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A new formulation of the predictive NRTL-PR model in terms of $k_{ij}$ mixing rules. Extension of the group contributions for the modeling of hydrocarbons in the presence of associating compounds

Joan Escandell$^a$, Evelyne Neau$^{a,*}$, Christophe Nicolas$^b$

$^a$ Laboratory M2P2, UMR 6181, University of Méditerranée, Faculty of Sciences of Luminy, 13288 Marseille, France
$^b$ Laboratory LMGEM, UMR 6117, University of Méditerranée, Faculty of Sciences of Luminy, 13288 Marseille, France

A generalized NRTL model was previously proposed for the modeling of non ideal systems and was extended to the prediction of phase equilibria under pressure according to the cubic NRTL-PR EoS. In this work, the model is reformulated with a predictive $k_{ij}$ temperature and composition dependent mixing rule and new interaction parameters are proposed between permanent gases, ethane and nitrogen with hydrocarbons, ethane with water and ethylene glycol. Results obtained for excess enthalpies, liquid–vapor and liquid–liquid equilibria are compared with those provided by the literature models, such as VTPR, PPR78, CPA and SRKm. A wide variety of mixtures formed by very asymmetric compounds, such as hydrocarbons, water and ethylene glycols are considered and special attention is paid to the evolution of $k_{ij}$ with respect to mole fractions and temperature.

1. Introduction

The description of phase equilibria occurring in complex systems such as petroleum fluids with water or glycol has become more and more important with the exploitation of reservoirs in extreme conditions. Besides theoretical association models, such as SAFT (Statistical Associating Fluid Theory) [1,2] CPA (Cubic Plus Association) [3] or the predictive QC-GEOs [4] equations, simple models based on the cubic Redlich–Kwong or Peng–Robinson EoS still represent a great interest for industrial applications.

In particular, petroleum industry currently describes phase equilibria by means of cubic EoS based on the EoS/C$^G$ approach; among them: the PPR78 (Predictive Peng–Robinson 1978) EoS [5] has gained an unquestionable success for the prediction of the binary interaction parameter $k_{ij}$ of nonpolar compounds, while the VTPR [6] (Volume Translated Peng–Robinson) model based on the UNIFAC group contribution model appears to be one of the most reliable simple model for the prediction of thermodynamic properties for a wide series of mixtures, involving solids and electrolytes. Nevertheless, these models appear not to be appropriate for the description of strong demixings occurring in mixtures containing water or glycols with hydrocarbons.

Due to these limitations, the modeling of reservoir fluids in the presence of associating compounds is mainly performed with empirical composition dependent mixing rules, such as the SRKm (Soave–Redlich–Kwong modified) and SRK-KD equations, respectively, proposed by Panagiotopoulos and Reid [7] and Kabadi and Danner [8]. The main interest of this correlation relies on the extensive set of interaction parameters available in industrial simulators, in particular for water–hydrocarbon mixtures; however, no specific parameters were developed for glycol–hydrocarbon systems, which are therefore modeled with standard values. In addition, the SRKm mixing rule suffers from the Michelsen–Kirstenmacher syndrome [9] which might affect the representation of highly dilute mixtures.

The NRTL-PR [10] equation of state was thus developed to provide a simple cubic EoS allowing a full prediction of phase equilibria occurring in highly nonideal systems. The model is based on the EoS/C$^G$ approach, in which the Peng–Robinson equation of state is associated with a generalized version of the NRTL model [11].

In this work, the model is reformulated with predictive $k_{ij}$ temperature and composition dependent mixing rules and new interaction parameters are proposed between permanent gases, ethane and nitrogen with hydrocarbons, ethane with water and ethylene glycol. Results obtained for excess enthalpies, liquid–vapor and liquid–liquid equilibria with the NRTL-PR group contributions are compared with those provided by the literature...
cubic models commonly used in petroleum industry. A wide variety of mixtures formed by very asymmetric compounds, such as hydrocarbons, water and ethylene glycols are considered and special attention is paid to the evolution of \( k_{ij} \) with respect to mole fractions and temperature.

2. The predictive NRTL-PR model with \( k_{ij} \) mixing rules

The NRTL-PR equation is based on the Peng–Robinson EoS [12]:

\[
P = \frac{RT}{v} - \frac{a}{\nu^2 + 2b\nu - b^2}
\]

For pure components, the attractive term \( a \) and the co-volume \( b \) are obtained with the critical properties \( T_c \) and \( P_c \) according to:

\[
a = a_c \alpha(T), \quad a_c = 0.45723553 \frac{RT_c^2}{P_c}, \quad b = 0.07779607 \frac{RT_c}{P_c}
\]

Concerning the \( \alpha(T) \) function, a theoretical analysis [13,14] based on the comparison of various literature expressions has shown that the Soave function leads to the most consistent behaviour in the range of temperature and pressures covered by industrial applications. The generalized Soave type function proposed by Robinson and Peng [15] was considered:

\[
\alpha(T) = \left[ 1 + m \left( 1 - \frac{T}{T_c} \right) \gamma \right]^2, \quad \text{with} \quad \gamma = 0.5
\]

and:

\[
m = 0.37464 + 1.54226(\alpha - 0.26992\omega^2) \quad \text{if} \quad \omega \approx 0.49
\]

\[
m = 0.379642 + 1.48503(\alpha - 0.164423\omega^2 + 0.016666\omega^3) \quad \text{if} \quad \omega > 0.49
\]

For mixtures, the attractive NRTL-PR term in Eq. (1) is expressed, either from the “EoS/GE” approach, as proposed in the original paper [10], or from a “\( k_{ij} \)” mixing rule, as is developed in this work. Hence:

(a) The alpha function \( \alpha \) is estimated using the approach based on the reference state recently developed in [16] (Appendix A):

\[
\alpha = \sum \frac{x_i \alpha_i}{C} \left[ \frac{E_{\text{NRTL-gen}}}{RT} - \sum \frac{x_i \ln \frac{P_i}{r}}{R} \right],
\]

\[
r = \sum x_i r_i, \quad C = 0.53
\]

where \( C \) is the reference state constant and \( r_i \) are the volume area factors characteristic of lattice fluid models; \( E_{\text{NRTL-gen}} \) is the generalized NRTL excess Gibbs energy proposed in [10]:

\[
E_{\text{NRTL-gen}} = RT \sum x_i \ln \frac{P_i}{r} + \sum x_i q_i G_{ij} \Gamma_{ji} / \sum x_i q_i G_{ii},
\]

\[
G_{ji} = \exp \left( \frac{\alpha_0 \Gamma_{ji} - RT}{RT} \right),
\]

where \( \Gamma_{ji} \) is the binary interaction parameter between molecules \( i \) and \( j \); \( \alpha_0 \) is the non randomness factor considered as a constant; \( q_i \) are the lattice fluid surface area factors.

The use of a linear dependence of the co-volume \( b \) with respect to mixture mole fractions leads to the NRTL-PR attractive term expressed as follows:

\[
a = abRT = b \left[ \sum x_i \frac{a_i}{b_i} - \sum x_i q_i G_{ji} \Gamma_{ji} / C \right],
\]

\[
b = \sum x_i b_i
\]

(b) In this work, the attractive term is also expressed in terms of a van der Waals type mixing rule:

\[
a = \sum x_i x_j \sqrt{a_i a_j} (1 - k_{ij})
\]

using, as demonstrated in Appendix B, the following temperature and composition dependent expression for the \( k_{ij} \) parameters:

\[
k_{ij} = k_{ij}^{(0)} + \rho_{ij}^{(0)} \left( \frac{b}{\sum x_i q_i G_{ii}} \right) + \rho_{ij}^{(0)} \left( \frac{b}{\sum x_i q_i G_{ii}} \right) = k_{ij}
\]

in which:

\[
k_{ij}^{(0)} = k_{ij}^{(0)} - \frac{(\delta_{ij} - \delta_{ij})^2}{2b_{ij}}, \quad \delta_{ij} = \sqrt{\frac{\omega_i}{\omega_j}}
\]

\[
\rho_{ij}^{(0)} = \frac{G_{ij} \Gamma_{ji} / C}{\sum x_i q_i G_{ii}} \quad \rho_{ij}^{(0)} = \frac{G_{ij} \Gamma_{ji} / C}{\sum x_i q_i G_{ii}} \quad \delta_{ij} = \sqrt{\frac{\omega_i}{\omega_j}}
\]

To provide a completely predictive version, the following parameter estimations have been proposed [10]:

- The surface area parameters \( q_i \) (Eqs. (9) and (10)) are estimated from the UNIFAC [17] subgroups \( Q_k \):

\[
q_i = \sum x_i Q_k
\]

where \( Q_k \) is the number of subgroup \( k \) in a molecule \( i \); for methane, carbon dioxide, nitrogen, hydrogen sulfide and ethylene glycol, the \( Q_k \) values of Holdelaun and Gmelning [18] and Skjold-Jorgensen et al. [19] were respectively considered (Table 1).

- The non randomness factor in Eq. (6) is fixed to the value \( \omega_0 = -1 \) as suggested by Marina and Tassios [20] for the modeling of strongly nonideal mixtures.

- The binary interaction parameters \( \Gamma_{ji} \) (Eqs. (7) and (10)) are estimated according to the following group contribution method:

\[
\Gamma_{ji} = -\sum K_{ik} \left( \theta_{ik} - \theta_{ik} \right) \Gamma_{ik}, \quad \Gamma_{kk} = 0
\]

where:

\[
\theta_{ik} = \frac{\sum x_i q_i Q_k}{q_i}
\]

Table 1

| Main groups K | Subgroups k | \( Q_k \) |
|--------------|-------------|----------|
| Paraffins    | PAR         | 0.848    |
|              | CH0         | 0.540    |
|              | CH1         | 0.600    |
|              | CH2         | 0.540    |
|              | CH3         | 0.228    |
|              | CH4         | 0.060    |
| Aromatics    | ARC         | 0.400    |
|              | C           | 0.120    |
| Ethane       | C2H6        | 1.224    |
| Ethylene glycol | MEG      | 1.400    |
| Methane      | C2H5        | 0.491    |
| Methanol     | C2H5OH      | 2.248    |
| Methanol     | C2H5OH      | 2.248    |
Fobj aqueous and ethylene glycol binary systems. The objective function for binary systems, the model is totally predictive (Table 1). Terms together with the global deviation values; for paraffin–paraffin systems, the NRTL-PR model predicts more important values of group interaction parameters (Table 2); hence, a variation of \( \Delta_i \) can be observed with respect to mole fractions, particularly in the vicinity of pure carbon dioxide.

\[
\Delta_i = \left( \frac{T}{T_0} - 1 \right) \quad (14)
\]

where \( T_0 \) is a reference temperature, arbitrarily chosen as 298.15 K.

The list of main groups and subgroups considered in this work is given in Table 1, while the values of the group interaction parameters \( \Gamma_{LK}^{(0)} \) and \( \Gamma_{LK}^{(1)} \) are detailed, respectively, in Tables 2a and 2b. It can be seen that:

- As in the UNIFAC model, no interactions are considered between subgroups belonging to the same main group, so that the modeling of paraffin mixtures requires no interaction energies (\( \Delta_i^{(0)} = 0 \)).

- Interaction parameters \( \Gamma_{LK} \) are assumed symmetric (\( \Gamma_{KL} = \Gamma_{LK} \)), except if only one of these groups is water or ethylene glycol.

Group parameters were fitted to a set of about 700 hydrocarbon binary systems (400 VLE and 300 excess enthalpies) and 70 LLE of aqueous and ethylene glycol binary systems. The objective function minimized was:

\[
F_{obj} = \frac{1}{N_p} \sum_{i} \left[ \Delta P_i P_i + \frac{1}{N_y} \sum_{j} \Delta y_j y_j + \frac{1}{N_h} \sum_{k} \Delta h_k h_k + \frac{1}{N_{2h}} \sum_{l} \Delta x_{2h}^l x_{2h}^l \right] + \frac{1}{N_{d}} \sum_{m} \Delta x_{d}^m x_{d}^m \quad (15)
\]

where \( \Delta P, \Delta y \) and \( \Delta h \) are, respectively, the deviations on bubble points, vapor mole fractions and excess enthalpies; \( \Delta x_{2h}^l \) and \( \Delta x_{d}^m \) are the deviations on the mole fraction of the dilute component, respectively, in the hydrocarbon (H) and polar (I) phases; \( N_p, N_y, N_h, N_{2h} \) and \( N_d \) are the numbers of data points for each function. Tables 3a and 3b give the detailed information on the data base considered for the estimation of the group contribution parameters together with the global deviation values; for paraffin–paraffin binary systems, the model is totally predictive (\( \Gamma_{KI} = \Gamma_{IK} = 0 \)), so that \( \Delta P, \Delta y \) are not indicated in Table 3a; for excess enthalpies, \( \Delta h \) values are usually meaningless and were not reported (Section 3.3).

### 3. Hydrocarbons and permanent gases

These mixtures are of great interest for petroleum industry and are commonly modeled with predictive models based on simple cubic EoS. The purpose of this section is to compare the behaviour of the proposed \( k_i \) NRTL-PR mixing rule with the PPR78 [5] and VTPR [6] models.

#### 3.1. Mole fraction and temperature dependence of \( k_i \) parameters

Fig. 1a illustrates NRTL-PR predictions of the \( k_i \) parameters with respect to mole fractions at a given temperature (\( T_0 = 300 \) K) and calls the following remarks:

- For cyclohexane–benzene and cyclohexane–eicosane systems, group interaction parameters \( \Gamma_{KI}^{(0)} \) and \( \Gamma_{KI}^{(1)} \) have very moderate values (Table 2), so that molecular interactions \( \Gamma_{ij} \) are almost negligible; hence, according to Appendix C (Eqs. (A3.1) and (A3.2)), the \( k_i \) parameters are practically independent on mixture mole fractions. For paraffin mixtures, which require no interaction energies (\( \Delta_i = 0 \)), the \( k_i \) parameters will be obviously strictly constant.

- For carbon dioxide–cyclohexane and carbon dioxide–eicosane systems, the NRTL-PR model predicts more important values of group parameters \( \Gamma_{KI} \) (Table 2); hence, a variation of \( k_i \) can be observed with respect to mole fractions, particularly in the vicinity of pure carbon dioxide.

Nevertheless, the observed variations of the \( k_i \) parameters at a given temperature are always extremely moderate, which presumes that the proposed NRTL-PR model and the PPR78 EoS with constant \( k_i \) values (Appendix C) should yield very close modeling of phase equilibria.

Fig. 1b shows the variation of \( k_i \) with respect to temperature, for the same systems at a given mole fraction (\( x_0 = 0.5 \)). In the current range of industrial applications (200–900 K), the \( k_i \) parameters are almost independent on mixture mole fractions. For paraffin mixtures, which require no interaction energies (\( \Delta_i = 0 \)), the \( k_i \) parameters will be obviously strictly constant.

Table 2a
NRTL-PR group interaction parameters \( \Gamma_{KI}^{(0)} \) (in J mol\(^{-1}\)).

| L | K | PAR | CYC | ARO | CH₄ | C₂H₆ | CO₂ | N₂ | H₂S | H₂O | MEG |
|---|---|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|
| PAR | 0.00 | 57.25 | 220.63 | 147.46 | 48.26 | 866.65 | 523.57 | 733.34 | 3258.30 | 2802.32 |
| CYC | 220.63 | 57.25 | 249.71 | 283.73 | 71.67 | 862.31 | 1035.59 | 731.54 | 3140.65 | 2768.55 |
| ARO | 147.46 | 249.71 | 0.00 | 555.61 | 552.46 | 820.70 | 1476.84 | 77.16 | 2792.91 | 2303.32 |
| CH₄ | 48.26 | 283.73 | 555.61 | 0.00 | 73.03 | 791.11 | 434.39 | 796.08 | 3300.41 | 3239.78 |
| C₂H₆ | 866.65 | 820.70 | 748.07 | 791.11 | 0.00 | 745.75 | 743.35 | – | – | – |
| CO₂ | 523.57 | 1035.59 | 1476.84 | 731.54 | 0.00 | 1670.19 | – | – | – | – |
| N₂ | 733.34 | 731.54 | 77.16 | 1016.15 | 796.08 | 743.35 | – | – | – | – |
| H₂S | 2387.95 | 2412.64 | 2343.02 | 2305.94 | 2265.04 | – | – | – | – | – |
| H₂O | 836.31 | 834.63 | 519.20 | 1281.26 | 881.95 | – | – | – | – | – |
| MEG | – | – | – | – | – | – | – | – | – | – | – |

Table 2b
NRTL-PR group interaction parameters \( \Gamma_{KI}^{(1)} \) (in J mol\(^{-1}\)).

| L | K | PAR | CYC | ARO | CH₄ | C₂H₆ | CO₂ | N₂ | H₂S | H₂O | MEG |
|---|---|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|
| PAR | 0.00 | –72.22 | 270.25 | 13.32 | –137.36 | 609.93 | 569.62 | –227.73 | –145.24 | –335.72 |
| CYC | –72.22 | 0.00 | 191.29 | 294.52 | 934.25 | 1491.76 | 1951.96 | –247.07 | –879.36 | 918.64 |
| ARO | 13.32 | 294.52 | –161.30 | 0.00 | 8.34 | 308.54 | –41.31 | –166.44 | –2007.73 | –550.04 |
| CH₄ | –137.36 | –172.44 | 934.25 | 8.34 | 0.00 | 526.65 | –18.84 | 120.77 | –825.32 | –5709.15 |
| C₂H₆ | 609.93 | 1491.76 | 308.54 | 526.65 | 0.00 | 165.42 | 368.65 | – | – | – |
| CO₂ | 59.69 | 1368.43 | 1953.96 | –4.31 | –18.84 | 165.42 | 0.00 | –171.30 | – | – |
| N₂ | –227.73 | 579.78 | –247.07 | –166.44 | 120.77 | –368.65 | –171.30 | 0.00 | – | – |
| H₂S | –3579.09 | –3871.15 | –2743.07 | –4185.03 | –3944.30 | – | – | – | 0.00 | –718.31 |
| H₂O | –1060.28 | –610.97 | –2048.06 | –1033.41 | 1527.06 | – | – | – | – | 0.00 |
parameters are rather constant for hydrocarbon mixtures; for systems containing carbon dioxide, a stronger variation is noticed with, according to Coutinho et al. [22], a minimum located about $T = 350 \, \text{K}$.

3.2. Vapor–liquid equilibrium (VLE) for binary systems

Deviations on bubble point pressures calculated with the PPR78, VTPR and NRTL-PR models for some binary mixtures are reported in Table 4; systems considered in this table were selected as the most representative of the results obtained for the modeling of the whole data set (Table 3a). As could be expected, the global deviations are close for all three models; indeed:

- Both VTPR and NRTL-PR equations derive from the “two-fluid” theory and express interactions $F_{ij}$ with group contributions depending only on main groups (Table 2).

- Even if the PPR78 equation is based on the “one-fluid” theory and makes use of numerous group interaction parameters, the model leads, for these systems, to a $k_{ij}$ behaviour very close to the one observed with the NRTL-PR equation (Fig. 1).

| Systems       | VLE | $N_{bs}$ | $N_p$ | $N_y$ | $F_{obj}$ | $\Delta\%$ | $\Delta y$ | $\bar{y}$ |
|---------------|-----|----------|-------|-------|-----------|------------|-----------|---------|
| Paraffins     |     | 58       | 3940  | 1523  | –         | –          | 1.79      | 0.0058  |
| Naphthenes    |     | 33       | 1841  | 905   | 1.79      | 0.0022     | 52        | 2806    |
| Aromatics     |     | 11       | 169   | 73    | 2.20      | 0.0125     | 56        | 2756    |
| CH$_4$        |     | 66       | 5395  | 3111  | 3.42      | 0.0084     | 35        | 1712    |
| Naphthenes    |     | 37       | 3119  | 2196  | 2.29      | 0.0117     | 51        | 1782    |
| Aromatics     |     | 29       | 1474  | 911   | 2.34      | 0.0098     | 1         | 36      |
| CH$_4$        |     | 22       | 3902  | 2354  | 7.80      | 0.0087     | 2         | 44      |
| Naphthenes    |     | 7        | 432   | 303   | 5.74      | 0.0069     | 1         | 36      |
| Aromatics     |     | 17       | 904   | 528   | 14.48     | 0.0159     | 1         | 1       |
| CH$_2$H$_6$   |     | 4        | 221   | 61    | 2.97      | 0.0078     | 1         | 1       |
| Aromatics     |     | 8        | 328   | 237   | 6.07      | 0.0079     | 1         | 1       |
| CH$_4$        |     | 1        | 373   | 335   | 1.69      | 0.0053     | 1         | 1       |
| Naphthenes    |     | 17       | 2203  | 946   | 5.09      | 0.0113     | 1         | 1       |
| Aromatics     |     | 4        | 221   | 61    | 2.97      | 0.0078     | 1         | 1       |
| Aromatics     |     | 8        | 328   | 237   | 6.07      | 0.0079     | 1         | 1       |
| Naphthenes    |     | 27       | 3036  | 2110  | 6.33      | 0.0123     | 3         | 1       |
| Aromatics     |     | 6        | 645   | 498   | 6.03      | 0.0116     | 1         | 1       |
| CH$_4$        |     | 23       | 2042  | 1306  | 9.90     | 0.0098     | 1         | 1       |
| Naphthenes    |     | 1        | 362   | 289   | 1.33      | 0.0082     | 1         | 1       |
| Aromatics     |     | 1        | 414   | 422   | 1.42      | 0.0120     | 1         | 1       |
| CO$_2$        |     | 14       | 1348  | 1121  | 10.10     | 0.0236     | 1         | 1       |
| Naphthenes    |     | 5        | 173   | 163   | 11.32     | 0.0129     | 1         | 1       |
| Aromatics     |     | 9        | 587   | 184   | 15.74     | 0.0107     | 1         | 1       |
| CH$_4$        |     | 1        | 497   | 438   | 1.29      | 0.0065     | 1         | 1       |
| Naphthenes    |     | 1        | 212   | 197   | 6.70      | 0.0139     | 1         | 1       |
| Aromatics     |     | 1        | 215   | 192   | 3.46      | 0.0132     | 1         | 1       |
| CO$_2$        |     | 14       | 564   | 419   | 4.93      | 0.0212     | 1         | 1       |
| Naphthenes    |     | 5        | 134   | 134   | 4.02      | 0.0120     | 1         | 1       |
| Aromatics     |     | 5        | 150   | 150   | 4.93      | 0.0085     | 1         | 1       |
| CH$_4$        |     | 1        | 117   | 114   | 6.90      | 0.0188     | 1         | 1       |
| Naphthenes    |     | 1        | 79    | 66    | 1.67      | 0.0187     | 1         | 1       |
| Aromatics     |     | 1        | 142   | 142   | 1.57      | 0.0167     | 1         | 1       |

a Systems containing both very low and high pressure data.
Table 3b

Water and ethylene glycol data base considered for the estimation of the group contribution parameters. \(N_b\) is the number of binary systems and \(N_{xx}, N_{xI}\) are the numbers of data points in the hydrocarbon and polar phases.

| Systems | VLE, LLE | \(N_b\) | \(N_{xx}\) | \(N_{xI}\) | \(F_{oh}\) | \(\Delta x^{2}\)% | \(\Delta x^{2}\)% |
|---------|----------|---------|---------|---------|---------|---------|---------|
| H\(_2\)O | Paraffins | 27 | 221 | 466 | 16.77 | 20.24 |
| | Naphthenes | 14 | 46 | 48 | 11.03 | 16.55 |
| | Aromatics | 24 | 319 | 670 | 11.26 | 20.34 |
| | CH\(_4\) | 1 | 276 | 428 | 11.04 | 5.09 |
| | C\(_2\)H\(_6\) | 1 | 91 | 174 | 9.04 | 11.63 |
| MEG | Paraffins | 3 | 18 | 43 | 3.99 | 7.90 |
| | Naphthenes | 2 | 11 | 6 | 8.87 | 3.90 |
| | Aromatics | 3 | 30 | 49 | 17.33 | 7.06 |
| | CH\(_4\) | 1 | 9 | 80 | 13.88 | 3.71 |
| | CH\(_2\)O | 1 | – | 21 | – | 13.33 |
| | H\(_2\)O | 1 | 245 | 114 | 3.92 | 1.68 |

However a comparison only based on numerical results can lead to erroneous conclusions, especially for systems containing both low and high pressure data. In this case, results expressed in terms of \(|\Delta P|/P_i\) (Eq. (15)) overestimate the importance of deviations occurring at very low pressure and only the analysis of the phase diagrams allows objective conclusions; such systems are indicated with an asterisk in Table 4.

- Hydrocarbon mixtures. For almost all systems the three models yield identical deviations on mixture bubble points; Fig. 2a represents the VLE predictions obtained for benzene–toluene system. Fig. 2b illustrates with the eicosane–cyclohexane system the case of mixtures noted with superscript letter (a) in Table 4; it shows that experimental pressures are extremely low, which explains why quite similar descriptions of the phase diagrams lead to rather different deviations \(\Delta P\%\).

- Permanent gas–hydrocarbon. Two type of mixtures are reported in Table 4 and call the following remarks:

Table 4

Hydrocarbons and permanent gases. Mean deviations \(\Delta P\%\) on calculated mixture bubble points by means of predictive models: PPR78, VTPR and NRTL-PR.

| Component (1) | Component (2) | \(N_p\) | \(T_{min}\) (K) | \(T_{max}\) (K) | PPR78 | VTPR | NRTL-PR | Ref. |
|---------------|---------------|---------|----------------|----------------|-------|-------|---------|------|
| Propane | Hexane | 40 | 273 | 313 | 3.15 | 1.28 | 1.61 | [34] |
| Hexane | Hexadecane | 120 | 293 | 623 | 3.62 | 3.02 | 3.28 | [35–38] |
| Propane | 2,3-Dimethyl butane | 58 | 348 | 488 | 2.14 | 2.52 | 2.90 | [39] |
| Propane | Methylcyclohexane | 25 | 313 | 473 | 3.73 | 3.89 | 2.96 | [40] |
| Eicosane | Cyclohexane\(^a\) | (27) | 305 | 317 | (2.01) | (5.67) | (2.58) | [41] |
| Benzene | Propane | 81 | 311 | 478 | 4.20 | 3.11 | 4.34 | [42] |
| Benzene | Hexadecane | 89 | 298 | 313 | 1.88 | 3.16 | 2.49 | [43–45] |
| 1,2,4-Trimeyethylbenzene | Decane\(^a\) | (44) | 374 | 433 | (1.24) | (4.33) | (2.17) | [46] |
| Benzene | Methylcyclohexane | 88 | 303 | 353 | 1.28 | 0.72 | 1.73 | [47–50] |
| Naphtalene | Cyclohexane | 37 | 372 | 480 | 3.55 | 3.65 | 3.54 | [51] |
| Benzene | Toluene | 170 | 273 | 393 | 3.14 | 3.85 | 3.10 | [52–58] |
| Ethylbenzene | o-Xylene | 32 | 368 | 403 | 0.71 | 1.00 | 0.65 | [59] |
| C\(_2\)H\(_6\) | Hexane | 97 | 298 | 450 | 6.35 | 5.57 | 7.00 | [60–62] |
| C\(_2\)H\(_6\) | Hexatriacontane | 25 | 373 | 573 | 8.55 | 7.88 | 8.23 | [63,64] |
| C\(_2\)H\(_6\) | Toluene | 30 | 313 | 473 | 3.93 | 4.75 | 4.61 | [65] |
| C\(_2\)H\(_6\) | 1,3,5-Trimethylbenzene | 25 | 313 | 473 | 7.33 | 6.12 | 3.16 | [40] |
| CO\(_2\) | Hexane | 110 | 273 | 393 | 3.76 | 2.92 | 2.90 | [60,66–68] |
| CO\(_2\) | Hexatriacontane | 33 | 373 | 573 | 3.76 | 2.92 | 2.90 | [64,69] |
| CO\(_2\) | Methylcyclohexane | 31 | 311 | 477 | 3.76 | 2.92 | 2.90 | [70] |
| CO\(_2\) | Benzene | 217 | 273 | 414 | 5.67 | 5.17 | 6.64 | [68,71–76] |
| CO\(_2\) | 2-Methylnaphtalene\(^a\) | (63) | 307 | 473 | (21.91) | (22.74) | (19.69) | [77–79] |
| H\(_2\)S | Butane | 63 | 366 | 418 | 2.53 | 2.23 | 1.46 | [80] |
| H\(_2\)S | Decane | 51 | 278 | 444 | 5.45 | 3.35 | 6.27 | [81] |
| H\(_2\)S | Cyclohexane | 24 | 323 | 423 | 3.84 | 4.43 | 2.81 | [82] |
| H\(_2\)S | Benzene | (24) | 323 | 423 | (1.15) | – | (1.80) | [82] |
| CH\(_4\) | Octane | 90 | 223 | 423 | 4.57 | 5.90 | 5.02 | [83,84] |
| CH\(_4\) | Eicosane | 35 | 323 | 573 | 12.75 | 13.22 | 13.74 | [85,86] |
| CH\(_4\) | m-Xylene\(^a\) | (68) | 295 | 582 | (8.31) | (10.38) | (5.62) | [87–91] |
| CH\(_4\) | Phenanthrene\(^a\) | (33) | 383 | 473 | (34.11) | (15.24) | (16.39) | [92,93] |
| N\(_2\) | Hexane\(^a\) | (43) | 306 | 488 | (17.10) | – | (9.02) | [94–96] |
| N\(_2\) | Isobutane | (52) | 255 | 394 | (6.94) | – | (8.66) | [97] |
| N\(_2\) | Propylcyclohexane\(^a\) | (33) | 314 | 473 | (13.55) | – | (6.49) | [98] |
| N\(_2\) | Toluene\(^a\) | (61) | 303 | 473 | (24.37) | – | (14.34) | [99,100] |
| CH\(_4\) | CH\(_2\)O | 381 | 91 | 283 | 1.59 | 1.90 | 1.56 | [101–110] |
| CH\(_4\) | CO\(_2\) | 395 | 153 | 301 | (3.69) | – | (2.54) | [102,121] |
| CH\(_4\) | H\(_2\)S | (84) | 277 | 344 | 2.23 | 3.18 | 1.35 | [122,123] |

\(-\) unbuplished parameters, () values not taken into consideration for the estimation of the global values.

\(^a\) Systems containing both very low and high pressure data.

Global 2406 3.38 3.44 3.37
Fig. 2. VLE of hydrocarbon mixtures. Predictions with the ( ) PPR78, ( ) VTPR and ( ) NRTL-PR models. (a) Benzene (1)–toluene (2) system at \( T = 353 \text{ K} \) (□), \( T = 373 \text{ K} \) (△) and \( T = 393 \text{ K} \) (♦)[56]. (b) Cyclohexane (1)–eicosane (2) system at \( T = 306 \text{ K} \) (□) and \( T = 317 \text{ K} \) (♦)[41].

- Systems containing ethane, carbon dioxide or hydrogen sulfide: the mixture critical points are, in many cases, located at moderate pressures and rather similar, satisfactory descriptions of VLE are obtained with the three cubic EoS (Table 4 and Fig. 3a and b for ethane–toluene and carbon dioxide–hexane mixtures).

- Mixtures of hydrocarbons with methane or nitrogen are, in many cases, of type III, according to the classification scheme of Scott and van Konynenburg[23], with critical points located at very high, or infinite, pressures, so that the modeling of the whole phase envelope is a quite impossible task with cubic EoS[24]. The PPR78 equation gives more priority to the high pressure domain, while the VTPR and NRTL-PR models account indistinctly for low and high pressures; consequently, deviations \( \Delta P \) given in Table 4 should be considered carefully. Fig. 4a and b illustrates the case of the nitrogen–hexane and methane–phenanthrene systems; numerous deviations located at low pressures are responsible, for the PPR78 model, of global deviations \( \Delta P \) totally misleading with respect to the phase envelopes, especially those described in Fig. 4a.

- Permanent gas–permanent gas. All the three predictive models consider permanent gases as “specific groups”; thus, the modeling of these systems only requires fitting a single group parameter and similar, good results are obtained with all models (Table 4).

3.3. Excess enthalpies for binary mixtures

For the majority of systems containing hydrocarbons and permanent gases, excess enthalpies are relatively small, so that relative deviations are even more meaningless than in the case of VLE. Results are illustrated with graphical examples for systems with significant excess enthalpies, such as aromatic–alkane, aromatic–napthene and permanent gas–hydrocarbon mixtures.

Fig. 5a and b represents respectively three toluene–alkane mixtures at \( T = 298 \text{ K} \) and the benzene–cyclohexane system at different temperatures. Both NRTL-PR and VTPR equations yield similar results and consistent behaviours with respect to the increase of the chain length and temperature. The PPR78 equation appears to be less accurate, which is probably due to the fact that excess enthalpies were not taken into account when fitting the numerous group interaction parameters.

3.4. Phase envelope of synthetic petroleum fluids

Two synthetic petroleum fluids not included in the data base are presented in Fig. 6; these mixtures of known composition are made up of rather “light” components, so that the estimation of the critical properties of the pure components is not questionable. It can be observed that all models allow a satisfactory representation of the phase envelopes.
Fig. 4. VLE of hydrocarbon–permanent gases. Predictions with the (■) PPR78, (●) VTPR and (▲) NRTL-PR models. (a) Nitrogen (1)–hexane (2) system at $T = 378$ K (□) and $T = 488$ K (♦) [95]. (b) Methane (1)–phenanthrene (2) system at $T = 473$ K (□) [93].

Fig. 5. Excess enthalpies of hydrocarbon mixtures. Predictions with the (■) PPR78, (●) VTPR and (▲) NRTL-PR models. (a) Toluene (1)–hexane (2) (□) [124], –dodecane (2) (♦) [125] and –hexadecane (2) (▲) [126] at $T = 298$ K. (b) Benzene (1)–cyclohexane (2) system at $T = 280$ K (□), $T = 323$ K (♦) and $T = 373$ K (▲) [127].

Fig. 6. Phase envelopes of synthetic petroleum fluids. Predictions with the (■) PPR78, (●) VTPR and (▲) NRTL-PR models. (a) $x_{\text{methane}} = 0.2453$, $x_{3\text{-methylpentane}} = 0.0498$, $x_{\text{hexane}} = 0.4029$, $x_{\text{benzene}} = 0.0508$, $x_{\text{cyclohexane}} = 0.0501$ and $x_{\text{heptane}} = 0.2011$ (□) [128]. (b) $x_{\text{carbon dioxide}} = 0.2507$, $x_{\text{naphtalene}} = 0.0330$ and $x_{\text{dodecane}} = 0.7163$ (□) [129].
4. Phase equilibria of water–hydrocarbons and ethylene glycol–hydrocarbons systems

The first part of this section concerns the NRTL-PR “\(k_{ij}\)” behaviour with respect to mole fraction and temperature. The second one details VLE and LLE predictions obtained with the NRTL-PR equation and other literature models, such as the cubic SRKm equations; as outlined in Section 1, the PPR78 and VTPR EoS are not appropriate for the modeling of the strong demixings occurring in this kind of mixtures and were not considered.

4.1. \(k_{ij}\) Parameters with respect to mole fraction and temperature

Fig. 7a shows that the NRTL-PR model provides a monotonous variation of the \(k_{ij}\) parameters from the hydrocarbon rich phase to the aqueous or glycol phase. It is also observed that, as expected, greater variations of \(k_{ij}\) are predicted for the water–paraffin systems which lead to the strongest demixings.

The evolution of \(k_{ij}\) parameters in each phase \((x_0^I = 0.01 \text{ and } x_0^II = 0.99)\) with respect to temperature is given by Fig. 7b. Continuous variations of \(k_{ij}\) are still obtained for both phases. As in the case of carbon dioxide–hydrocarbon mixtures, the SRKm mixing rule reduces, for binary mixtures, to a linear \(k_{ij}\) correlation \((C_{ij} = 1)\) of the Adachi and Sugie type [25]; it must also be recalled [26] that, for multicomponent systems, these mixing rules suffer from the Michelsen–Kirstenmacher syndrome [9] which might affect the representation of highly dilute mixtures.

Table 5 presents, for isobaric and isothermal VLLE, the global deviations \(\Delta x_{ij}^{II}\%\) and \(\Delta x_{ij}^{II}\%\) on the mole fraction of the dilute components, respectively, in the aqueous (I) and hydrocarbon (II) phases. On the whole, it can be observed that, whatever the range of pressure or temperature, the NRTL-PR model yields a very accurate prediction of the solubilities in both phases. The SRKm equation provides, in general, a rather similar description of the hydrocarbon phases, but fails in correlating the aqueous phase, which is also characterized by the smallest solubilities.

The detailed analysis of LLE under atmospheric pressure is performed in Fig. 8 for water with hexane, cyclohexane, benzene and ethylbenzene. Contrary to the VLE of hydrocarbon mixtures, which usually cover the whole range of molar fractions, these LLE present very low solubilities in both phases, especially in the aqueous phase; for this reason Fig. 8 only describe the solubility of the more dilute compound in each phase. For all systems considered, the NRTL-PR model provides satisfactory results for both phases. At the exception of the water–cyclohexane system (Fig. 8b), the SRKm equation correctly represents the organic phase, but introduces large deviations on the solubility in the aqueous phase; in all cases, the SRKM model does not succeed in correlating both phases.

Fig. 9 illustrate VLE results for the water–methane system, which was widely studied in the literature from: very low temperatures (275 K), with phase diagrams very close to those observed in Fig. 8 for LLE, to high temperatures (633 K), with phase envelopes similar to those described in Figs. 3 and 4 for the VLE of hydrocarbon mixtures. This system was therefore chosen for a general comparison of the literature \(k_{ij}\) mixing rules used for the description of the VLE of water–hydrocarbon mixtures; for this purpose, besides the NRTL-PR and SRKm modelings, the whole water–methane data set was also correlated by means of a constant \(k_{ij}\) parameter and of a linear \(k_{ij}(x)\) mixing rule of the Adachi and Sugie type, using, in each case, a linear variation of \(k_{ij}\) with respect to the inverse of temperature. Results of the various correlations at \(T = 377.59\) K and 603.15 K are reported in Fig. 9, together with the values of the fitted \(k_{ij}\) parameters. It can be observed that:

- At the lowest temperature, the solubilities in the two phases are extremely low, so that all models seem to provide satisfactory phase envelopes (Fig. 9a1); but, Fig. 9b1 gives evidence that, except the NRTL-PR model, all other correlations yield in reality a very poor description of the aqueous phase.
- At the highest temperature (Fig. 9a2 and b2) the experimental VLE phase envelope is similar to one of the hydrocarbon mixtures and all models are able to represent both the liquid and the vapor phases.

The variations of the \(k_{ij}\) with respect to the water mole fraction, at the two temperatures, are reported in Fig. 9 c1 and c2 for the various models in the two phase region; their analysis shows that:

- Contrary to the other models, the NRTL-PR equation yields a consistent evolution of \(k_{ij}\) between the lowest and the highest temperature; this regular behaviour explains the satisfactory results thus obtained, in both phases, at \(T = 377.59\) K and 603.15 K.
- The SRKm equation, as well as the \(k_{ij}(x)\) and constant \(k_{ij}\) mixing rules, provide rather similar and satisfactory parameters at \(T = 603.15\) K; however, at the lowest temperature, these models predict completely abnormal values in the aqueous phase, which are responsible of the erroneous description of this phase at \(T = 377.59\) K.

Fig. 9 also confirms that a constant \(k_{ij}\) mixing rule should be avoided; this is obviously the reason why the CPA model was successfully developed by adding the association term to this simple mixing rule.

4.2. Vapor–liquid and liquid–liquid equilibria (VLLE) for water–hydrocarbon systems

4.2.1. Comparison with the SRKm EoS

Results obtained with the NRTL-PR model are compared in Table 5 and Figs. 8 and 9 with the SRKm equation using the literature interaction \(k_{ij}\) parameters reported in Appendix D.1. As can be observed in this appendix, for almost all systems, except for water with methane, methylcyclohexane and benzene, the SRKm mixing rule reduces, for binary mixtures, to a linear \(k_{ij}\) correlation \((C_{ij} = 1)\) of the Adachi and Sugie type [25]; it must also be recalled [26] that, for multicomponent systems, these mixing rules suffer from the Michelsen–Kirstenmacher syndrome [9] which might affect the representation of highly dilute mixtures.

The VLE of water–ethane system, in a wide range of temperatures (310–410 K) and pressures (10–1000 bar), are illustrated in Fig. 10a and b. They show that, whatever the temperature and pressures considered, both models are able to describe accurately the solubilities in each phase.

The same satisfactory modeling is observed, in Fig. 11a and b, for the LLE of water–octane and water–toluene systems. However, for both systems, the NRTL-PR model is the only one which represents the minimum of solubility experimentally observed in the aqueous phase at low temperatures.

Finally, the great advantage of the proposed NRTL-PR model, with respect to the CPA equation, is to allow very good predictions of the solubilities in both polar and organic phases but, without requiring fitted \(k_{ij}\) parameters.

4.3. VLE and LLE for ethylene glycol–hydrocarbon systems

4.3.1. Comparison with the SRKm EoS

Table 6 compares, for the modeling of VLE of glycol–hydrocarbon mixtures with the NRTL-PR and SRKm models, the global deviations on the mole fraction of the dilute components in each phase.
Table 5
Water–hydrocarbon mixtures. Mean deviations between experimental and calculated mole fractions, in the hydrocarbon (II) and aqueous (I) phases, with the SRKm (specific parameters, Appendix D.1) and NRTL-PR models.

| Component (2) | Isothermal data (T(K)) | SRKm | NRTL-PR |
|---------------|-------------------------|------|---------|
|               | T<sub>min</sub> | T<sub>max</sub> | N<sub>II</sub> | N<sub>I</sub> | Δx<sub>II</sub>% | Δx<sub>I</sub>% | Δx<sub>II</sub>% | Δx<sub>I</sub>% | Ref. |
| Methane       | 275               | 633   | 220    | 369    | 9.28       | 64.17     | 9.28       | 5.90       | [130–151] |
| Pentane       | 573               | 603   | 11     | –      | –          | 26.67     | –          | 18.52      | [152]     |
| Heptane       | 568               | 603   | 6      | –      | –          | 95.36     | –          | 20.61      | [154]     |
| Octane        | 498               | 538   | 18     | –      | –          | 26.54     | –          | 12.90      | [155]     |
| Decane        | 498               | 548   | 28     | –      | –          | 35.36     | –          | 15.43      | [156]     |
| Benzene       | 298               | –     | –      | 5      | –          | 53.46     | –          | 5.52       | [158]     |
| Toluene       | 298               | 583   | 11     | 5      | 5.21       | 29.81     | 3.37       | 21.79      | [154]     |
| Ethylbenzene  | 298               | –     | –      | 4      | –          | 79.04     | –          | 31.10      | [159]     |
| m-Xylene      | 298               | –     | –      | 4      | –          | 69.81     | –          | 29.82      | [159]     |
| p-Xylene      | 298               | –     | –      | 2      | –          | 69.19     | –          | 41.13      | [159]     |
| Global        | 277               | 406   | 12.87  | 63.40  | 9.90       | 7.31      |

| Component (2) | Isobaric data (P/bar) | SRKm | NRTL-PR |
|---------------|------------------------|------|---------|
|               | P<sub>min</sub> | P<sub>max</sub> | N<sub>II</sub> | N<sub>I</sub> | Δx<sub>II</sub>% | Δx<sub>I</sub>% | Δx<sub>II</sub>% | Δx<sub>I</sub>% | Ref. |
| Pentane       | 1                   | 5     | 12     | 35     | 42.07       | 14.35     | 14.08       | 13.83      | [152]     |
| Hexane        | 1                   | 200   | 25     | 37     | 26.16       | 63.16     | 13.93       | 15.85      | [153]     |
| Heptane       | 1                   | –     | 17     | 23     | 13.51       | 31.11     | 25.44       | 29.03      | [154]     |
| Octane        | 1                   | 70    | 13     | 11     | 24.97       | 16.79     | 24.09       | 16.36      | [155]     |
| Decane        | 1                   | –     | 4      | –      | 7.47        | –         | 12.56       | –          | [156]     |
| 2-Methybutane | 1                   | –     | 15     | 8      | 9.21        | 49.68     | 12.58       | 39.42      | [152]     |
| Cyclohexane   | 1                   | 5     | 16     | 21     | 28.25       | 18.58     | 14.67       | 12.62      | [157]     |
| Methylcyclohexane | 1               | –     | 4      | 9      | 21.38       | 8.00      | 3.91        | 14.95      | [154]     |
| Benzene       | 1                   | 625   | 144    | 173    | 6.77        | 53.96     | 8.58        | 19.20      | [158]     |
| Toluene       | 1                   | 2000  | 45     | 140    | 10.88       | 15.24     | 8.15        | 9.46       | [154]     |
| Ethylbenzene  | 1                   | 1000  | 27     | 107    | 15.49       | 73.13     | 13.11       | 16.76      | [159]     |
| o-Xylene      | 1                   | –     | 3      | 13     | 1.82        | 52.35     | 19.59       | 38.28      | [159]     |
| m-Xylene      | 1                   | 60    | 13     | 34     | 25.49       | 63.93     | 13.93       | 21.68      | [159]     |
| p-Xylene      | 1                   | 2     | 11     | 40     | 25.34       | 422.16    | 7.33        | 23.77      | [159]     |
| Global        | 349                 | 651   | 14.09  | 67.04  | 11.54       | 17.29     |

For these systems, no specific SRKm parameters were found in the literature, so that calculations were performed with the “standard values” given in Appendix D.2. Results presented in Table 6 show that, as for aqueous mixtures, the SRKm equation does not succeed in correlating the weakest solubilities, which, in this case, correspond to the hydrocarbon phase (see Fig. 13); the use of standard k<sub>ij</sub> parameters, instead of fitted ones, is probably responsible for the worse results obtained for this kind of mixtures. On the contrary, the NRTL-PR model is able to predict accurate solubilities in each phase; it should be also mentioned that, with respect to water–hydrocarbon mixtures, better results are obtained, since these mixtures present larger solubilities in the hydrocarbon and polar phases.

4.3.2. Comparison with the CPA model
Figs. 12 and 13 illustrate results obtained with the NRTL-PR and CPA models, respectively, for VLE and LLE data:
- For the VLE of ethylene glycol–methane, the NRTL-PR model, even slightly less precise than the CPA model in the glycol phase (Fig. 12a), gives a very accurate description of the solubility of ethylene glycol in methane (Fig. 12b).

Fig. 7. NRTL-PR predictions of k<sub>ij</sub> for (—) water (1)–heptane (2), (—·—) water (1)–benzene (2) and (—·—·—) ethylene glycol (1)–toluene (2) systems: (a) k<sub>ij</sub>(T<sub>0</sub>,X<sub>0</sub>) at T<sub>0</sub> = 300 K and (b) k<sub>ij</sub>(T,X<sub>i</sub>) for (—) X<sub>i</sub> = 0.01 and (—·—·—) X<sub>i</sub> = 0.99.
Fig. 8. LLE of water–hydrocarbon systems under atmospheric pressure. Modeling with the ( ) SRKm and ( ) NRTL-PR models. (a) Water (1)–hexane (2): hydrocarbon phase (II) (△) [160] and aqueous phase (I) (■) [160], (♦) [161], (●) [162]; (b) Water (1)–cyclohexane (2): hydrocarbon phase (II) (△) [163], (○) [164] and aqueous phase (I) (▲) [165]; (c) Water (1)–benzene (2): hydrocarbon phase (II) (△) [160], (♦) [168], (+) [169] and aqueous phase (I) (■) [160], (▲) [166], (○) [167]; (d) Water (1)–ethylbenzene (2): hydrocarbon phase (II) (△) [170] and aqueous phase (I) (♦) [171], (●) [173], (▲) [172].

Table 6
Ethylene glycol–hydrocarbon mixtures. Mean deviations between experimental and calculated mole fractions, in the hydrocarbon (II) and glycol (I) phases, with the SRKm (standard parameters, Appendix D.2) and NRTL-PR models.

| Component (2) | Isothermal data (T/K) | SRKm | NRTL-PR |
|---------------|----------------------|------|---------|
|               | Tmin | Tmax | N_d  | N_a  | Δx1% | Δx2% | Δx1% | Δx2% | Ref.   |
| Methane       | 273  | 398  | 9    | 80   | 55.84 | 24.04 | 13.88 | 3.71 | [179–182] |
| Ethane        | 283  | 303  | –    | 21   | –     | 126.94 | –     | 13.33 | [181–183] |
| Propane       | 298  | 398  | –    | 31   | –     | 109.34 | –     | 8.76  | [184] |
| Global        | 9    | 132  |      |      | 55.84 | 60.44 | 13.88 | 6.43  |        |

| Component (2) | Isobaric data (P/bar) | SRKm | NRTL-PR |
|---------------|-----------------------|------|---------|
|               | P_min | P_max | N_d  | N_a  | ΔΔx1% | ΔΔx2% | ΔΔx1% | ΔΔx2% | Ref.   |
| Hexane        | 1     | –     | 5    | 5    | 91.96 | 20.14 | 2.26  | 7.78  | [185] |
| Heptane       | 1     | –     | 13   | 7    | 90.90 | 27.80 | 3.82  | 4.19  | [185,186] |
| Cyclohexane   | 1     | –     | 5    | –    | 92.42 | 244.51 | 7.16  | –     | [186] |
| Methylcyclohexane | 1      | –     | 6    | 6    | 91.87 | 87.40 | 10.48 | 3.90  | [185] |
| Benzene       | 1     | –     | 10   | 17   | >500  | 87.40 | 16.72 | 11.55 | [186–189] |
| Toluene       | 1     | –     | 20   | 19   | >500  | 72.08 | 17.63 | 2.00  | [188,190] |
| o-Xylene      | 1     | –     | –    | 13   | 98.31 | 87.46 | –     | 8.59  | [190] |
| Global        | 59    | 67    | >90  |      | 85.74 | 11.52 | 6.53  |        |
Fig. 9. VLE of water (1)–methane (2) system. Modeling with (■) PR, (♦) SRKm and (△) NRTL-PR models. (1) System at $T = 377.59 \, \text{K}$ (■) [134], (♦) [135], (△) [143]; (2) System at $T = 603.15 \, \text{K}$ (■, □) [146]. (a) Phase envelope; (b) Solubilities in aqueous (I) and hydrocarbon (II) phases; (c) Variation of $k_{ij}$ with respect to water mole fractions. $k_{12} = -0.1719 + 217.1/T$; $k_{12}(x) = k_{12}^0 + k_{12}^1(x_1 - x_2)$, $k_{12}^0 = -0.1510 + 300.3/T$, $k_{12}^1 = -0.6647 + 300.0/T$.

Fig. 13 represent the LLE of ethylene glycol with paraffins and aromatics predicted with the NRTL-PR model and correlated with the CPA model, with fitted $k_{ij}$ parameters; results obtained with the NRTL-PR model, but using $I_{ij}$ interaction parameters fitted on binary mixtures (NRTL-PRfitted), are also reported in these figures. It can also be observed that, with respect to aqueous mixtures, solubilities do not present an experimental minimum at low temperatures.

- On the whole, all models provide satisfactory representation of the solubilities in both phases; the use of fitted $k_{ij}$ parameters slightly improves the correlation of phase equilibria.

4.4. LLE for water–ethylene glycol–hydrocarbon mixtures

Fig. 14 represents the VLE of water–ethylene glycol mixture at two temperatures modeled with the CPA and NRTL-PR equations.
Fig. 10. VLE of water (1)–ethane (2) system. Modeling with the (-----) CPA and (-----) NRTL-PR models at $T = 310$ K (□), $T = 344$ K (○), $T = 378$ K (△), $T = 411$ K (◇) and $T = 444$ K (●): (a) hydrocarbon [174] and (b) aqueous [175] phases (CPA curves and $k_{ij}$ values taken from Li and Firoozabadi [192]).

Fig. 11. LLE of water–hydrocarbon systems. Modeling with the (-----) CPA and (-----) NRTL-PR models. (a) Water (1)–octane (2): aqueous phase (I) (■) [176] and hydrocarbon phase (II) (□) [176] (CPA curves from Voutsas et al. [193], $k_{ij} = 0.03$). (b) Water (1)–toluene (2): aqueous phase (I) (■) [160], (●) [177], (♦) [178] and hydrocarbon phase (II) (□) [160], (○) [177], (♦) [178] (CPA curves from Folas et al. [194] with $k_{ij} = 0.0095$, BETCR = 0.06).

Due to the simplicity of the system considered, the modeling only requires fitting a single binary interaction parameter and very good results are obtained with both models.

Table 7 concerns the description of the LLE of ternary systems containing water and ethylene glycol, respectively, with benzene and toluene; in this case, predictions with the NRTL-PR model are compared, not only with the CPA equation, but also with the NRTL-PR$_{\text{fitted}}$ version using, like CPA, binary interaction parameters $\Gamma_{ij}$ fitted on the binary water–hydrocarbon and ethylene glycol–hydrocarbon systems. It can be observed that:

- Even based on group contributions, the NRTL-PR model succeeds in predicting the phase equilibria with a precision comparable to the CPA model, but with adjustable parameters.
- By fitting one $\Gamma_{ij}$ parameter, the NRTL-PR$_{\text{fitted}}$ model leads to more reliable results than the CPA equation.

Fig. 12. VLE of ethylene glycol–hydrocarbon systems. Modeling with the (-----) CPA and (-----) NRTL-PR models. Ethylene glycol (1)–methane (2) system: (a) solubility in the polar phase at $T = 283$ K (■) [181], $T = 323$ K (●) and $T = 373$ K (▲) [182]; (b) solubility in the hydrocarbon phase at $T = 278$ K (x), $T = 298$ K (○) and $T = 373$ K (♦) [179] (CPA curves from Haghighi et al. [195] with $k_{ij} = 0.0004 + 0.0498 T$).
The NRTL-PR equation of state previously proposed \[9\] as a EoS/GE model for the prediction of phase equilibria occurring in highly nonideal systems was reformulated in terms of a predictive composition dependent mixing rule. Special attention was paid to the evolution of \(k_{ij}\) parameters with respect to mole fraction and temperature and a wide variety of nonideal mixtures containing hydrocarbons, water and ethylene glycols were considered. Results obtained for excess enthalpies, liquid–vapor and liquid–liquid equilibria were compared with those provided by the literature models commonly used in petroleum industry, such as the VTPR, PPR78 and CPA equations, for hydrocarbon mixtures, and the SRKm and CPA models, for water or glycol systems with hydrocarbons.

For hydrocarbon mixtures, the \(k_{ij}\) parameters have always extremely moderate variations, so that the proposed NRTL-PR model is very similar to the PPR78 EoS with constant \(k_{ij}\) values. Results obtained with the group contribution NRTL-PR, VTPR and PPR78 equations for the modeling of VLE and excess enthalpies of binary mixtures, or for the phase envelopes of synthetic petroleum fluids, are quite similar. The main advantage of the NRTL-PR and VTPR models is to drive from the two fluid lattice theory and to make use of a restricted number of group interaction parameters.

For water or ethylene glycol with hydrocarbons, the NRTL-PR model provides a monotonous variation of the \(k_{ij}\) parameters from the hydrocarbon rich phase to the polar phase and, contrary to the SRKm and other classical mixing rules, predicts a consistent behaviour with respect to temperature; this explains the great improvement introduced by the NRTL-PR model for the prediction of the solubilities in both the organic and the polar phases. Comparison with results obtained, for the same systems, with the CPA equation shows that the two models lead to rather similar accurate description of the solubilities in both phases; nevertheless, the NRTL-PR model requires no fitted \(k_{ij}\) parameters and is able to represent the minimum of solubility experimentally observed in the aqueous phase at low temperatures.

The extension to other oxygenated compounds is under development. Preliminary results obtained with acetone and alcohols are quite satisfactory, which shows that the NRTL-PR group contribution can be extended to other “polar” functional groups.

**Fig. 13.** LLE of ethylene glycol–hydrocarbon systems. Modeling with the (-----) CPA, ( ) NRTL-PR and ( ) NRTL-PR\textsubscript{model} models. Solubilities in the polar (I) and hydrocarbon (II) phases. (a) Ethylene glycol (1)–hexane (2) ( ) \[185\] (CPA curves from Folas et al. [196] with \(k_{ij} = 0.059\); NRTL-PR\textsubscript{model}: \(T = 2989 - 657,033/T\), \(T = 2964 - 43,303/T\)) and ethylene glycol (1)–benzene (2) ( ) \[185\], ( ) \[187\], ( ) \[189\] (CPA curves from Folas et al. [188] with \(k_{ij} = 0.049\), BETCR = 0.04; NRTL-PR\textsubscript{model}: \(T = 2423 - 492,442/T\), \(T = 2731 - 33,819/T\)). (b) Ethylene glycol (1)–heptane (2) ( ) \[185\], ( ) \[187\] (CPA curves from Folas et al. [194] with \(k_{ij} = 0.031\); NRTL-PR\textsubscript{model}: \(T = 2554 - 608,309/T\), \(T = 1950 - 102,371/T\)) and Ethylene glycol (1)–toluene (2) ( ) \[188\], ( ) \[189\] (CPA curves from Folas et al. [195] with \(k_{ij} = 0.055\), BETCR = 0.045; NRTL-PR\textsubscript{model}: \(T = 2279 - 489,683/T\), \(T = 2194 + 30,955/T\)).

**Table 7** Ethylene glycol–water–hydrocarbon mixtures. Mean deviations between experimental and calculated mole fractions, in the hydrocarbon (II) and polar (I) phases, with the CPA, NRTL-PR\textsubscript{model} (with \(F_{ij}\) parameters fitted on the binary systems) and predictive NRTL-PR models.

| Systems | \(T\) (K) | CPA | NRTL-PR\textsubscript{model} | NRTL-PR |
|---------|--------|-----|----------------|--------|
| MEG(1)–H\(_2\)O(2)–benzene(3) | 298 | 17,5 | 11,9 | 19,4 | 8,5 | 9,2 | 14,8 | 9,87 | 15,83 | 10,79 |
| MEG(1)–H\(_2\)O(2)–toluene(3) | 298 | 22,5 | 19,3 | 20,6 | 7,0 | 10,7 | 19,0 | 13,15 | 6,53 | 22,28 |
| MEG(1)–H\(_2\)O(2)–hexane(3) | 323 | 16,1 | 5,2 | 24,8 | 7,2 | 4,8 | 15,7 | 13,67 | 4,12 | 8,71 |

Experimental data and CPA results from Folas et al. [188]. NRTL-PR\textsubscript{model} parameters: H\(_2\)O (1)–benzene (2): \(T = 2985 - 866,784/T\), \(T = 3565 - 232,283/T\); MEG (1)–benzene (2): \(T = 2423 - 492,442/T\), \(T = 2731 - 33,819/T\); H\(_2\)O (1)–toluene (2): \(T = 5364 - 899,732/T\), \(T = 3667 - 244,207/T\); MEG (1)–toluene (2): \(T = 2279 - 489,683/T\), \(T = 2194 + 30,955/T\).

**Fig. 14.** VLE of water–ethylene glycol. Modeling with the (-----) CPA and ( ) NRTL-PR models at \(T = 343\) K ( ) and \(T = 363\) K ( ) [191] (CPA curves from Haghighi et al. [195] with \(k_{ij} = 0.2313 + 5.6294 \times 10^{-4} T\)).


List of symbols

a attractive term
b co-volume
C reference state constant
F \text{obj} objective function
\gamma_{ij} molal Gibbs energy
k_{ij} EOS interaction parameter between molecules i and j
P pressure
Q group surface area factor
q molecular surface area factor
R ideal gas constant
r volume area factor
T temperature
V volume
\nu molar volume
VLE vapor–liquid equilibria
LLE liquid–liquid equilibria
VLE \text{vapor–liquid and liquid–liquid equilibria}

Greek letters
\alpha alpha function
\alpha_0 non randomness factor
\xi^{(0)} \text{interaction parameters between molecules i and j}
\xi^{(1)} \text{parameters of the group contribution method}
v_{ik} number of subgroup k in a molecule i
\omega acentric factor

Subscript and superscript
c critical property
E excess property at constant pressure

Appendix A. The generalized reference state at constant volume

The method is based on the EoS/C^E approach. The attractive term a of the EoS is estimated by assuming that, in a given reference state \( V^0 \), the excess Helmholtz energies at constant volume, \( A^{EV} \), derived from the EoS and from a low pressure model are equal:

\[
\frac{A^{EV}(T, V^0, n)_{\text{EoS}}}{nRT} = \frac{A^{EV}(T, x)}{nRT} \approx \frac{g^E(T, x)}{RT}
\]  

(A1.1)

with, for a cubic EoS:

\[
\frac{A^{EV}(T, V^0, n)_{\text{EoS}}}{nRT} = A^{\text{res}}(T, V^0, n) - \sum_i \sum_j A^{\text{res}}(T, V^0, n_i) + RT \sum_i n_i \ln \frac{V^0}{V^0_i} = -\sum_i \ln \left( \frac{1 - \eta^0_i}{1 - \eta^0} \right) - \alpha C(\eta^0) + \sum_i x_i \alpha_i C(\eta^0) + \sum_i x_i \ln \frac{V^0}{V^0_i} \approx \frac{g^E(T, x)}{RT}
\]

and:

\[
A^{EV}(T, V^0) = \sum_i V^0_i, \quad C(\eta^0) = \frac{1}{(e_1 - e_2^2)} \ln \left( \frac{1 + e_1 \eta^0}{1 + e_2 \eta^0} \right),
\]

\[
C(\eta^0) = \frac{1}{(e_1 - e_2^2)} \ln \left( \frac{1 + e_1 \eta^0}{1 + e_2 \eta^0} \right)
\]  

(A1.3)

A.1. Application to the literature reference states

From Eqs. (A1.2) and (A1.3) it is possible to deduce the classical literature reference states (zero pressure [27,28], MHV1 [29], infinite pressure [30], constant packing fraction [31]) as follows:

- To eliminate the volumes in Eq. (A1.2), packing fractions in the reference state (\( \eta^0 = nb/V^0 \) and \( \eta^0 = nb_i/V^0_i \)) are assumed equal;
- The functions \( C(\eta^0) = C(\eta^0) \) are fixed at a constant value C. Leading to the zero pressure relation (Michelsen approach):

\[
\frac{g^E(T, x)}{RT} = C \left[ -\alpha + \sum_i x_i \alpha_i \right] + \sum_i x_i \ln \frac{b_i}{B}, \quad C = \text{constant}
\]  

(A1.4)

and to the following a\( M \) function:

\[
a^M = \alpha - \sum_i x_i \alpha_i = \frac{1}{C_0} \left[ \frac{g^E}{RT} - \sum_i x_i \ln \frac{b_i}{B} \right]
\]  

(A1.5)

Nevertheless, as was shown by Kontogeorgis and Vlamos [32], the a\( M \) function should, in principle, only depend on the residual part \( g^E/RT \) of the excess Gibbs energy model; therefore:

- Predictive models based on the zero pressure (VTPR [6], UMR–PRU [33]) or on the constant packing fraction (PPR78 [5]) reference states assume that the volume factors \( r_i \) and \( r \) of the combinatorial Flory term are equal to the EoS co-volumes \( b_i \) and \( b \);
- Only the residual part of the excess model should be employed with the infinite pressure or constant packing fraction reference states.

However, the problem still remains unsolved when using low pressure models with parameters determined without an EoS.

A.2. Generalized reference state

In order to solve this problem, the following approach was considered:

- The reference volumes \( V^0 \) and \( V^0 \) in Eq. (A1.2) are expressed directly from the volume factors \( r_i \) and \( r \) used with the C\( E \) model and no more from the EoS co-volumes.
- Then, to eliminate the volumes in Eq. (A1.2), the packing fractions in the reference state are assumed to satisfy the condition: \( 1 - \eta^0 = \Pi(1 - \eta^0_i)^{n_i}, \) instead of the classical equality: \( \eta^0 = \eta^0_i; \)
- Finally, functions \( C(\eta^0) \) and \( C(\eta^0) \) are fixed at the same constant C\( 0 \) value, which leads to:

\[
\frac{g^E(T, x)}{RT} = C_0 \left[ -\alpha + \sum_i x_i \alpha_i \right] + \sum_i x_i \ln \frac{r_i}{r}, \quad C_0 = \text{constant}
\]  

(A1.6)

and to the expression of the a\( M \) function:

\[
a^M = \alpha - \sum_i x_i \alpha_i = \frac{1}{C_0} \left[ \frac{g^E}{RT} - \sum_i x_i \ln \frac{r_i}{r} \right]
\]  

(A1.7)

Since any value can be chosen for the C\( 0 \) parameter (for instance, in the case of the Peng–Robinson EoS: 0.53, 0.63 or 1.0 as with the zero pressure, infinite pressure or constant packing fraction reference states respectively), we refer to this mixing rule as “a generalized reference state”.


Appendix B. The \( k_{ij} \) NRTL-PR model

The aim of this section is to express the attractive term \( a \) of the NRTL-PR EoS given by Eq. (7) according to a “\( k_{ij} \)” mixing rule, which, therefore, satisfies the following relation:

\[
a = \alpha bRT = b \left[ \sum_i a_i \frac{a_i}{b_i} - \sum_i x_i q_i \frac{\sum_j x_j G_{ji}/C}{\sum_j x_i q_i G_{ji}} \right]
\]

\[
= \sum_i \sum_j x_i x_j \sqrt{a_i} \sqrt{a_j} (1 - k_{ij}) \tag{A2.1}
\]

Parameters \( k_{ij} \) having symmetric values \( (k_{ij} = k_{ji}) \), the above condition assures that all the terms in the left side of Eq. (A2.1) must be expressed as symmetric double sums with respect to \( i \) and \( j \) components. For this purpose:

- The first term is written as follows:
  \[
b \sum_i a_i \frac{a_i}{b_i} = \sum_i \sum_j x_i x_j \frac{a_i}{b_i} = \left[ \frac{1}{2} \sum_i \sum_j x_i x_j b_i b_j \right] \left[ \frac{a_i}{b_i} + \frac{a_j}{b_j} \right] \tag{A2.2}
\]

- while the second term is developed according to:
  \[
b \sum_i x_i q_i G_{ji}/C = \left[ \frac{1}{2} \sum_i \sum_j x_i x_j \right] \left[ \frac{G_{ij} \Gamma_{ij}/C}{\sum_j x_i q_i G_{ji}} + \frac{G_{ji} \Gamma_{ji}/C}{\sum_i x_i q_i G_{ji}} \right] \tag{A2.3}
\]

Thus, from Eq. (A2.1) binary interaction parameters \( k_{ij} \) satisfy the following relation:

\[
\sqrt{a_i} \sqrt{a_j} (1 - k_{ij}) = \frac{1}{2} \left[ b_i b_j \left( \frac{a_i}{b_i} + \frac{a_j}{b_j} \right) \right] - \frac{1}{2} \left[ b_i b_j \left( \frac{G_{ij} \Gamma_{ij}/C}{\sum_j x_i q_i G_{ji}} + \frac{G_{ji} \Gamma_{ji}/C}{\sum_i x_i q_i G_{ji}} \right) \right]
\]

which leads to the final formulation of \( k_{ij} \):

\[
k_{ij} = k_{ij}^{(0)} + \rho_{ij}^{(0)} \left[ \frac{b}{\sum_j x_i q_i G_{ji}} \right] + \rho_{ji}^{(0)} \left[ \frac{b}{\sum_i x_i q_i G_{ji}} \right] = k_{ij} \tag{A2.5}
\]

where:

\[
k_{ij}^{(0)} = \frac{k_{ji}^{(0)}}{2 \sqrt{\delta_{bi} \delta_{bj}}} = 1 - \frac{b_i b_j}{2 \sqrt{\delta_{bi} \delta_{bj}}} \left( \frac{a_i}{b_i} + \frac{a_j}{b_j} \right) = \left( \frac{\delta_{bi} - \delta_{bj}}{2 \delta_{bi} \delta_{bj}} \right)^2
\]

with:

\[
\delta_{bi} = \sqrt{\frac{a_i}{b_i}} \tag{A2.6}
\]

and:

\[
\rho_{ij}^{(0)} = \frac{q_i G_i \Gamma_{ij}/C}{2 \sqrt{\delta_{bi} \delta_{bj}}} \quad \rho_{ji}^{(0)} = \frac{G_j \Gamma_{ji}/C}{2 \delta_{bj} \delta_{aj}}, \quad \text{with} \quad \delta_{bi} = \frac{\sqrt{a_i}}{q_i}
\]

\[
\tag{A2.7}
\]

Appendix C. Lattice models with constant \( k_{ij} \) mixing rules with respect to mole fractions.

C.1. NRTL-PR model

For simple mixtures, in which molecular interactions are sufficiently small \( (\Gamma_{ij} \approx 0) \) not to disturb the “random” distribution of molecules, the repartition coefficients in Eq. (6) are assumed close to unit \( (G_{ii} \approx 1) \), so that the attractive term \( a \) in Eq. (7) or (A2.1) is expressed according to the “one fluid lattice model” as:

\[
a = \alpha bRT = b \left[ \sum_i x_i \frac{a_i}{b_i} - \frac{1}{2} \sum_i \sum_j x_i x_j b_i b_j \frac{q_i q_j E_{ij}/C}{q} \right] \tag{A3.1}
\]

with:

\[
q = \sum_i x_i q_i, \quad E_{ij} = E_{ji} = \Gamma_{ij} + \Gamma_{ji} \approx 0 \tag{A3.2}
\]

or, according to Eqs. (9) and (10) or (A2.5), to the following “\( k_{ij} \)” mixing rule:

\[
k_{ij} = k_{ij}^{(0)} + \rho_{ij}^{(0)} + \rho_{ji}^{(0)} \left( \frac{b_i b_j}{q} \right) \approx k_{ij}^{(0)} \tag{A3.3}
\]

According to the method proposed for the calculation of the \( \Gamma_{ij} \) interaction parameters (Eq. (12)), only hydrocarbon mixtures, for which the \( \Gamma_{ij}^{(0)} \) and \( \Gamma_{ij}^{(1)} \) parameters detailed in Table 2 have rather small values, can be considered as “random mixtures”.

C.2. PPR78 EoS

Whatever the kind of mixture considered, the attractive term a proposed by Pénéloux et al. [31] and Jaubert and co-workers [5] with the PPR78 EoS is expressed according to a “one fluid lattice model” \( (G_{ii} = 1) \) as:

\[
a = \alpha bRT = b \left[ \sum_i x_i \frac{a_i}{b_i} - \frac{1}{2} \sum_i \sum_j x_i x_j b_i b_j E_{ij} \right] \tag{A3.4}
\]

or with the “\( k_{ij} \)” mixing rule:

\[
k_{ij} = - \frac{b_i b_j}{2 \delta_{bi} \delta_{bj}} E_{ij} \tag{A3.5}
\]

It can be noticed that, for simple mixtures, the NRTL-PR mixing rule (Eqs. (A3.1) and (A3.2)) is equivalent to the PPR78 one (Eq. (A3.4)), except that it makes use of dimensionless area parameters \( q_i \) instead of co-volumes \( b_i \) (obviously the use of parameters \( q_i \approx b_i \) would lead to similar \( k_{ij} \) values). Nevertheless, for all other mixtures, the PPR78 model assumes, contrary to the NRTL-PR model, that \( k_{ij} \) parameters are independent on mole fractions.

Appendix D. SRKm model

The SRKm (Soave–Redlich-Kwong modified) mixing rule proposed by Panagiotopoulos and Reid [7] expresses the attractive term a of the EoS according to:

\[
a = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \sqrt{\frac{a_i}{a_i} (1 - K_{ij})}, \quad b = \sum_{i=1}^{c} x_i b_i
\]

\[
K_{ij} = k_{ij} - (k_{ij} - k_{ji}) \left( \frac{x_j}{x_i + x_j} \right) c_q, \quad k_{ij} = k_{ij}^{(0)} + \frac{k_{b1} b_i + k_{b2} b_j}{T^2}
\]

\[
\tag{A4.1}
\]
D.1. Literature interaction parameters between water (1) and hydrocarbon (2)

| Component (2) | $k_{A1}$ | $k_{A2}$ | $k_{C1}$ | $k_{C2}$ | $C_{12}$ | Component (2) | $k_{A1}$ | $k_{A2}$ | $k_{C1}$ | $k_{C2}$ | $C_{12}$ |
|---------------|---------|---------|---------|---------|-------|---------------|---------|---------|---------|---------|-------|
| Methane       | 0.1171  | 131.7   | 0       | 0       | 0.7606 | Penetane      | −0.0673 | 506.46  | −91.4163 | 1       |       |
| Hexane        | 1.7921  | −1167.81| 161363  | 1       | 1.2235 | Heptane       | 0.8464  | −523.23 | 587.015  | 1       |       |
| Octane        | 3.0148  | −1563.34| 239464  | 1       | −1     | Cyclohexane   | −0.0543 | −116.05 | 0        | 1       |       |
| 2-Methylbutane| 0.3637  | −220.69 | 7372.16 | 1       | 0.2021 | Benzene       | 0.8769  | −498.18 | 578.129  | 1       |       |
| Methyleneclorohane | 0.5075 | −368.75 | 36169.4 | 1       | 1.6618 | Ethylbenzene  | 0.6501  | −548.67 | 73399.5  | 1       |       |
| Toluene       | 0.6948  | −52.54  | 0       | 1       | 0.6792 | m-Xylene      | 0.9392  | −142.47 | 0        | 1       |       |
| o-Xylene      | 0.2844  | −164.52 | 0       | 1       | 0.0928 | n-Xylene      | 0.3702  | −26.73  | 164411   | 0.015   | 0.295 |
| p-Xylene      | 0.3027  | 0       | 0       | 1       | −0.008 |             | 0.1764  | −106.53 | 0        | 1       |       |

D.2. Standard interaction parameters between water (1) or ethylene glycol (1) and hydrocarbon (2)

| Component (2) | $k_{A1}$ | $k_{A2}$ | $k_{C1}$ | $k_{C2}$ | $C_{12}$ | Component (2) | $k_{A1}$ | $k_{A2}$ | $k_{C1}$ | $k_{C2}$ | $C_{12}$ |
|---------------|---------|---------|---------|---------|-------|---------------|---------|---------|---------|---------|-------|
| Alcane        | 0.5     | 0       | 0       | 1       | −0.06 | Naphthene     | 0.445   | 0       | 0        | 1       |       |
| Aromatic      | 0.315   | 0       | 0       | 1       | −0.06 |             | −0.06   | 0       | 0        | 1       |       |

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