21}=-314.0$ $B_{10\text{-}21}=1673$	$A_{11\text{-}21}=-225.8$ $B_{11\text{-}21}=1476$	$A_{12\text{-}21}=268.3$ $B_{12\text{-}21}=268.3$	$A_{13\text{-}21}=70.10$ $B_{13\text{-}21}=823.5$	$A_{14\text{-}21}=145.8$ $B_{14\text{-}21}=823.5$	NOT AVAILABLE	$A_{16\text{-}21}=830.8$ $B_{16\text{-}21}=-137.9$	$A_{17\text{-}21}=151.3$ $B_{17\text{-}21}=165.1$	$A_{18\text{-}21}=163.0$ $B_{18\text{-}21}=322.2$	$A_{19\text{-}21}=630.0$ $B_{19\text{-}21}=573.1$	$A_{20\text{-}21}=483.1$ $B_{20\text{-}21}=2417$

Table 4. Group interaction parameters of the PPR78 model: $\left(A_{kl}=A_{lk}\right)/MPa$ and $\left(B_{kl}=B_{lk}\right)/MPa$.

with:
$$\begin{cases} F_{obj,bubble} = 100 \sum_{i=1}^{n_{bubble}} 0.5 \left(\frac{|\Delta x|}{x_{1,exp}} + \frac{|\Delta x|}{x_{2,exp}} \right)_i \quad with \ |\Delta x| = |x_{1,exp} - x_{1,cal}| = |x_{2,exp} - x_{2,cal}| \\[2ex] F_{obj,dew} = 100 \sum_{i=1}^{n_{dew}} 0.5 \left(\frac{|\Delta y|}{y_{1,exp}} + \frac{|\Delta y|}{y_{2,exp}} \right)_i \quad with \ |\Delta y| = |y_{1,exp} - y_{1,cal}| = |y_{2,exp} - y_{2,cal}| \\[2ex] F_{obj,crit.\ comp} = 100 \sum_{i=1}^{n_{crit}} 0.5 \left(\frac{|\Delta x_c|}{x_{c1,exp}} + \frac{|\Delta x_c|}{x_{c2,exp}} \right)_i \quad with \ |\Delta x_c| = |x_{c1,exp} - x_{c1,cal}| = |x_{c2,exp} - x_{c2,cal}| \\[2ex] F_{obj,crit.\ pressure} = 100 \sum_{i=1}^{n_{crit}} \left(\frac{|P_{cm,exp} - P_{cm,cal}|}{P_{cm,exp}} \right)_i \end{cases}$$

n_{bubble}, n_{dew} and n_{crit} are the number of bubble points, dew points and mixture critical points respectively. x_1 is the mole fraction in the liquid phase of the most volatile component and x_2 the mole fraction of the heaviest component (it is obvious that $x_2 = 1 - x_1$). Similarly, y_1 is the mole fraction in the gas phase of the most volatile component and y_2 the mole fraction of the heaviest component (it is obvious that $y_2 = 1 - y_1$). x_{c1} is the critical mole fraction of the most volatile component and x_{c2} the critical mole fraction of the heaviest component. P_{cm} is the binary critical pressure. For all the data points included in our database, the objective function defined by Eq. (36) is only:

$$F_{obj} = 7.6 \% \tag{37}$$

The average overall deviation on the liquid phase composition is:

$$\overline{\Delta x}\% = \frac{\overline{\Delta x_1}\% + \overline{\Delta x_2}\%}{2} = \frac{F_{obj,bubble}}{n_{bubble}} = \underline{\underline{7.4 \ \%}} \tag{38}$$

The average overall deviation on the gas phase composition is:

$$\overline{\Delta y}\% = \frac{\overline{\Delta y_1}\% + \overline{\Delta y_2}\%}{2} = \frac{F_{obj,dew}}{n_{dew}} = \underline{\underline{8.0 \ \%}} \tag{39}$$

The average overall deviation on the critical composition is:

$$\overline{\Delta x_c}\% = \frac{\overline{\Delta x_{c1}}\% + \overline{\Delta x_{c2}}\%}{2} = \frac{F_{obj,crit.\ comp}}{n_{crit}} = \underline{\underline{7.1 \ \%}} \tag{40}$$

The average overall deviation on the binary critical pressure is:

$$\overline{\Delta P_c}\% = \frac{F_{obj,crit.\ pressure}}{n_{crit}} = \underline{\underline{4.9 \ \%}} \tag{41}$$

Taking into account the scatter of the experimental data which inevitably makes increase the objective function value, we can assert that the PPR78 model is a very accurate thermodynamic model. In conclusion, thanks to this predictive model it is today possible to

estimate the k_{ij} for any mixture containing alkanes, aromatics, naphthenes, CO_2, N_2, H_2S, H_2, mercaptans, water and alkenes for any temperature. We thus can say that the PPR78 model is able to cover all the compounds that an engineer of a petroleum company is likely to encounter. We are proud to announce that the PPR78 model is now integrated in two famous process simulators: PRO/II commercialized by Invensys and ProSimPlus developed by the French company PROSIM. Figure 2 graphically illustrates the accuracy of the PPR78 model.
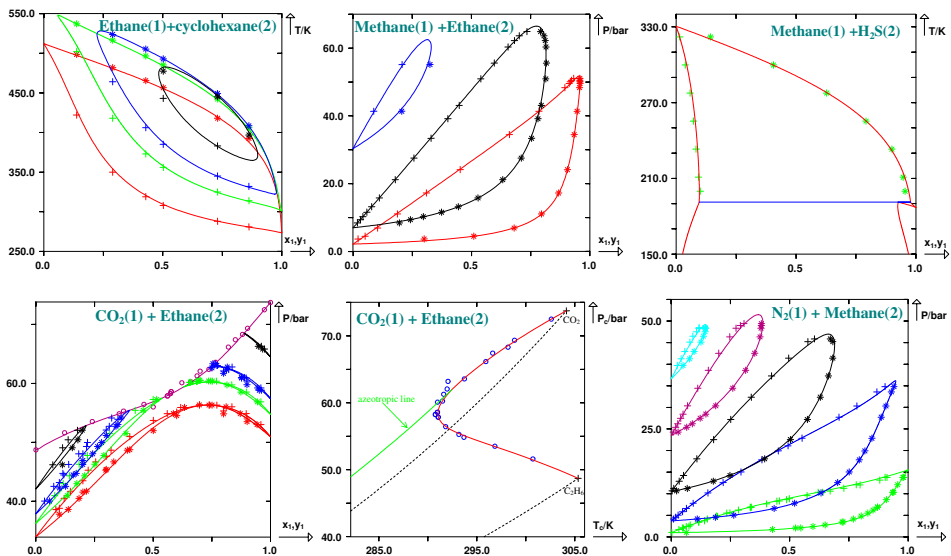
Fig. 2. Illustration of the accuracy of the PPR78 model. The symbols are the experimental data points. The full lines are the predictions with the PPR78 model.

5.2.2.2 On the temperature dependence of the k_{ij} parameter

In mixtures encountered in the petroleum and gas processing industries it is today accepted that the binary interaction parameter k_{ij} depends on temperature. This temperature dependence has been described by a few authors. The very good paper by (Coutinho et al., 1994) gives an interesting review of the different publications dealing with this subject. The same authors give a theoretical explanation for the temperature dependence of the k_{ij} and conclude that this parameter varies quadratically with the inverse temperature ($1/T$). Using Eq. (35), it is simple to plot k_{ij} versus temperature for a given binary system. As an illustration, Figure 3 presents plots of k_{ij} with respect to the reduced temperature of the heavy n-alkane for three binary systems: methane/propane, methane/n-hexane and methane/n-decane. The shapes of the curves are similar to the ones published by Coutinho et al. At low temperature, k_{ij} is a decreasing function of temperature. With increasing the temperature, the k_{ij} reaches a minimum and then increases again. The minimum is located at a reduced temperature close to 0.55, independent of the binary system. This minimum moves to $T_r = 0.6$ for the system methane/n-C_{30} (results not shown in Figure 3). From Figure 3, we can unambiguously conclude that it is necessary to work with temperature-dependent k_{ij}.
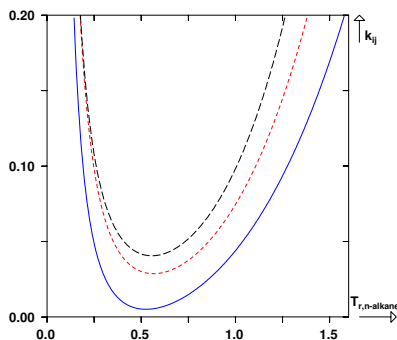
Fig. 3. Temperature dependence of predicted k_{ij} by means of Eq. (35). Solid line: system methane/propane. Short dashed line: system methane/n-hexane. Long dashed line: system methane/n-decane. In abscissa, T_r is the reduced temperature of the heavy n-alkane (respectively propane, n-hexane, n-decane).

5.2.3 Soave's group-contribution method (GCM)

In a recent paper, (Soave et al., 2010) also developed a GCM aimed at predicting temperature-dependent k_{ij} for the well known SRK EoS. Six groups are defined: group1 = CH$_4$, group2 = CO$_2$, group3 = N$_2$, group4 = H$_2$S, group5 = *alkyl group* and group6 = *aromatic group*. The last two groups are introduced to model alkanes and aromatic compounds. This small number of groups is an advantage since it reduces the number of group parameters to be estimated and it allows a faster estimation of the k_{ij}. Indeed, the calculation of a double sum as the one contained in Eq. (35) is time consuming and strongly affected by the number of groups. Very accurate results are obtained on binary systems. As shown by (Jaubert & Privat, 2010), the accuracy of Soave's GCM - although not tested on many experimental data – is similar to what is observed with the PPR78 model. Whether a naphthenic group was added, this GCM could be applied to predict the phase behaviour of reservoir fluids.

5.3 k_{ij}(T) values: how to switch from a cubic EoS to another one?

As explained in the previous sections, the key point when using cubic EoS to describe complex mixtures like petroleum fluids is to give appropriate values to the binary interaction parameters (k_{ij}). We however know by experience that the k_{ij}, suitable for a given EoS (e.g. the PR EoS) cannot be directly used for another one (e.g. the SRK EoS). Moreover, numerical values of k_{ij} are not only specific to the considered EoS but they also depend on the alpha-function (Soave, Twu, Mathias-Copeman, etc.) involved in the mathematical expression of the a_i parameter. This assessment makes it impossible for petroleum engineers to use various equations of state and to test different alpha functions. Indeed, they usually have tables containing the numerical values of the k_{ij} only for the most widely used EoS and alpha function in their company. To overcome this limitation, (Jaubert & Privat, 2010) had the idea to establish a relationship between the k_{ij} of a first EoS (k_{ij}^{EoS1}) and those of a second one (k_{ij}^{EoS2}). As a consequence, knowing the numerical values of the k_{ij} for the first EoS makes it possible to deduce the corresponding values for any other cubic EoS. The obtained

relationship is given just below (Eq. (43)). To understand the notations, let us consider two cubic equations of state (EoS1 and EoS2) deriving from Van der Waals' equation i.e. having the general form given in Eq. (12). At this step, we define the following quantities:

$$
\begin{cases}
C_{EoS} = \dfrac{1}{r_1 - r_2} \cdot \ln\left(\dfrac{1 - r_2}{1 - r_1}\right) \text{ if } r_1 \neq r_2 \text{ and } C_{EoS} = \dfrac{1}{1 - r_1} \text{ if } r_1 = r_2 \\[3mm]
\xi_{1 \to 2} = \dfrac{C_{EoS1} \cdot \Omega_b^{EoS1}}{C_{EoS2} \cdot \Omega_b^{EoS2}} \\[3mm]
\delta_i^{EoS} = \dfrac{\sqrt{a_i^{EoS}}}{b_i^{EoS}}
\end{cases}
\tag{42}
$$

After some derivation, the obtained relationship is:

$$
k_{ij}^{EoS2} = \frac{2\xi_{1 \to 2} k_{ij}^{EoS1} \delta_i^{EoS1} \delta_j^{EoS1} + \xi_{1 \to 2}\left(\delta_i^{EoS1} - \delta_j^{EoS1}\right)^2 - \left(\delta_i^{EoS2} - \delta_j^{EoS2}\right)^2}{2\delta_i^{EoS2} \delta_j^{EoS2}}
\tag{43}
$$

Eq. (43) can also be used if we work with the same EoS (let us say the PR EoS) but if we decide to only change the $a_i(T)$ function (e.g. we initially work with a Soave-type function for which the k_{ij} are known and we decide to work with a Mathias and Copeman function for which the k_{ij} are unknown). In this latter case, $\xi_{1 \to 2} = 1$, but Eq. (43) in which the δ parameters depend on the $a(T)$ function will lead to a relationship between the k_{ij} to be used with the first $a(T)$ function and those to be used with the second one.

As previously explained, the PPR78 model is a GCM designed to predict the k_{ij} of the PR EoS. The coupling of this GCM with Eq. (43) makes it possible to predict the temperature-dependent k_{ij} of any desired EoS using the GC concept. Let us indeed consider a cubic EoS (see Eq. (12)) noted EoS1 hereafter, and let us define:

$$
\xi_{PR \to EoS1} = \frac{C_{PR} \cdot \Omega_b^{PR}}{C_{EoS1} \cdot \Omega_b^{EoS1}}
\tag{44}
$$

By combining Eqs. (35) and (43), we can write:

$$
k_{ij}^{EoS1}(T) = \frac{-\dfrac{1}{2}\left[\displaystyle\sum_{k=1}^{N_s}\sum_{l=1}^{N_s}(\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl})\xi_{PR \to EoS1} A_{kl}^{PR} \cdot \left(\dfrac{298.15}{T/K}\right)^{\left(\dfrac{B_{kl}^{PR}}{A_{kl}^{PR}} - 1\right)}\right] - \left(\dfrac{\sqrt{a_i^{EoS1}(T)}}{b_i^{EoS1}} - \dfrac{\sqrt{a_j^{EoS1}(T)}}{b_j^{EoS1}}\right)^2}{2\dfrac{\sqrt{a_i^{EoS1}(T) \cdot a_j^{EoS1}(T)}}{b_i^{EoS1} \cdot b_j^{EoS1}}}
\tag{45}
$$

Using Eq. (45), it is thus possible to calculate by GC, the temperature-dependent k_{ij} for any desired cubic EoS (EoS1), with any desired $a_i(T)$ function, using the group contribution parameters (A_{kl}^{PR} and B_{kl}^{PR}) we determined for the PPR78 model. Eq. (45) can also be used if we work with the PR EoS but with a different $a_i(T)$ function than the one defined by Eq. (10). In this latter case, $\xi_{PR \to EoS1} = 1$, but Eq. (45) will lead to k_{ij} values different of those

obtained from the PPR78 model. Eq. (45) was extensively used by (Jaubert & Privat, 2010) in the particular case where EoS1 is the SRK EoS. They concluded that the accuracy obtained with the SRK EoS was similar to the one obtained with the PPR78 model. The resulting model, based on the SRK EoS and for which the k_{ij} are estimated from the GCM developed for the PPR78 model was called PR2SRK. In conclusion, we can claim that the PPR78 model is a *universal* GCM since it can predict the k_{ij} for any desired EoS with any desired $a_i(T)$ function at any temperature for any mixture containing hydrocarbons, permanent gases, and water.

5.4 Other mixing rules

Cubic EoS with Van der Waals one-fluid mixing rules lead to very accurate results at low and high pressures for *simple* mixtures (few polar, hydrocarbons, gases). They also allow the prediction of many more properties than phase equilibria (e.g. excess properties, heat capacities, etc.). Such mixing rules can however not be applied with success to polar mixtures. In return, g^E models (activity-coefficient models) are applicable to low pressures and are able to correlate polar mixtures. It thus seems a good idea to combine the strengths of both approaches, i.e. the cubic EoS and the activity coefficient models and thus to have a single model suitable for phase equilibria of polar and non-polar mixtures and at both low and high pressures. This combination of EoS and g^E models is possible via the so-called EoS/g^E models which are essentially mixing rules for the energy parameter of cubic EoS. As explained in the recent book by (Kontogeorgis & Folas, 2010), the starting point for deriving EoS/g^E models is the equality of the excess Gibbs energies from an EoS and from an explicit activity coefficient model at a suitable reference pressure. The activity coefficient model may be chosen among the classical forms of molar excess Gibbs energy functions (Redlich-Kister, Margules, Wilson, Van Laar, NRTL, UNIQUAC, UNIFAC…). Such models are pressure-independent (they only depend on temperature and composition) but the same quantity from an EoS depends on pressure, temperature and composition explaining why a reference pressure needs to be selected before equating the two quantities. In order to avoid confusion, we will write with a special font ($\mathcal{G}^E$) the selected activity coefficient model and with a classical font (g^E) the excess Gibbs energy calculated from an EoS by:

$$\frac{g^E}{RT} = \sum_{i=1}^{p} z_i \cdot \ln\left(\frac{\hat{\varphi}_i}{\varphi_{pure\,i}}\right) \qquad (46)$$

where $\hat{\varphi}_i$ is the fugacity coefficient of component i in the mixture and $\varphi_{pure\,i}$ the fugacity coefficient of the pure compound. The starting equation to derive EoS/g^E models is thus:

$$\left[g^E / (RT) \right]_P = \mathcal{G}^E / (RT) \qquad (47)$$

where subscript *P* indicates that a reference pressure has to be chosen.

5.4.1 The infinite pressure reference

The basic assumption of the method is the use of the infinite pressure as the reference pressure.

5.4.1.1 The Huron-Vidal mixing rules

The first systematic successful effort in developing an EoS/g^E model is that of (Huron & Vidal, 1979). Starting from Eq. (47), they obtained:

$$\begin{cases} \dfrac{a(T,\mathbf{x})}{b(\mathbf{x})} = \displaystyle\sum_{i=1}^{p} x_i \dfrac{a_i(T)}{b_i} - \dfrac{G^E}{C_{EoS}} \\[2em] b(\mathbf{x}) = \displaystyle\sum_{i=1}^{p} x_i b_i \end{cases} \tag{48}$$

where C_{EoS} is defined by Eq. (42). A positive feature of the Huron-Vidal mixing rule includes an excellent correlation of binary systems. A limitation is that it does not permit use of the large collections of interaction parameters of G^E models which are based on low-pressure VLE data (e.g. the UNIFAC tables). Indeed, the excess Gibbs energy at high pressures is, in general, different from the value at low pressures at which the parameters of the G^E models are typically estimated.

5.4.1.2 The Van der Waals one-fluid (VdW1f) mixing rules

The classical VdW1f mixing rules used in the PPR78 and PR$_2$SRK model write:

$$a(T,\mathbf{x}) = \sum_{j=1}^{p} x_i x_j \sqrt{a_i a_j} \left[1 - k_{ij}(T) \right] \qquad \text{and} \qquad b(\mathbf{x}) = \sum_{i=1}^{p} x_i b_i \tag{49}$$

We here want to give proof that such mixing rules are in fact strictly equivalent to the Huron-Vidal mixing rules if a Van-Laar type G^E model is selected in Eq. (48). Indeed, by sending Eq. (49) in Eq. (48), one has:

$$\begin{aligned} \frac{G^E}{C_{EoS}} &= \sum_{i=1}^{p} x_i \frac{a_i(T)}{b_i} - \frac{a(T,\mathbf{x})}{b(\mathbf{x})} = \sum_{i=1}^{p} x_i \cdot \frac{a_i(T)}{b_i} - \frac{\displaystyle\sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \sqrt{a_i \cdot a_j} \cdot \left[1 - k_{ij}(T)\right]}{\displaystyle\sum_{j=1}^{p} x_j \cdot b_j} \\[2em] &= \frac{\displaystyle\sum_{i=1}^{p} x_i \cdot \frac{a_i(T)}{b_i} \times \sum_{j=1}^{p} x_j \cdot b_j - \sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \sqrt{a_i \cdot a_j} \cdot \left[1 - k_{ij}(T)\right]}{\displaystyle\sum_{j=1}^{p} x_j \cdot b_j} \end{aligned} \tag{50}$$

We can write:

$$\sum_{i=1}^{p} x_i \cdot \frac{a_i(T)}{b_i} \times \sum_{j=1}^{p} x_j \cdot b_j = \sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \frac{a_i \cdot b_j}{b_i} = \frac{1}{2}\sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \frac{a_i \cdot b_j}{b_i} + \frac{1}{2}\sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \frac{a_j \cdot b_i}{b_j} \tag{51}$$

Thus,

$$\frac{G^E}{C_{EoS}} = \frac{\sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \left[\frac{1}{2}\frac{a_i \cdot b_j}{b_i} + \frac{1}{2}\frac{a_j \cdot b_i}{b_j} - \sqrt{a_i \cdot a_j} \cdot \left[1 - k_{ij}(T)\right]\right]}{\sum_{j=1}^{p} x_j \cdot b_j}$$

$$= \frac{\sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \cdot b_i \cdot b_j \left[\frac{1}{2}\frac{a_i}{b_i^2} + \frac{1}{2}\frac{a_j}{b_j^2} - \frac{\sqrt{a_i}}{b_i}\cdot\frac{\sqrt{a_j}}{b_j} \cdot \left[1 - k_{ij}(T)\right]\right]}{\sum_{j=1}^{p} x_j \cdot b_j} \tag{52}$$

At this step, we introduce for clarity: $\delta_i = \sqrt{a_i}/b_i$ which has the Scatchard-Hildebrand solubility parameter feature, and we define the parameter E_{ij} by:

$$E_{ij} = \delta_i^2 + \delta_j^2 - 2\delta_i\delta_j\left[1 - k_{ij}(T)\right] \tag{53}$$

Eq. (52) thus writes:
$$\frac{G^E}{C_{EoS}} = \frac{1}{2}\cdot\frac{\sum_{i=1}^{p}\sum_{j=1}^{p} x_i \cdot x_j \cdot b_i \cdot b_j \cdot E_{ij}(T)}{\sum_{j=1}^{p} x_j \cdot b_j} \tag{54}$$

Eq. (54) is the mathematical expression of a Van Laar-type G^E model. We thus demonstrated that it is rigorously equivalent to use a Van Laar-type G^E model in the Huron-Vidal mixing rules or to use classical mixing rules with temperature-dependent k_{ij}. From Eq. (53) we have:

$$k_{ij}(T) = \frac{E_{ij}(T) - (\delta_i - \delta_j)^2}{2\delta_i\delta_j} \tag{55}$$

Eq. (55) thus establishes a connection between E_{ij} of the Van Laar-type G^E model and k_{ij} of the classical mixing rules.

5.4.1.3 The Wong-Sandler mixing rules

It can be demonstrated that the Huron Vidal mixing rules violate the imposed by statistical thermodynamics quadratic composition dependency of the second virial coefficient:

$$B = \sum_{i=1}^{p}\sum_{j=1}^{p} x_i x_j B_{ij} \tag{56}$$

To satisfy Eq. (56), (Wong and Sandler, 1992) decided to revisit the Huron-Vidal mixing rules. Since they made use of the infinite pressure as the reference pressure, like Huron and Vidal, they obtained:

$$a(T, \mathbf{x}) = b(\mathbf{x}) \sum_{i=1}^{p} x_i \frac{a_i(T)}{b_i} - \frac{G^E}{C_{EoS}} \tag{57}$$

However, knowing that the second virial coefficient from a cubic EoS is given as:

$$B = b - \frac{a}{RT} \tag{58}$$

eq. (56) writes:

$$b(\mathbf{x}) = \frac{a(T, \mathbf{x})}{RT} + \sum_{i=1}^{p} \sum_{j=1}^{p} x_i x_j B_{ij} \tag{59}$$

Substituting Eq. (57) in Eq. (59), we get:

$$b(\mathbf{x}) = \frac{\displaystyle\sum_{i=1}^{p} \sum_{j=1}^{p} x_i x_j B_{ij}}{1 + \dfrac{G^E}{C_{EoS}} - \displaystyle\sum_{i=1}^{p} x_i \dfrac{a_i(T)}{b_i}} \tag{60}$$

The following choice for the cross virial coefficient is often used:

$$B_{ij} = \frac{1}{2}(B_i + B_j)(1 - k_{ij}) \tag{61}$$

Eq. (61) makes unfortunately appear an extra binary interaction parameter (k_{ij}), the value of which can be estimated through various approaches.

Substituting Eq. (58) in Eq.(61), one has:

$$B_{ij} = \frac{\left(b_i - \dfrac{a_i}{RT}\right) + \left(b_j - \dfrac{a_j}{RT}\right)}{2}(1 - k_{ij}) \tag{62}$$

The Wang-Sandler mixing rules thus write:

$$\begin{cases} b(T, \mathbf{x}) = \dfrac{\displaystyle\sum_{i=1}^{p} \sum_{j=1}^{p} x_i x_j \dfrac{\left(b_i - \dfrac{a_i}{RT}\right) + \left(b_j - \dfrac{a_j}{RT}\right)}{2}(1 - k_{ij})}{1 + \dfrac{G^E}{C_{EoS}} - \displaystyle\sum_{i=1}^{p} x_i \dfrac{a_i(T)}{b_i}} \\ \\ a(T, \mathbf{x}) = b(\mathbf{x}) \displaystyle\sum_{i=1}^{p} x_i \dfrac{a_i(T)}{b_i} - \dfrac{G^E}{C_{EoS}} \end{cases} \tag{63}$$

We can thus conclude that the Wong-Sandler mixing rules differ from the Huron-Vidal mixing rules in the way of estimating the covolume. In Eq. (63), *b* has become temperature-

dependent. Many papers illustrate the key success of the Wong-Sandler mixing rules to predict VLE using existing low pressure parameters from activity coefficients models. However parameters for gas-containing systems are not available in activity coefficient models like UNIFAC which limits the applicability of these mixing rules to such systems.

5.4.2 The zero-pressure reference

The zero-pressure reference permits a direct use of G^E interaction parameter tables. Starting from Eq. (47) and by setting $P = 0$, one obtains:

$$
\begin{cases}
\dfrac{G^E}{RT} = Q(\alpha) - \sum_{i=1}^{p} x_i \cdot Q(\alpha_i) + \sum_{i=1}^{p} x_i \cdot \ln\left(\dfrac{b_i}{b}\right) \text{ with } \alpha = \dfrac{a}{bRT} \\[2mm]
Q(\alpha) = -\ln\left(\dfrac{1-\eta_0(\alpha)}{\eta_0(\alpha)}\right) - \dfrac{\alpha}{r_1 - r_2}\ln\left(\dfrac{1-\eta_0(\alpha)\cdot r_2}{1-\eta_0(\alpha)\cdot r_1}\right) \\[2mm]
\eta_0(\alpha) = \dfrac{r_1 + r_2 + \alpha + \sqrt{(r_1+r_2+\alpha)^2 - 4(r_1 r_2 + \alpha)}}{2(r_1 r_2 + \alpha)} \text{ submitted to: } \alpha \geq \alpha_{\lim} \\[2mm]
\alpha_{\lim} = -r_1 - r_2 + 2 + 2\sqrt{1 - r_1 - r_2 + r_1 r_2}
\end{cases}
\tag{64}
$$

After selecting a mixing rule for the covolume, Eq. (64) becomes an implicit mixing rule for the energy parameter, which means that an iterative procedure is needed for calculating the energy parameter.

5.4.2.1 The MHV-1 mixing rule

In order to obtain an explicit mixing rule and to address the limitation introduced by the presence of $\alpha_{\lim}$ (Michelsen, 1990) proposed to define a linear approximation of the Q function by:

$$
Q(\alpha) = q_0 + q_1 \cdot \alpha
\tag{65}
$$

Doing so, Eq. (64) writes:

$$
\alpha = \sum_{i=1}^{p} x_i \cdot \alpha_i + \frac{1}{q_1}\left[\frac{G^E}{RT} - \sum_{i=1}^{p} x_i \cdot \ln\left(\frac{b_i}{b}\right)\right]
\tag{66}
$$

Eq. (66) is the so called MHV-1 (modified Huron-Vidal first order) mixing rule usually used with a linear mixing rule for the covolume parameter. Michelsen advices to use $q_1 = -0.593$ for the SRK EoS, $q_1 = -0.53$ for the PR EoS and $q_1 = -0.85$ for the VdW EoS.

5.4.2.2 The PSRK model

(Holderbaum & Gmehling, 1991) proposed the PSRK (predictive SRK) model based on the MHV-1 mixing rule. These authors however use a slightly different q_1 value than the one proposed by Michelsen. They select: $q_1 = -0.64663$. In order to make their model predictive, Holderbaum and Gmehling combine the SRK EoS with a predictive G^E model (the original

or the modified Dortmund UNIFAC). Moreover they developed extensive parameter table, including parameters for gas-containing mixtures. The PSRK model may thus be used to model petroleum fluids. No comparison was performed between PSRK and PPR78 but we can expect similar results.

5.4.2.3 The UMR-PR and VTPR models

The UMR-PR (universal mixing rule-Peng Robinson) and the VTPR (volume translated Peng Robinson) models, both use the MVH-1 mixing rule. They were respectively developed by (Ahlers & Gmehling, 2001, 2002) and by (Voutsas et al., 2004). In both cases, the same translated form of the PR EoS is used. The Twu $a(T)$ function is however used in the VTPR model whereas the Mathias-Copeman expression is used in the UMR-PR model. Both models incorporate the UNIFAC G^E model in Eq. (66). However, in order to be able to properly correlate asymmetric systems, only the residual part of UNIFAC is used in the VTPR model. These authors indeed assume that the combinatorial part of UNIFAC and $\sum x_i \cdot \ln(b_i/b)$ in Eq. (66) cancel each other. In the UMR-PR model the residual part of UNIFAC but also the Staverman-Guggenheim contribution of the combinatorial term is used. These authors indeed assume that the Flory-Huggins combinatorial part of UNIFAC and $\sum x_i \cdot \ln(b_i/b)$ in Eq. (66) cancel each other. A novel aspect of these models is the mixing rule used for the covolume parameter. Both models give better results than PSRK. The equations to be used are:

$$\underline{\underline{VTPR:}}$$

$$\alpha = \sum_{i=1}^{p} x_i \cdot \alpha_i + \frac{1}{q_1}\left[\frac{G_{residual}^{E,UNIFAC}}{RT}\right] \tag{67}$$

$$b = \sum_{i=1}^{p}\sum_{j=1}^{p} x_i x_j b_{ij} \ \text{ with: } b_{ij} = \left(\frac{b_i^{1/s} + b_j^{1/s}}{2}\right) \text{ and } s = \frac{4}{3}$$

$$\underline{\underline{UMP-PR:}}$$

$$\alpha = \sum_{i=1}^{p} x_i \cdot \alpha_i + \frac{1}{q_1}\left[\frac{G_{residual}^{E,UNIFAC}}{RT} + \frac{G_{\text{Staverman-Guggenheim combinatorial contribution}}^{E,UNIFAC}}{RT}\right] \tag{68}$$

$$b = \sum_{i=1}^{p}\sum_{j=1}^{p} x_i x_j b_{ij} \ \text{ with: } b_{ij} = \left(\frac{b_i^{1/s} + b_j^{1/s}}{2}\right) \text{ and } s = 2$$

The mixing rule described by Eq. (67), was also applied to the SRK EoS (Chen et al., 2002) in order to define a new version of the PSRK model. In this latter case, the SRK EoS was combined with a Mathias-Copeman alpha function.

5.4.2.4 The LCVM model

The LCVM model (Boukouvalas et al., 1994) is based on a mixing rule which is a **L**inear **C**ombination of the **V**idal and **M**ichelsen (MHV-1) mixing rules:

$$\alpha_{LCVM} = \lambda \cdot \alpha_{Huron-Vidal} + (1 - \lambda) \cdot \alpha_{Michelsen} \tag{69}$$

From Eq. (48), one has:

$$\alpha_{Huron-Vidal} = \sum_{i=1}^{p} x_i \cdot \alpha_i - \frac{\mathcal{G}^E}{R \cdot T \cdot C_{EoS}} \tag{70}$$

whereas $\alpha_{Michelsen}$ is given by Eq. (66). The LCVM as used today is based on the original UNIFAC $\mathcal{G}^E$ model and the value $\lambda = 0.36$ should be used in all applications. Their authors use a translated form of the PR EoS and obtain accurate results especially for asymmetric systems.

5.4.2.5 The MHV-2 mixing rule

In order to increase the accuracy of the MHV-1 mixing rule, (Dahl & Michelsen, 1990) proposed a quadratic approximation of the Q function by:

$$Q(\alpha) = q_0 + q_1 \cdot \alpha + q_2 \cdot \alpha^2 \tag{71}$$

thus defining the MHV-2 model. It is advised to use $q_1 = -0.4783$ and $q_2 = -0.0047$ for the SRK EoS; $q_1 = -0.4347$ and $q_2 = -0.003654$ for the PR EoS. Doing so, Eq. (64) writes:

$$\frac{\mathcal{G}^E}{RT} = q_1 \left(\alpha - \sum_{i=1}^{p} x_i \cdot \alpha_i \right) + q_2 \left(\alpha^2 - \sum_{i=1}^{p} x_i \cdot \alpha_i^2 \right) + \sum_{i=1}^{p} x_i \cdot \ln\left(\frac{b_i}{b} \right) \tag{72}$$

Eq. (72) does not yield anymore to an explicit mixing rule but instead has to be solved in order to determine α. For such a mixing rule, parameter tables are available for many gases. As a general rule, MHV-2 provides a better reproduction of the low-pressure VLE data than MHV-1.

6. Energetic aspects: estimation of enthalpies from cubic EoS

Engineers use principles drawn from thermodynamics to analyze and design industrial processes. The application of the first principle (also named *energy rate balance*) to an open multi-component system at steady state writes:

$$\dot{W} + \dot{Q} = \sum \dot{n}_{out} h_{out} \quad - \quad \sum \dot{n}_{in} h_{in} \tag{73}$$

where $\dot{W}$ and $\dot{Q}$ are the net rates of energy transfer resp. by work and by heat; $\dot{n}$ is the molar flowrate and h denotes the molar enthalpy of a stream. Subscripts *in* and *out* resp. mean *inlet* and *outlet* streams. Note that kinetic-energy and potential-energy terms are supposed to be zero in Eq. (73). According to classical thermodynamics, the molar enthalpy of a *p*-component homogeneous system at a given temperature *T*, pressure *P* and composition **z** (mole fraction vector) is:

$$\underbrace{h(T,P,\mathbf{z})}_{\substack{\text{molar enthalpy} \\ \text{of an inlet or} \\ \text{an outlet stream}}} = \sum_{i=1}^{p} z_i \left[h_{pure\,i}(T,P) - h_{pure\,i}^{ref} \right] \quad + \quad h^M(T,P,\mathbf{z}) \tag{74}$$

wherein $h_{pure\,i}(T,P)$ is the molar enthalpy of pure component i at the same temperature and pressure as the mixture, $h_{pure\,i}^{ref}$ is the molar enthalpy of pure component i in its reference state, i.e. at a reference temperature T_{ref}, pressure P_{ref} and aggregation state. Note that this term is specific to each component i and does not depend on the temperature and pressure of the stream. $h^M(T,P,\mathbf{z})$ is the molar enthalpy change on isothermal and isobaric mixing. This section is dedicated to explain how to calculate these terms when a cubic equation of state (as defined in Eq. (12)) is used with Soave's alpha function (see Eq. (15)) and classical mixing rules involving a temperature-dependent k_{ij} (see Eq. (49)).

6.1 Calculation of pure-component enthalpies

At this step, the concept of *residual molar enthalpy* h^{res} needs to be introduced: h^{res} is a difference measure for how a substance deviates from the behaviour of a perfect gas **having the same temperature T** as the real substance. The molar enthalpy of a pure fluid can thus be written as the summation of the molar enthalpy of a perfect gas having the same temperature as the real fluid plus a residual term:

$$h_{pure\,i}(T,P) = h_{pure\,i}^{pg}(T) + h_{pure\,i}^{res}\left(T, v_{pure\,i}(T,P)\right) \tag{75}$$

where the superscript *pg* stands for *perfect gas*; $v_{pure\,i}(T,P)$ is the molar volume of the pure fluid i at temperature T and pressure P; it can be calculated by solving the cubic EoS (see Eq. (13)) at given T and P. Since cubic EoS are explicit in pressure (i.e. they give the pressure as an explicit function of variables T and v), the expression of the residual molar enthalpy can be naturally written in variables T and v:

$$h_{pure\,i}^{res}(T,v) = \frac{RTb_i}{v - b_i} - \frac{a_i(T)\,v}{(v - r_1 b_i)(v - r_2 b_i)} + \frac{1}{b(r_1 - r_2)} \left(a_i - T \frac{da_i}{dT} \right) \cdot \ln\left(\frac{v - r_1 b_i}{v - r_2 b_i} \right) \tag{76}$$

If employing Soave's alpha function, then:

$$\frac{da_i}{dT} = -a_{c,i} m_i \left[1 + m_i \left(1 - \sqrt{T / T_{c,i}} \right) \right] / \sqrt{T \cdot T_{c,i}} \tag{77}$$

Finally, according to Eq. (75), the difference of pure-fluid enthalpy terms in Eq. (74) writes:

$$\begin{aligned} h_{pure\,i}(T,P) - h_{pure\,i}^{ref} = & \left[h_{pure\,i}^{pg}(T) - h_{pure\,i}^{pg}\left(T_{ref}\right) \right] \\ & + \left[h_{pure\,i}^{res}\left(T, v_{pure\,i}(T,P)\right) - h_{pure\,i}^{res}\left(T, v_{pure\,i}(T_{ref}, P_{ref})\right) \right] \end{aligned} \tag{78}$$

wherein the h_i^{res} function is given by Eq. (76). Let us recall that:

$$\left[h_{pure\,i}^{pg}(T) - h_{pure\,i}^{pg}\left(T_{ref}\right) \right] = \int_{T_{ref}}^{T} c_{P,pure\,i}^{pg}(T)\,dT \tag{79}$$

where $c_{P,i}^{pg}(T)$ denotes the molar heat capacity at constant pressure of the pure perfect gas i.

6.2 Calculation of the enthalpy change on mixing

By definition, the molar enthalpy change on mixing h^M is the difference between the molar enthalpy of a solution and the sum of the molar enthalpies of the components which make it up, all at the same temperature and pressure as the solution, *in their actual state* (see Eq. (74)) weighted by their mole fractions z_i. Consequently to this definition, h^M can be expressed in terms of residual molar enthalpies:

$$h^M(T,P,\mathbf{z}) = h^{res}(T,v,\mathbf{z}) - \sum_{i=1}^{p} z_i\, h^{res}_{pure\,i}(T,v_{pure\,i}(T,P)) \tag{80}$$

where v is the molar volume of the mixture at T, P and $\mathbf{z}$. To calculate this molar volume, Eq. (13) has to be solved. The residual molar enthalpy of pure component i is given by Eq. (76) and the residual molar enthalpy of the mixture is given by Eq. (81):

$$h^{res}\left(T,v,\mathbf{z}\right) = \frac{RT\,b(\mathbf{z})}{v-b(\mathbf{z})} - \frac{a(T,\mathbf{z})\,v}{\left[v-r_1b(\mathbf{z})\right]\left[v-r_2b(\mathbf{z})\right]} + \frac{1}{b(\mathbf{z})\left(r_1-r_2\right)}\left[a(T,\mathbf{z}) - T\left(\frac{\partial a}{\partial T}\right)_{\mathbf{z}}\right]\cdot\ln\left[\frac{v-r_1b(\mathbf{z})}{v-r_2b(\mathbf{z})}\right] \tag{81}$$

If classical mixing rules with temperature-dependent k_{ij} are considered, then:

$$\left(\frac{\partial a}{\partial T}\right)_{\mathbf{z}} = \sum_{i=1}^{p}\sum_{j=1}^{p} z_i z_j \left[\left[1-k_{ij}(T)\right]\frac{a_j(T)\cdot\frac{da_i}{dT} + a_i(T)\cdot\frac{da_j}{dT}}{2\sqrt{a_i(T)a_j(T)}} - \frac{dk_{ij}}{dT}\sqrt{a_i(T)a_j(T)}\right] \tag{82}$$

From Eqs. (80), (81) and (82), it appears that the use of a temperature-dependent k_{ij} allows a better flexibility of the h^M function (see the term dk_{ij}/dT in Eq. (82)). As a consequence, a better accuracy on the estimation of the molar enthalpies is expected when temperature-dependent k_{ij} rather than constant k_{ij} are used.

6.3 Practical use of enthalpies of mixing and illustration with the PPR78 model

As previously explained, the molar enthalpy of a multi-component phase is obtained by adding a pure-component term and a molar enthalpy change on mixing term (see Eq. (74)). When molecules are few polar and few associated (and this is often the case within petroleum blends), pure-component terms provide an excellent estimation of the molar enthalpy of the mixture. Therefore, the enthalpy-of-mixing term can be seen as a correction, just aimed at improving the first estimation given by pure-component ground terms. In other words, with few-polar and few-associated molecules, h^M terms are generally nearly negligible with respect to pure-component terms in the energy rate balance. Typically, h^M terms are very small in alkane mixtures and are not negligible in petroleum mixtures containing CO_2, H_2O or alcohols. When parameters involved in k_{ij} correlations are not directly fitted on enthalpy-of-mixing data (and this is, for instance, the case with the PPR78 model), the relative deviations between calculated and experimental h^M data can be very important and reach values sometimes greater than 100 %. However, as explained in the

introduction part of this section, since h^M quantities are only used to evaluate the molar enthalpies, h_{in} and h_{out}, involved in the energy rate balance, only absolute deviations and their effect on the accuracy of the energy balance are of interest. When experimental and calculated h^M values are very low (typically < 100 J/mol), the energy rate balance is not significantly affected by high relative deviations. On the contrary, if h^M values are very important (e.g. > 3000 J/mol), important absolute deviations on h^M can have a detrimental impact on the energy rate balance even if the corresponding relative deviation remains low. Note that in such a case, h^M terms can become dominant with respect to pure-component enthalpy terms. As an illustration, the PPR78 was used to predict isothermal and isobaric curves h^M vs. z_1 of two binary mixtures: n-hexane + n-decane and N_2 + CO_2 (see Figure 4).
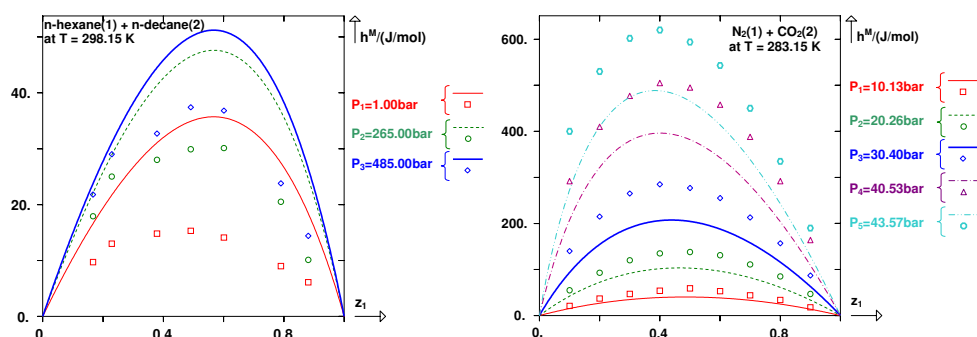
Fig. 4. Representation of molar enthalpy change on isothermal isobaric mixing vs. mole fraction z_1. *Symbols:* experimental data. *Full lines:* predicted curves with the PPR78 model.

One observes that enthalpies of mixing of an alkane mixture (not too much dissymmetric in size) are very low. The PPR78 model predicts h^M with an acceptable order of magnitude (and as a consequence, only pure-component enthalpy terms will govern the energy rate balance). Regarding the binary mixture N_2 + CO_2, it clearly appears that the orders of magnitude of h^M are around ten times bigger than those with the n-hexane + n-heptane system. Deviations between predicted values and experimental data are around 100 – 150 J/mol at the most, which remains acceptable and should very few affect the energy rate balance. When at the considered temperature and pressure, a liquid-vapour phase equilibrium occurs, the corresponding h^M vs. z_1 curve is made up of three different parts: a homogeneous liquid part, a liquid-vapour part and a homogeneous gas part. The liquid-vapour part is a straight line, framed by the two other parts. Figure 5 gives an illustration of the kind of curves observed in such a case. For system exhibiting vapour-liquid equilibrium (VLE) at given T and P, it is possible to show that the essential part of the enthalpy-of-mixing value is due to the vaporization enthalpies of the pure compounds. As a consequence, a good agreement between experimental and predicted h^M vs. z_1 curves of binary systems exhibiting VLE, mainly attests of the capacity of the EoS to model vaporization enthalpies of pure components rather than its capacity to estimate h^M.
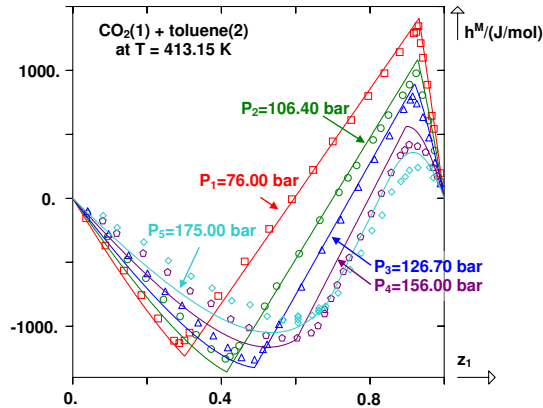
Fig. 5. System $CO_2(1)$ + toluene(2): representation of molar enthalpy change on isothermal isobaric mixing vs. mole fraction z_1. *Symbols:* experimental data. *Full lines:* predicted curves with the PPR78 model.

7. Prediction of the thermodynamic behaviour of petroleum fluids

Dealing with petroleum fluids, many difficulties appear. Indeed, such mixtures contain a huge number of various compounds, such as paraffins, naphthenes, aromatics, gases (CO_2, H_2S, N_2, …), mercaptans and so on. A proper representation involves to accurately quantifying the interactions between each pair of molecules, which is obviously becoming increasingly difficult if not impossible as the number of molecules is growing. To avoid such a fastidious work, an alternative solution lies in using a predictive model, able to estimate the interactions from mere knowledge of the structure of molecules within the petroleum blend. For this reason, it is advised to use predictive cubic EoS (PPR78, PR2SRK, PSRK) to model petroleum fluid phase behaviour. As an illustration of the capabilities of such models, some phase envelops of petroleum fluids predicted with the PPR78 model are shown and commented hereafter.

7.1 Prediction of natural gases

As an example, (Jarne et al., 2004) measured 110 upper and lower dew-point pressures for two natural gases containing nitrogen, carbon dioxide and alkanes up to n-C_6. The composition of the fluids and the accuracy of the PPR78 model can be seen in Figure 6. The average deviation on these 110 pressures is only 2.0 bar which is close to the experimental uncertainty.
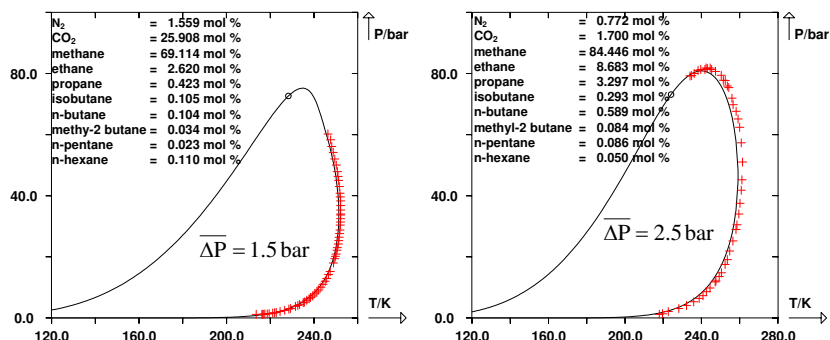
Fig. 6. Solid line: (P,T) phase envelopes of Jarne et al.'s natural gases predicted with the PPR78 model. +: experimental upper and lower dew-point pressures. ○: predicted critical point.

7.2 Prediction of gas condensates

(Gozalpour et al., 2003) measured 6 dew-point pressures for a gas condensate containing 5 normal alkanes ranging from methane to n-hexadecane. Figure 7 puts in evidence that with an average deviation of 3.0 %, the PPR78 model is able to accurately predict these data.
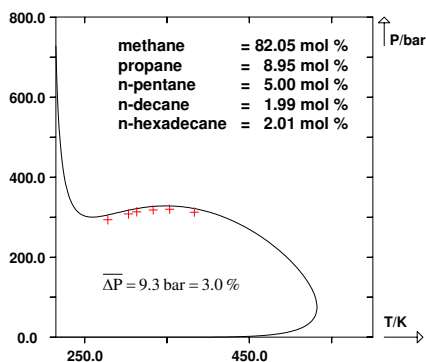
Fig. 7. Solid line: (P,T) phase envelope of Gozalpour et al.'s gas condensates predicted with the PPR78 model. +: experimental dew-point pressures. ○: predicted critical point.

7.3 Prediction of gas injection experiments

(Turek et al., 1984) performed swelling tests at two temperatures on a crude oil containing 10 n-alkanes ranging from methane to n-tetradecane. The injected gas is pure CO_2. 22 mixture saturation pressures were measured. The composition of the crude oil along with the accuracy of the PPR78 model to predict these data are shown in Figure 8. With an average deviation of 2.8 bar (i.e. 2.3 %), we can conclude that the PPR78 model is able to predict these data with high accuracy. It is here important to recall that no parameter is fitted on the experimental data.
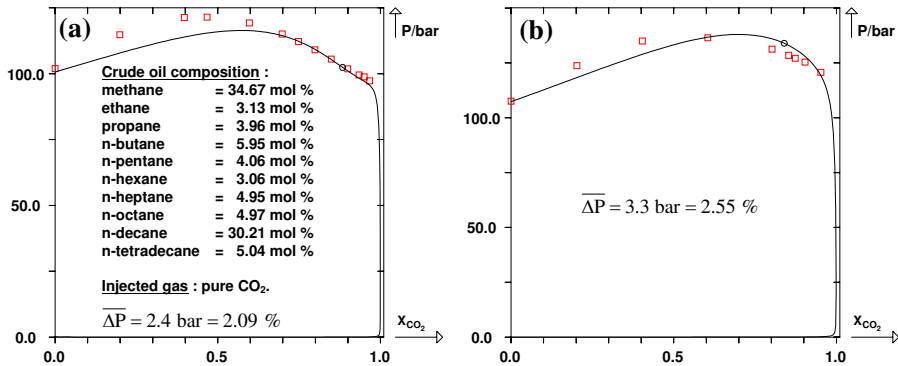
Fig. 8. Solid line: variation of mixture saturation pressure with added CO_2 to a synthetic crude oil (swelling test) predicted with the PPR78 model. a) T/K = 322 and b) T/K = 338.7. b): experimental bubble-point and dew-point pressures. ○: predicted critical point.

8. Conclusion

A complete account of all cubic equations of state is not easy to provide; however, according to (Valderrama, 2003), it is not adventurous to estimate that there must be about 150 RK-type equations and a total of 400 cubic EoS proposed to date in the literature. There are in general small differences in the VLE correlation among all these cubic EoS provided the same way of obtaining the pure parameters and the same mixing/combining rules are used. This is why, in the petroleum industry, only two cubic EoS are generally used: the SRK and the PR EoS. Such cubic EoS have many advantages but also shortcomings. The main advantages are:

- they are simple and capable of fast calculations
- they apply in both liquid and vapour phases
- they are applicable over wide ranges of pressures and temperatures
- they allow a good correlation for non-polar systems encountered in the petroleum industry
- they estimate accurate densities if a volume translation is used
- accurate correlations and GCM are available to estimate the k_{ij}

The outstanding book by (Kontogeorgis & Folas, 2010), cites the following sentence by (Tsonopoulos & Heidman, 1986) which summarizes well the advantages of such models: *cubic EoS are simple, reliable, and allow the direct incorporation of critical conditions. We, in the petroleum industry, continue to find that simple cubic EoS such as RKS and PR are very reliable high-pressure VLE models, and we have not yet found in our work any strong incentive for using non-cubic EoS*. Among the shortcomings, we can cite:

- often a temperature-dependent interaction parameter is needed
- poor correlation of polar/associating systems. The use of two interaction parameters (k_{ij} and l_{ij}) highly improves the results but such parameters can not be easily estimated knowing only the structure of the molecules
- Unsatisfactory correlation of LLE especially with highly immiscible systems (e.g. water or glycols with alkanes)

To conclude, predictive cubic EoS (PPR78, PR2SRK, PSRK, VTPR, UMR-PR) make a perfect job to simulate the phase behaviour of crude oils, gas condensate and natural gases. For processes in which water and/or glycol are present (e.g. transportation processes), it is advised to use more complex EoS like the CPA (Cubic-Plus-Association) by (Derawi et al., 2003) or equation deriving from the SAFT (Statistical Associating Fluid Theory) which are however non predictive (many parameters have to be fitted on experimental data).

9. Acknowledgment

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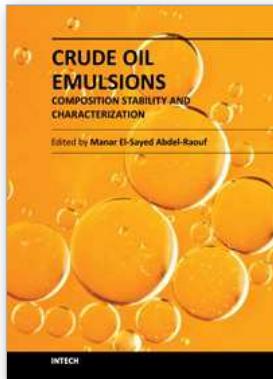
Crude Oil Emulsions- Composition Stability and Characterization

Edited by Prof. Manar El-Sayed Abdul-Raouf

Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

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