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Joan Escandell, Evelyne Neau, Christophe Nicolas. A new formulation of the predictive NRTL-PR model in terms of kij mixing rules. Extension of the group contributions for the modeling of hydrocarbons in the presence of associating compounds. *Fluid Phase Equilibria*, 2011, 301 (1), pp.80-97. 10.1016/j.fluid.2010.11.009 . hal-01464747

HAL Id: hal-01464747

<https://hal.science/hal-01464747>

Submitted on 3 Sep 2020

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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

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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 SRK_m. 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-GCEoS [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/G^E 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 SRK_m (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 SRK_m 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/G^E 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

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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]:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \quad (1)$$

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:

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

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:

$$\alpha(T) = \left[1 + m \left(1 - \left(\frac{T}{T_c} \right)^\gamma \right) \right]^2, \quad \text{with } \gamma = 0.5 \quad (3)$$

and:

$$\begin{aligned} m &= 0.37464 + 1.54226\omega - 0.26992\omega^2 & \text{if } \omega < 0.49 \\ m &= 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 & \text{if } \omega > 0.49 \end{aligned} \quad (4)$$

For mixtures, the attractive NRTL-PR term in Eq. (1) is expressed, either from the “EoS/G^E” 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 $\alpha = a/bRT$ is estimated using the approach based on the reference state recently developed in [16] (Appendix A):

$$\begin{aligned} \alpha &= \sum_i x_i \alpha_i - \frac{1}{C} \left[\frac{g_{NRTL-gen}^E}{RT} - \sum_i x_i \ln \frac{r_i}{r} \right], \\ r &= \sum_i x_i r_i, \quad C = 0.53 \end{aligned} \quad (5)$$

where C is the reference state constant and r_i are the volume area factors characteristic of lattice fluid models; $g_{NRTL-gen}^E$ is the generalized NRTL excess Gibbs energy proposed in [10]:

$$\begin{aligned} g_{NRTL-gen}^E &= RT \sum_i x_i \ln \frac{r_i}{r} + \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_l x_l q_l G_{li}}, \\ G_{ji} &= \exp - \left(\frac{\alpha_0 \Gamma_{ji}}{RT} \right) \end{aligned} \quad (6)$$

where Γ_{ji} is the binary interaction parameter between molecules i and j ; α_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:

$$\begin{aligned} a &= \alpha b RT = b \left[\sum_i x_i \frac{a_i}{b_i} - \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji} / C}{\sum_l x_l q_l G_{li}} \right], \\ b &= \sum_i x_i b_i \end{aligned} \quad (7)$$

Table 1

Main groups, subgroups and subgroup surface area parameters of the NRTL-PR model.

Main groups K		Subgroups k	Q_k
Paraffins	PAR	CH ₃	0.848
		CH ₂	0.540
		CH	0.228
Naphthenes	CYC	C	0.000
		CH ₂	0.540
		CH, C	0.228
		CH	0.400
Aromatics	ARO	C	0.120
		CH ₄	1.124
		C ₂ H ₆	1.696
Methane	CH ₄	CH ₄	0.982
Ethane	C ₂ H ₆	C ₂ H ₆	0.930
Carbon dioxide	CO ₂	CO ₂	1.202
Nitrogen	N ₂	N ₂	1.400
Hydrogen sulfide	H ₂ S	H ₂ S	2.248
Water	H ₂ O	H ₂ O	
Ethylene glycol	MEG	MEG	

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

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i} \sqrt{a_j} (1 - k_{ij}) \quad (8)$$

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

$$k_{ij} = k_{ij}^{(0)} + \rho_{ij}^{(0)} \left[\frac{b}{\sum_l x_l q_l G_{lj}} \right] + \rho_{ji}^{(0)} \left[\frac{b}{\sum_l x_l q_l G_{li}} \right] = k_{ji} \quad (9)$$

in which:

$$\begin{aligned} k_{ij}^{(0)} &= k_{ji}^{(0)} = - \frac{(\delta_{bi} - \delta_{bj})^2}{2\delta_{bi}\delta_{bj}} & \text{with: } \delta_{bi} &= \frac{\sqrt{a_i}}{b_i} \\ \rho_{ij}^{(0)} &= \frac{G_{ij} \Gamma_{ij} / C}{2\delta_{qi}\delta_{qj}}, \quad \rho_{ji}^{(0)} = \frac{G_{ji} \Gamma_{ji} / C}{2\delta_{qi}\delta_{qj}} & \text{with: } \delta_{qi} &= \frac{\sqrt{a_i}}{q_i} \end{aligned} \quad (10)$$

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 :

$$q_i = \sum_k \nu_{ik} Q_k \quad (11)$$

where ν_{ik} 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 Holderbaum and Gmelhing [18] and Skjold-Jorgensen et al. [19] were respectively considered (Table 1).

- The non randomness factor in Eq. (6) is fixed to the value $\alpha_0 = -1$ as suggested by Marina and Tassios [20] for the modeling of strongly nonideal mixtures.

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

$$\Gamma_{ji} = - \sum_K \theta_{iK} \sum_L (\theta_{iL} - \theta_{jL}) \Gamma_{LK}, \quad \Gamma_{KK} = 0 \quad (12)$$

$$\text{with: } \theta_{iK} = \sum_k \frac{\nu_{ik(K)} Q_k}{q_i} \quad (13)$$

where $\nu_{ik(K)}$ is the number of subgroups k belonging to the main group K in a molecule i .

According to previous works [21] related to the correlation of data with simple equations of state, the following variation with

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

L\K	PAR	CYC	ARO	CH ₄	C ₂ H ₆	CO ₂	N ₂	H ₂ S	H ₂ O	MEG
PAR	0.00	57.25	220.63	147.46	48.26	866.65	523.57	733.34	3258.30	2802.32
CYC	57.25	0.00	249.71	283.73	71.67	862.31	1035.59	731.54	3140.65	2768.55
ARO	220.63	249.71	0.00	555.61	552.46	820.70	1476.84	77.16	2792.91	2303.32
CH ₄	147.46	283.73	555.61	0.00	73.03	748.07	231.80	1016.15	3309.45	2851.39
C ₂ H ₆	48.26	71.67	552.46	73.03	0.00	791.11	434.39	796.08	3300.41	3239.78
CO ₂	866.65	862.31	820.70	748.07	791.11	0.00	743.75	743.35	-	-
N ₂	523.57	1035.59	1476.84	231.80	434.39	743.75	0.00	1670.19	-	-
H ₂ S	733.34	731.54	77.16	1016.15	796.08	743.35	1670.19	0.00	-	-
H ₂ O	2387.95	2421.64	2343.02	2305.94	2265.04	-	-	-	0.00	124.48
MEG	836.31	834.63	519.20	1281.26	881.95	-	-	-	124.48	0.00

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

L\K	PAR	CYC	ARO	CH ₄	C ₂ H ₆	CO ₂	N ₂	H ₂ S	H ₂ O	MEG
PAR	0.00	-72.22	270.25	13.32	-137.36	609.93	59.69	-227.73	-145.24	-335.72
CYC	-72.22	0.00	191.29	294.52	-172.44	524.20	1368.43	579.78	-285.83	-561.09
ARO	270.25	191.29	0.00	-163.10	934.25	1491.76	1953.96	-247.07	-879.36	918.64
CH ₄	13.32	294.52	-163.10	0.00	8.34	308.54	-4.31	-166.44	-2007.73	-550.04
C ₂ H ₆	-137.36	-172.44	934.25	8.34	0.00	526.65	-18.84	120.77	-825.32	-5709.15
CO ₂	609.93	524.20	1491.76	308.54	526.65	0.00	165.42	-368.65	-	-
N ₂	59.69	1368.43	1953.96	-4.31	-18.84	165.42	0.00	-171.30	-	-
H ₂ S	-227.73	579.78	-247.07	-166.44	120.77	-368.65	-171.30	0.00	-	-
H ₂ O	-3579.09	-3871.15	-2743.07	-4185.03	-3944.30	-	-	-	0.00	-718.31
MEG	-1060.28	-610.97	-2048.06	-1033.41	1527.06	-	-	-	-718.31	0.00

respect to temperature is considered:

$$\Gamma_{LK} = \Gamma_{LK}^{(0)} + \Gamma_{LK}^{(1)} \left(\frac{T^0}{T} - 1 \right) \quad (14)$$

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 ($\Gamma_{ij} = \Gamma_{ji} = 0$).
- Interaction parameters Γ_{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:

$$F_{obj} = \frac{1}{N_p} \sum_i \frac{|\Delta P_i|}{P_i} + \frac{1}{N_y} \sum_i |\Delta y_i| + \frac{1}{N_h} \sum_i \frac{|\Delta h_i|}{h_i} + \frac{1}{N_{xI}} \sum_i \frac{|\Delta x_{1i}^I|}{x_{1i}^I} + \frac{1}{N_{xI}} \sum_i \frac{|\Delta x_{2i}^I|}{x_{2i}^I} \quad (15)$$

where ΔP , Δy and Δh are, respectively, the deviations on bubble points, vapor mole fractions and excess enthalpies; Δx_{1i}^I and Δx_{2i}^I are the deviations on the mole fraction of the dilute component, respectively, in the hydrocarbon (II) and polar (I) phases; N_p , N_y , N_h , N_{xI} and N_{xI} 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 ($\Gamma_{KL} = \Gamma_{LK} = 0$), so that ΔP , Δy are not indicated in Table 3a; for excess enthalpies,

Δh 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_{ij} parameters

Fig. 1a illustrates NRTL-PR predictions of the k_{ij} 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 $\Gamma_{LK}^{(0)}$ and $\Gamma_{LK}^{(1)}$ have very moderate values (Table 2), so that molecular interactions Γ_{ij} are almost negligible; hence, according to Appendix C (Eqs. (A3.1) and (A3.2)), the k_{ij} parameters are practically independent on mixture mole fractions. For paraffin mixtures, which require no interaction energies ($\Gamma_{ij} = 0$), the k_{ij} 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 Γ_{LK} (Table 2); hence, a variation of k_{ij} can be observed with respect to mole fractions, particularly in the vicinity of pure carbon dioxide.

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

Fig. 1b shows the variation of k_{ij} with respect to temperature, for the same systems at a given mole fraction ($x_1^0 = 0.5$). In the current range of industrial applications (200–900 K), the k_{ij}

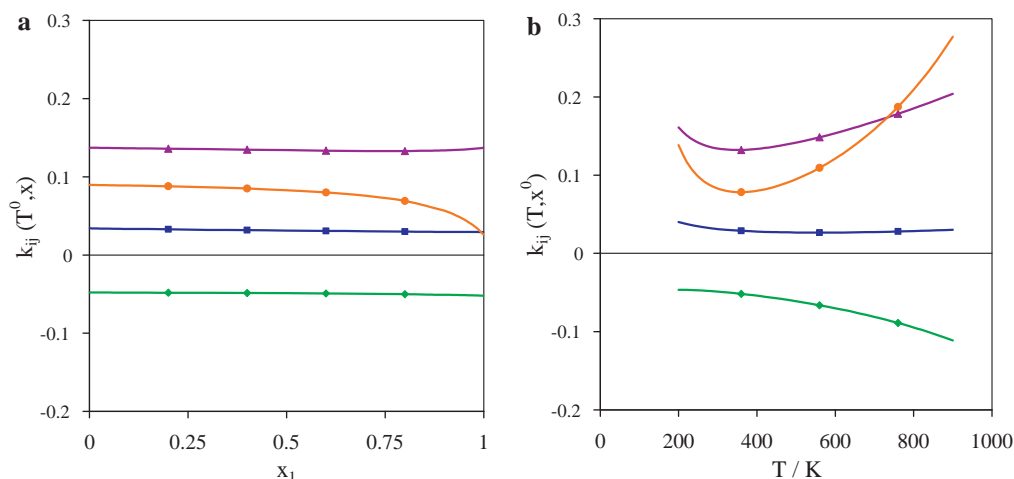


Fig. 1. NRTL-PR predictions of k_{ij} for (■) cyclohexane (1)–benzene (2), (◆) cyclohexane (1)–eicosane (2), (▲) carbon dioxide (1)–cyclohexane (2), and (●) carbon dioxide (1)–eicosane (2) systems: (a) $k_{ij}(T^0, x)$ at $T^0 = 300$ K and (b) $k_{ij}(T, x^0)$ for $x_1^0 = 0.5$.

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 $T = 350$ 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 Γ_{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).

Table 3a

Hydrocarbon data base considered for the estimation of the group contribution parameters. N_{bs} is the number of binary systems and N_p , N_y , N_h , are the numbers of data points for each function.

Systems	VLE	F_{obj}			h^E			
		N_{bs}	N_p	N_y	$\Delta P\%$	Δy	N_{bs}	N_h
Paraffins	–Paraffins	58	3940	1523	–	–	98	1963
Naphthenes	–Paraffins	33	1841	905	1.79	0.0058	52	2806
	–Naphthenes	11	169	73	2.20	0.0022	14	1025
Aromatics	–Paraffins	66	5395	3111	3.42	0.0125	56	2756
	–Naphthenes	37	3119	2196	2.29	0.0084	35	1712
CH ₄	–Aromatics	29	1474	911	2.34	0.0117	51	1782
	–Paraffins	22	3902	2354	7.80	0.0087	2	44
	–Naphthenes	7	432	303	5.74	0.0069	1	36
C ₂ H ₆	–Aromatics	17	904	528	14.48 ^a	0.0159		
	–Paraffins	17	2203	946	5.09	0.0113		
	–Naphthenes	4	221	61	2.97	0.0078		
	–Aromatics	8	328	237	6.07	0.0079		
CO ₂	–CH ₄	1	373	335	1.69	0.0053	1	11
	–Paraffins	27	3036	2110	6.33	0.0123	3	1401
	–Naphthenes	6	645	498	6.03	0.0116	1	536
	–Aromatics	23	2042	1306	9.90 ^a	0.0088	1	751
N ₂	–CH ₄	1	362	289	1.33	0.0082		
	–C ₂ H ₆	1	414	422	1.42	0.0120		
	–Paraffins	14	1348	1121	10.10 ^a	0.0236		
	–Naphthenes	5	173	163	11.32 ^a	0.0129		
	–Aromatics	9	587	184	15.74 ^a	0.0107		
	–CH ₄	1	497	438	1.29	0.0065	1	12
H ₂ S	–C ₂ H ₆	1	212	197	6.70	0.0139		
	–CO ₂	1	215	192	3.46	0.0132		
	–Paraffins	14	564	419	4.91	0.0212		
	–Naphthenes	5	134	134	4.02	0.0120		
	–Aromatics	5	150	150	4.93	0.0085		
	–CH ₄	1	117	114	6.90	0.0188		
	–C ₂ H ₆	1	79	66	1.67	0.0187		
	–CO ₂	1	142	142	1.97	0.0167		
	–N ₂	1	74	71	6.28	0.0116		

^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_{bs} is the number of binary systems and N_{xll} , N_{xl} are the numbers of data points in the hydrocarbon and polar phases.

Systems		VLE, LLE			F_{obj}	
		N_{bs}	N_{xll}	N_{xl}	$\Delta x_1^I\%$	$\Delta x_2^I\%$
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	3.39	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
	–C ₂ H ₆	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 $|\Delta P_i|/P_i$ (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 $\Delta P\%$.

For all these systems, it can also be concluded that the use of interactions only between main groups, as for VTPR and NRTL-PR, or between numerous groups, like with PPR78, has few influence on the prediction of the phase diagrams.

- 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-Trimethylbenzene	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	<i>o</i> -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	7.58	10.23	8.67	[64,69]
CO ₂	Methylcyclohexane	31	311	477	7.04	6.98	8.06	[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	<i>m</i> -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	(143)	306	488	(17.10)	–	(9.02)	[94–96]
N ₂	Isobutane	(52)	255	394	(6.94)	–	(6.86)	[97]
N ₂	Propylcyclohexane ^a	(33)	314	473	(13.55)	–	(6.49)	[98]
N ₂	Toluene ^a	(61)	303	473	(24.37)	–	(14.34)	[96,99,100]
CH ₄	C ₂ H ₆	381	91	283	1.59	1.90	1.56	[101–110]
CH ₄	CO ₂	395	153	301	1.72	2.16	1.34	[106,109–119]
CH ₄	H ₂ S	(84)	277	344	(3.69)	–	(2.54)	[120,121]
C ₂ H ₆	H ₂ S	59	200	283	2.23	3.18	1.35	[122,123]
<i>Global</i>		2406			3.38	3.44	3.37	

– unpublised parameters, () values not taken into consideration for the estimation of the global values.

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

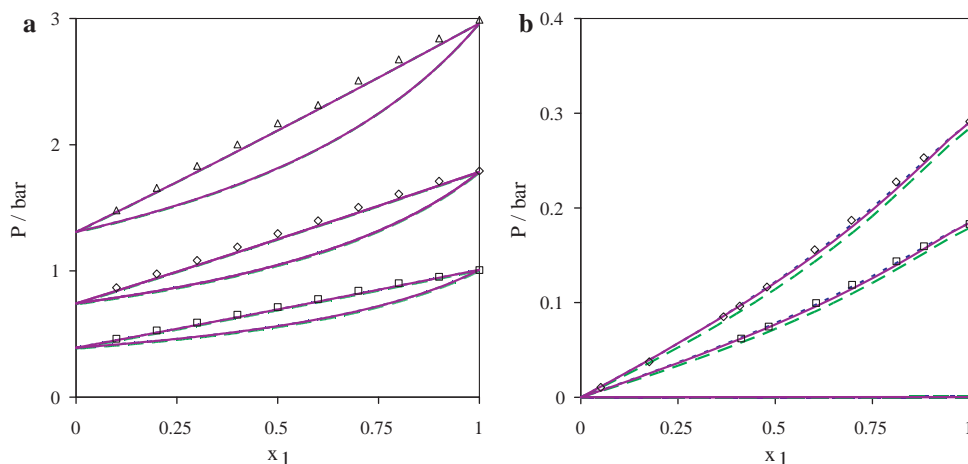


Fig. 2. VLE of hydrocarbon mixtures. Predictions with the (■ ■ ■ ■) PPR78, (■ ■ ■ ■) VTPR and (—) NRTL-PR models. (a) Benzene (1)–toluene (2) system at $T=353\text{ K}$ (□), $T=373\text{ K}$ (◇) and $T=393\text{ K}$ (△) [56]. (b) Cyclohexane (1)–eicosane (2) system at $T=306\text{ K}$ (□) and $T=317\text{ K}$ (◇) [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–naphthene 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.

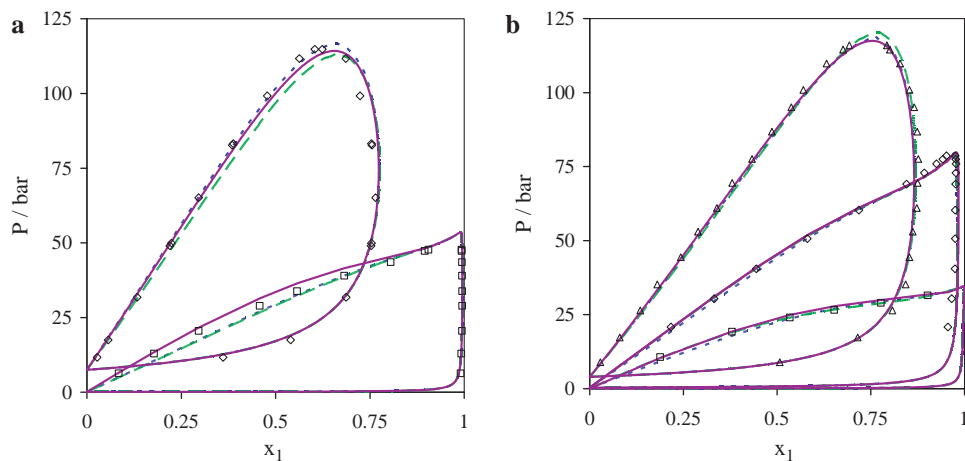


Fig. 3. VLE of hydrocarbon–permanent gases. Predictions with the (■ ■ ■ ■) PPR78, (■ ■ ■ ■) VTPR and (—) NRTL-PR models. (a) Ethane (1)–toluene (2) system at $T=313\text{ K}$ (□) and $T=473\text{ K}$ (◇) [65]. (b) Carbon dioxide (1)–hexane (2) system at $T=273\text{ K}$ (□) [66], $T=313\text{ K}$ (◇) [67] and $T=393\text{ K}$ (△) [68].

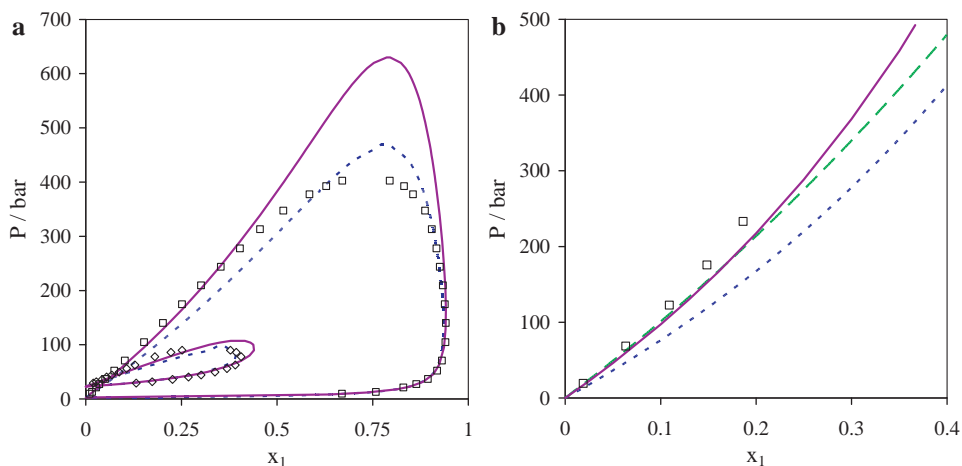


Fig. 4. VLE of hydrocarbon-permanent gases. Predictions with the (---) PPR78, (---) VTPR and (—) NRTL-PR models. (a) Nitrogen (1)-hexane (2) system at $T=378$ K (\square) and $T=488$ K (\diamond) [95]. (b) Methane (1)-phenanthrene (2) system at $T=473$ K (\square) [93].

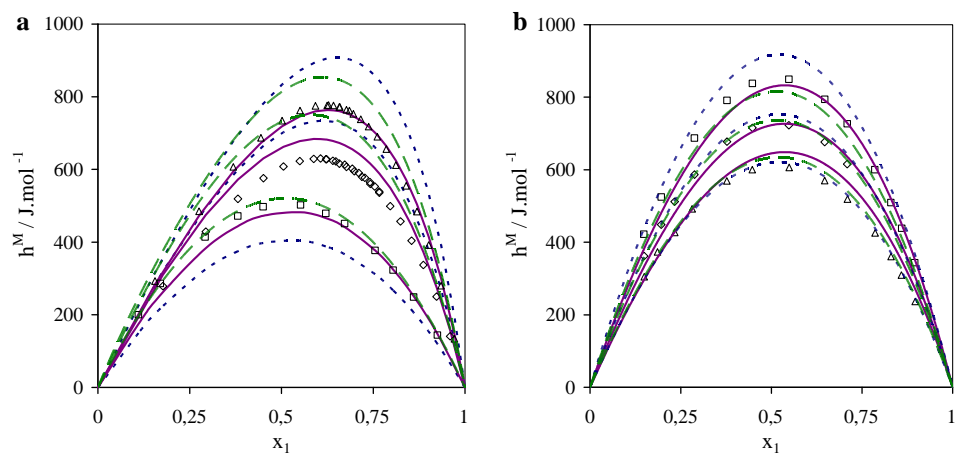


Fig. 5. Excess enthalpies of hydrocarbon mixtures. Predictions with the (---) PPR78, (---) VTPR and (—) NRTL-PR models. (a) Toluene (1)-hexane (2) (\square) [124], -dodecane (2) (\diamond) [125] and -hexadecane (2) (\triangle) [126] at $T=298$ K. (b) Benzene (1)-cyclohexane (2) system at $T=280$ K (\square),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

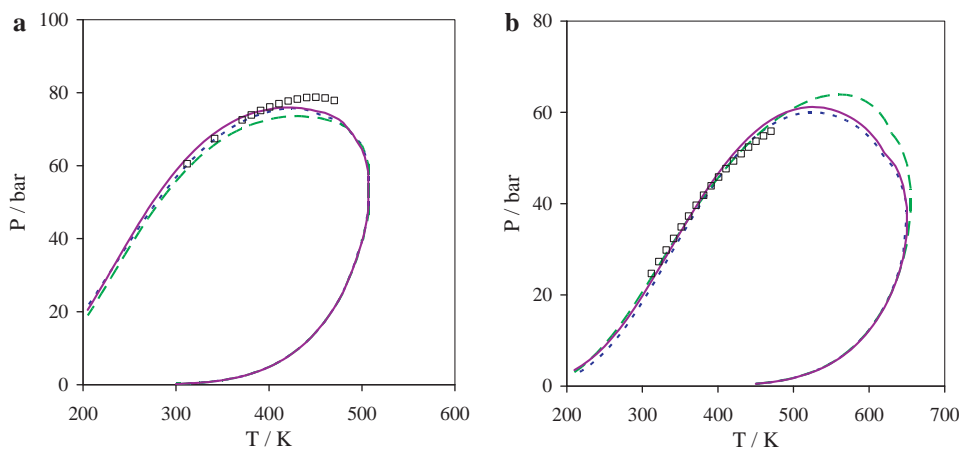


Fig. 6. Phase envelopes of synthetic petroleum fluids. Predictions with the (---) PPR78, (---) VTPR and (—) NRTL-PR models. (a) $x_{\text{methane}}=0.2453$, $x_{3\text{-methylpentane}}=0.0498$, $x_{\text{hexane}}=0.4029$, $x_{\text{benzene}}=0.0508$, $x_{\text{cyclohexane}}=0.0501$ and $x_{\text{heptane}}=0.2011$ (\square) [128]. (b) $x_{\text{carbon dioxide}}=0.2507$, $x_{\text{naphtalene}}=0.0330$ and $x_{\text{dodecane}}=0.7163$ (\square) [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 SRK [7] and CPA [3] 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 ($x_1^0 = 0.01$ and $x_1^0 = 0.99$) 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 (Fig. 1b), a minimum located around 350 K is observed for the hydrocarbon rich phase of water–heptane and ethylene glycol–toluene systems.

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

4.2.1. Comparison with the SRK EoS

Results obtained with the NRTL-PR model are compared in Table 5 and Figs. 8 and 9 with the SRK 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 SRK 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 $\Delta x_2^I\%$ and $\Delta x_2^{II}\%$ 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 very accurate prediction of the solubilities in both phases. The SRK 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 SRK equation correctly represents the organic phase, but introduces large deviations on the solubility in the aqueous phase; in all cases, the SRK 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 compar-

ison of the literature k_{ij} mixing rules used for the description of the VLLE of water–hydrocarbon mixtures; for this purpose, besides the NRTL-PR and SRK models, 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 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 SRK 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.

4.2.2. Comparison with the CPA equation

Figs. 10 and 11 present the comparison between the NRTL-PR and the CPA equations.

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 SRK EoS

Table 6 compares, for the modeling of VLLE of glycol–hydrocarbon mixtures with the NRTL-PR and SRK 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.

Isothermal data (T (K))					SRKm		NRTL-PR		Ref.
Component (2)	T_{\min}	T_{\max}	N_{xII}	N_{xI}	$\Delta x_1^{II}\%$	$\Delta x_2^{II}\%$	$\Delta x_1^{I}\%$	$\Delta x_2^{I}\%$	
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]
<i>m</i> -Xylene	298	–	–	4	–	69.81	–	29.82	[159]
<i>p</i> -Xylene	298	–	–	2	–	69.19	–	41.13	[159]
<i>Global</i>			277	406	12.87	63.40	9.90	7.31	

Isobaric data (P /bar)					SRKm		NRTL-PR		Ref.
Component (2)	P_{\min}	P_{\max}	N_{xII}	N_{xI}	$\Delta x_1^{II}\%$	$\Delta x_2^{II}\%$	$\Delta x_1^{I}\%$	$\Delta x_2^{I}\%$	
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-Methylbutane	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	8.80	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]
<i>o</i> -Xylene	1	–	3	13	1.82	52.35	19.59	38.28	[159]
<i>m</i> -Xylene	1	60	13	34	25.49	63.93	13.93	21.68	[159]
<i>p</i> -Xylene	1	2	11	40	25.34	422.16	7.33	23.77	[159]
<i>Global</i>			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_{ij} parameters, instead of fitted ones, is probably responsible of 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).

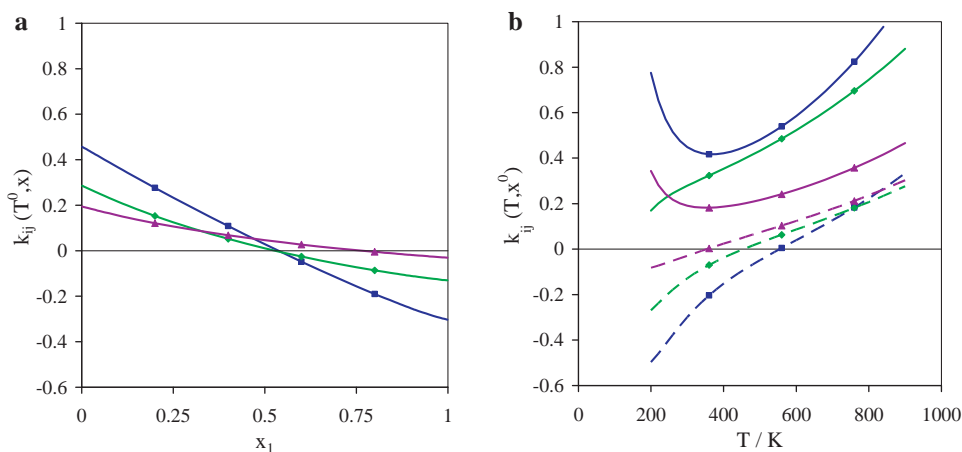


Fig. 7. NRTL-PR predictions of k_{ij} for (—■—) water (1)–heptane (2), (—◆—) water (1)–benzene (2) and (—▲—) ethylene glycol (1)–toluene (2) systems: (a) $k_{ij}(T^0, x)$ at $T^0 = 300$ K and (b) $k_{ij}(T, x^0)$ for (—) $x_1^0 = 0.01$ and (---) $x_1^0 = 0.99$.

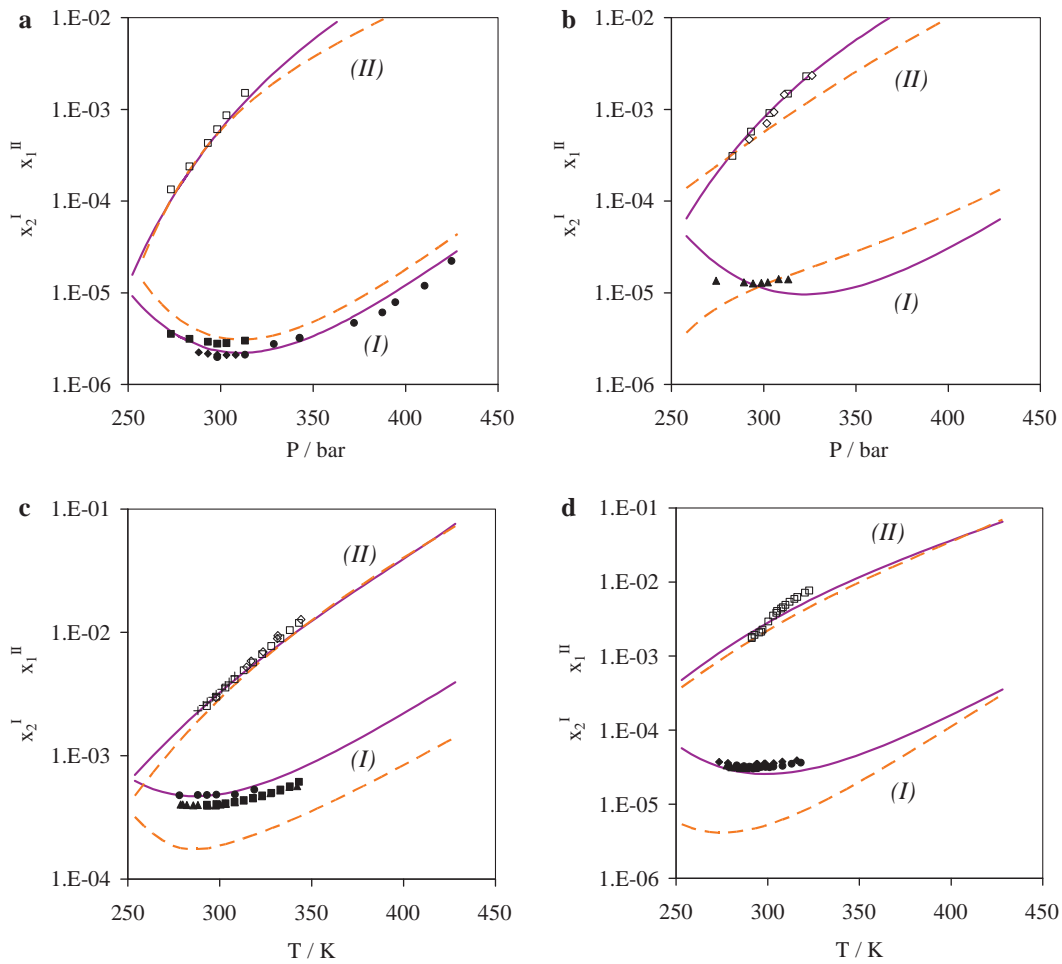


Fig. 8. LLE of water-hydrocarbon systems under atmospheric pressure. Modeling with the (—) SRKm and (—) NRTL-PR models. (a) Water (1)-hexane (2): hydrocarbon phase (II) (□) [160] and aqueous phase (I) (■) [160], (◆) [161], (●) [162]; (b) Water (1)-cyclohexane (2): hydrocarbon phase (II) (□) [163], (◇) [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.

Isothermal data (T (K))					SRKm		NRTL-PR		Ref.
Component (2)	T_{min}	T_{max}	N_{xII}	N_{xI}	$\Delta x_1^{II}\%$	$\Delta x_2^I\%$	$\Delta x_1^{II}\%$	$\Delta x_2^I\%$	
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]
<i>Global</i>			9	132	55.84	60.44	13.88	6.43	
Isobaric data (P (bar))					SRKm		NRTL-PR		Ref.
Component (2)	P_{min}	P_{max}	N_{xII}	N_{xI}	$\Delta x_1^{II}\%$	$\Delta x_2^I\%$	$\Delta x_1^{II}\%$	$\Delta x_2^I\%$	
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	-	7.16	-	[186]
Methylcyclohexane	1	-	6	6	91.87	244.51	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]
<i>o</i> -Xylene	1	-	-	13	98.31	87.46	-	8.59	[190]
<i>Global</i>			59	67	>90	85.74	11.52	6.53	

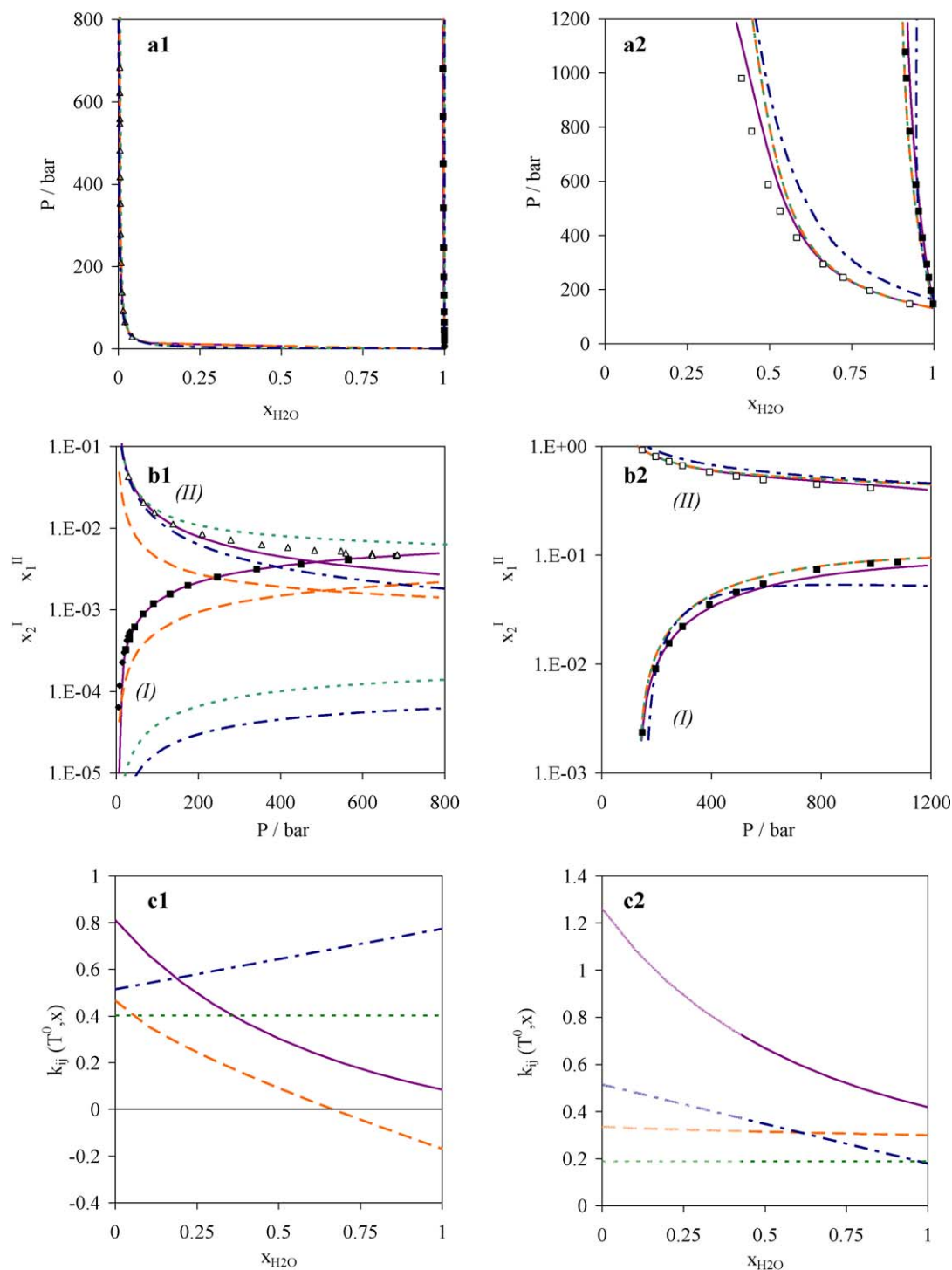


Fig. 9. VLE of water (1)–methane (2) system. Modeling with (—) PR $[k_{ij}]^*$, (---) PR $[k_{ij}(x)]^*$ (---) SRKm and (—) NRTL-PR models. (1) System at $T = 377.59$ K (■) [134], (◆) [135], (△) [143]; (2) System at $T = 603.15$ K (■, □) [146]. (a) Phase envelope; (b) Solubilities in aqueous (I) and hydrocarbon (II) phases; (c) Variation of k_{ij} with respect to water mole fractions. $*[k_{12}^0 = -0.1719 + 217.1/T]$ $*[k_{12}(x) = k_{12}^0 + k_{12}^1(x_1 - x_2)$, $k_{12}^0 = -0.1510 + 300.3/T$, $k_{12}^1 = -0.6647 + 300.0/T]$.

- 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 Γ_{ij} interaction parameters fitted on binary mixtures (NRTL-PR_{fitted}), 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.

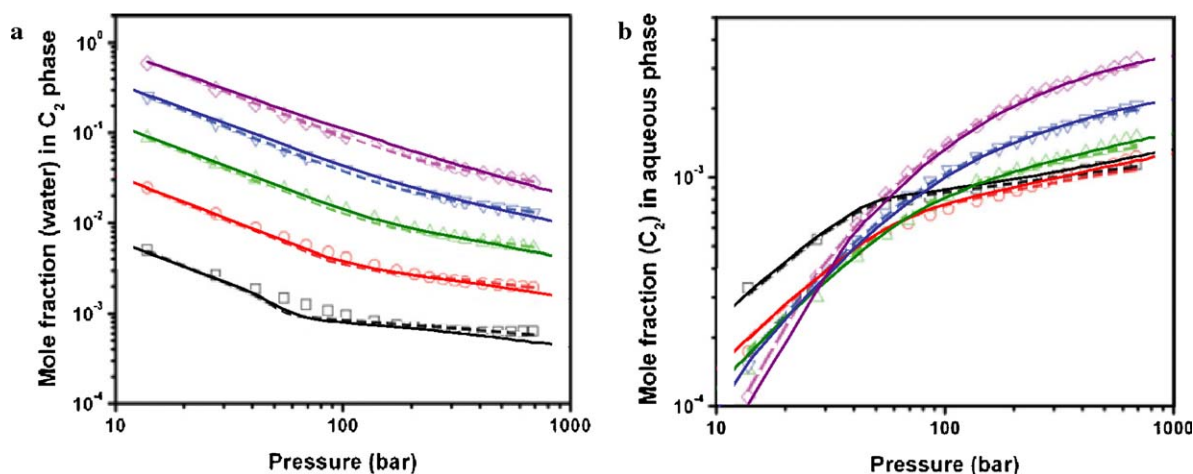


Fig. 10. VLE of water (1)–ethane (2) system. Modeling with the (---) CPA and (—) NRTL-PR models at $T=310\text{ K}$ (\square), $T=344\text{ K}$ (\circ), $T=378\text{ K}$ (\triangle), $T=411\text{ K}$ (∇) and $T=444\text{ K}$ (\diamond): (a) hydrocarbon [174] and (b) aqueous [175] phases (CPA curves and k_{ij} values taken from Li and Firoozabadi [192]).

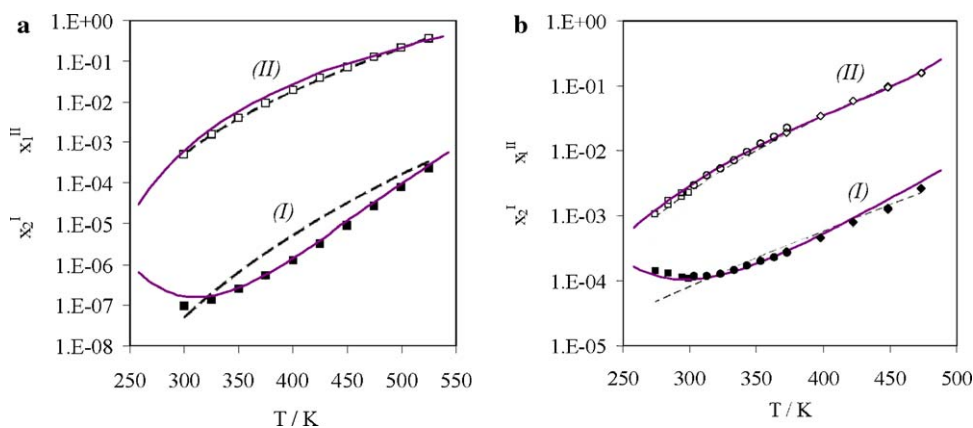


Fig. 11. LLE of water–hydrocarbon systems. Modeling with the (---) CPA and (—) NRTL-PR models. (a) Water (1)–octane (2): aqueous phase (I) (\blacksquare) [176] and hydrocarbon phase (II) (\square) [176] (CPA curves from Voutsas et al. [193], $k_{ij} = -0.03$). (b) Water (1)–toluene (2): aqueous phase (I) (\blacksquare) [160], (\bullet) [177], (\blacklozenge) [178] and hydrocarbon phase (II) (\square) [160], (\circ) [177], (\diamond) [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_{fitted} version using, like CPA, binary interaction parameters Γ_{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 Γ_{ij} parameter, the NRTL-PR_{fitted} model leads to more reliable results than the CPA equation.

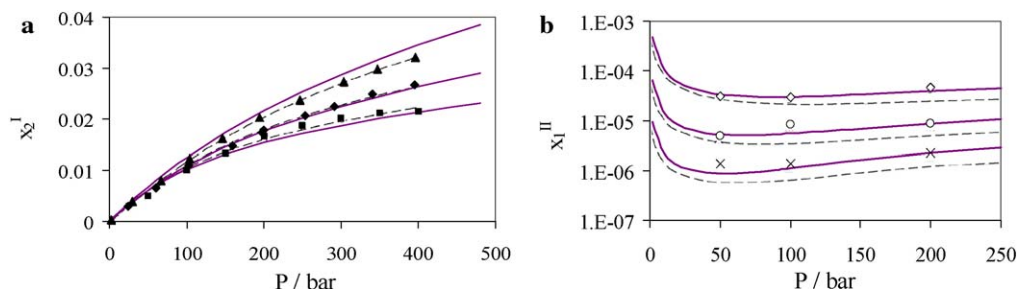


Fig. 12. VLE of ethylene glycol–hydrocarbon systems. Modeling with the (---) CPA and (—) NRTL-PR models. Ethylene glycol (1)–methane (2) system: (a) solubility in the polar phase at $T=283\text{ K}$ (\blacksquare) [181], $T=323\text{ K}$ (\blacklozenge) and $T=373\text{ K}$ (\blacktriangle) [182]; (b) solubility in the hydrocarbon phase at $T=278\text{ K}$ (\times), $T=298\text{ K}$ (\circ) and $T=373\text{ K}$ (\diamond) [179] (CPA curves from Haghghi et al. [195] with $k_{ij} = 0.0004 + 0.0498 T$).

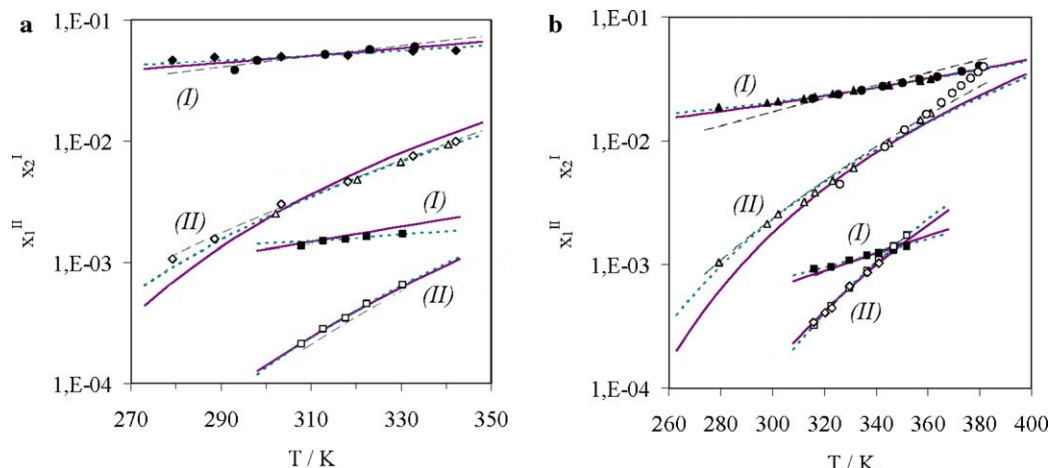


Fig. 13. LLE of ethylene glycol-hydrocarbon systems. Modeling with the (---) CPA, (—) NRTL-PR and (■ ■ ■) NRTL-PR_{fitted} models. Solubilities in the polar (I) and hydrocarbon (II) phases. (a) Ethylene glycol (1)-hexane (2) (■, □) [185] (CPA curves from Folas et al. [196] with $k_{ij} = 0.059$; NRTL-PR_{fitted}: $\Gamma_{21} = 2989 - 657,033/T$, $\Gamma_{12} = 2964 - 43,303/T$) and ethylene glycol (1)-benzene (2) (◆, ◇) [185], (●) [187], (△) [186] (CPA curves from Folas et al. [188] with $k_{ij} = 0.049$, BETCR=0.04; NRTL-PR_{fitted}: $\Gamma_{21} = 2423 - 492,442/T$, $\Gamma_{12} = 2731 - 33,819/T$). (b) Ethylene glycol (1)-heptane (2) (■, □) [185], (◇) [186] (CPA curves from Folas et al. [194] with $k_{ij} = 0.031$; NRTL-PR_{fitted}: $\Gamma_{21} = 2554 - 608,309/T$, $\Gamma_{12} = 1950 - 102,371/T$) and Ethylene glycol (1)-toluene (2) (▲, △) [188], (●, ○) [190] (CPA curves from Folas et al. [194] with $k_{ij} = 0.055$, BETCR = 0.045; NRTL-PR_{fitted}: $\Gamma_{21} = 2279 - 489,683/T$, $\Gamma_{12} = 2194 + 30,955/T$).

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_{fitted} (with Γ_{ij} parameters fitted on the binary systems) and predictive NRTL-PR models.

Systems	T (K)	CPA			NRTL-PR _{fitted}			NRTL-PR		
		Δx_1^I %	Δx_2^II %	Δx_3^I %	Δx_1^I %	Δx_2^II %	Δx_3^I %	Δx_1^I %	Δx_2^II %	Δx_3^I %
MEG(1)-H ₂ O(2)-benzene(3)	298	17,5	11,9	19,4	8,5	9,3	14,8	9,87	15,83	10,79
	323	16,1	5,2	24,8	7,2	4,8	15,7	13,67	4,12	8,71
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
	323	7,5	11,0	13,3	3,5	11,8	15,4	3,58	18,22	20,95

Experimental data and CPA results from Folas et al. [188]. NRTL-PR_{fitted} parameters: H₂O (1)-benzene (2): $\Gamma_{21} = 5285 - 866,874/T$, $\Gamma_{12} = 3565 - 232,283/T$; MEG (1)-benzene (2): $\Gamma_{21} = 2423 - 492,442/T$, $\Gamma_{12} = 2731 - 33,819/T$; H₂O (1)-toluene (2): $\Gamma_{21} = 5364 - 899,732/T$, $\Gamma_{12} = 3667 - 244,207/T$. MEG (1)-toluene (2): $\Gamma_{21} = 2279 - 489,683/T$, $\Gamma_{12} = 2194 + 30,955/T$; H₂O (1)-MEG (2): $\Gamma_{21} = 843 - 214,161/T$, $\Gamma_{12} = \Gamma_{21}$.

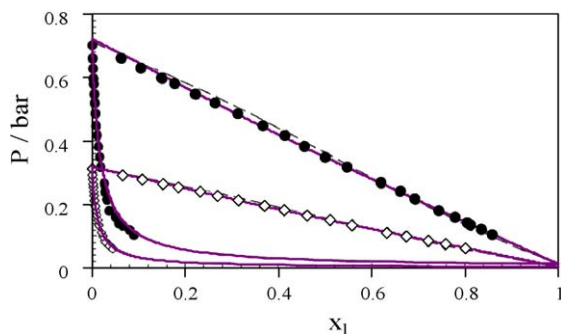


Fig. 14. VLE of water-ethylene glycol. Modeling with the (---) CPA and (—) NRTL-PR models at $T = 343$ K (◇) and $T = 363$ K (●) [191] (CPA curves from Haghighi et al. [195] with $k_{ij} = -0.2313 + 5.6294 \times 10^{-4} T$).

5. Conclusion

The NRTL-PR equation of state previously proposed [9] as a EoS/ G^E 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 SRK_m 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 derive 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 SRK_m 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.

List of symbols

a	attractive term
b	co-volume
C	reference state constant
F_{obj}	objective function
G_{ji}	non randomness parameter between molecules i and j
g	molar Gibbs energy
k_{ji}	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
x	mole fraction
v	molar volume
VLE	vapor–liquid equilibria
LLE	liquid–liquid equilibria
VLE	vapor–liquid and liquid–liquid equilibria

Greek letters

α	alpha function
α_0	non randomness factor
Γ_{ji}	interaction parameters between molecules i and j
$\Gamma_{LK}^{(0)}, \Gamma_{LK}^{(1)}$	parameters of the group contribution method
ν_{ik}	number of subgroup k in a molecule i
ω	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/ G^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:

$$\frac{A^{EV}(T, V^0, n)_{EoS}}{nRT} = \frac{A^{EV}(T, x)}{nRT} \approx \frac{g^E(T, x)}{RT} \quad (A1.1)$$

with, for a cubic EoS:

$$\begin{aligned} \frac{A^{EV}(T, V^0, n)_{EoS}}{nRT} &= A^{res}(T, V^0, n) - \sum_i A_i^{res}(T, V_i^0, n_i) + RT \sum_i n_i \ln \frac{V_i^0}{V^0} \\ &= - \sum_i x_i \ln \left(\frac{1 - \eta^0}{1 - \eta_i^0} \right) - \alpha C(\eta^0) + \sum_i x_i \alpha_i C(\eta_i^0) \\ &\quad + \sum_i x_i \ln \frac{V_i^0}{V^0} \approx \frac{g^E(T, x)}{RT} \end{aligned} \quad (A1.2)$$

and:

$$\begin{aligned} V^0 &= \sum V_i^0, \quad C(\eta^0) = \frac{1}{(e_1 - e_2)} \ln \left(\frac{1 + e_1 \eta^0}{1 + e_2 \eta^0} \right), \\ C(\eta_i^0) &= \frac{1}{(e_1 - e_2)} \ln \left(\frac{1 + e_1 \eta_i^0}{1 + e_2 \eta_i^0} \right) \end{aligned} \quad (A1.3)$$

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 $\eta_i^0 = nb_i/V_i^0$) are assumed equal;
- The functions $C(\eta^0) = C(\eta_i^0)$ are fixed at a constant value C .
Leading to the zero pressure relation (Michelsen approach):

$$\frac{g^E(T, x)}{RT} = C \left[-\alpha + \sum_i x_i \alpha_i \right] + \sum_i x_i \ln \frac{b_i}{b}, \quad C = \text{constant} \quad (A1.4)$$

and to the following α^M function:

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = \frac{1}{C} \left[\frac{g^E}{RT} - \sum_i x_i \ln \frac{b_i}{b} \right] \quad (A1.5)$$

Nevertheless, as was shown by Kontogeorgis and Vlamos [32], the α^M function should, in principle, only depend on the residual part g_{res}^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_i^0 and V^0 in Eq. (A1.2) are expressed directly from the volume factors r_i and r used with the G^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: $1 - \eta^0 = \Pi(1 - \eta_i^0)^{x_i}$, instead of the classical equality: $\eta^0 = \eta_i^0$;
- Finally, functions $C(\eta^0)$ and $C(\eta_i^0)$ are fixed at the same constant C_0 value, which leads to:

$$\frac{g^E(T, x)}{RT} = C_0 \left[-\alpha + \sum_i x_i \alpha_i \right] + \sum_i x_i \ln \frac{r_i}{r}, \quad C_0 = \text{constant} \quad (A1.6)$$

and to the expression of the α^M function:

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = \frac{1}{C_0} \left[\frac{g^E}{RT} - \sum_i x_i \ln \frac{r_i}{r} \right] \quad (A1.7)$$

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:

$$a = \alpha bRT = b \left[\sum_i x_i \frac{a_i}{b_i} - \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}/C}{\sum_j x_j q_j G_{ji}} \right] \\ = \sum_i \sum_j x_i x_j \sqrt{a_i} \sqrt{a_j} (1 - k_{ij}) \quad (\text{A2.1})$$

Parameters k_{ij} having symmetric values ($k_{ij} = k_{ji}$), the above condition assumes 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:

$$b \sum_i x_i \frac{a_i}{b_i} = \sum_i \sum_j x_i x_j b_j \frac{a_i}{b_i} = \frac{1}{2} \sum_i \sum_j x_i x_j b_j b_i \left[\frac{a_i}{b_i^2} + \frac{a_j}{b_j^2} \right] \quad (\text{A2.2})$$

- while the second term is developed according to:

$$b \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}/C}{\sum_l x_l q_l G_{li}} = \frac{1}{2} \sum_i \sum_j x_i x_j \times \\ \left[b q_i q_j \left(\frac{G_{ji} \Gamma_{ji}/C}{\sum_l x_l q_l G_{li}} + \frac{G_{ij} \Gamma_{ij}/C}{\sum_l x_l q_l G_{lj}} \right) \right] \quad (\text{A2.3})$$

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

$$\sqrt{a_i} \sqrt{a_j} (1 - k_{ij}) = \frac{1}{2} \left[b_i b_j \left(\frac{a_i}{b_i^2} + \frac{a_j}{b_j^2} \right) \right] \\ - \frac{1}{2} \left[b q_i q_j \left(\frac{G_{ji} \Gamma_{ji}/C}{\sum_l x_l q_l G_{li}} + \frac{G_{ij} \Gamma_{ij}/C}{\sum_l x_l q_l G_{lj}} \right) \right] \quad (\text{A2.4})$$

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

$$k_{ij} = k_{ij}^{(0)} + \rho_{ij}^{(0)} \left[\frac{b}{\sum_l x_l q_l G_{lj}} \right] + \rho_{ji}^{(0)} \left[\frac{b}{\sum_l x_l q_l G_{li}} \right] = k_{ji} \quad (\text{A2.5})$$

where:

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

$$\text{with : } \delta_{bi} = \frac{\sqrt{a_i}}{b_i} \quad (\text{A2.6})$$

and:

$$\rho_{ij}^{(0)} = \frac{q_i q_j G_{ij} \Gamma_{ij}/C}{2 \sqrt{a_i} \sqrt{a_j}} = \frac{G_{ij} \Gamma_{ij}/C}{2 \delta_{qi} \delta_{qj}}, \quad \rho_{ji}^{(0)} = \frac{G_{ji} \Gamma_{ji}/C}{2 \delta_{qi} \delta_{qj}} \quad \text{with : } \delta_{qi} = \frac{\sqrt{a_i}}{q_i} \quad (\text{A2.7})$$

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 ($G_{ji} \approx 1$), so that the attractive term a in Eq. (7) or (A2.1) is expressed according to the "one fluid lattice model" as:

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

with:

$$q = \sum_i x_i q_i, \quad E_{ij} = E_{ji} = \Gamma_{ij} + \Gamma_{ji} \approx 0 \quad (\text{A3.2})$$

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

$$k_{ij} = k_{ij}^{(0)} + (\rho_{ij}^{(0)} + \rho_{ji}^{(0)}) \left(\frac{b}{q} \right) \approx k_{ij}^{(0)} \\ \text{since : } \rho_{ij}^{(0)} + \rho_{ji}^{(0)} \approx \frac{E_{ij}/C}{2 \delta_{qi} \delta_{qj}} \approx 0 \quad (\text{A3.3})$$

According to the method proposed for the calculation of the Γ_{ij} interaction parameters (Eq. (12)), only hydrocarbon mixtures, for which the $\Gamma_{KL}^{(0)}$ and $\Gamma_{KL}^{(1)}$ 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 Pénélox et al. [31] and Jaubert and co-workers [5] with the PPR78 EoS, is expressed according to a "one fluid lattice model" ($G_{ji} = 1$) as:

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

or with the " k_{ij} " mixing rule:

$$k_{ij} = \frac{-(\delta_{bi} - \delta_{bj})^2 + E_{ij}}{2 \delta_{bi} \delta_{bj}} \quad (\text{A3.5})$$

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. SRK_m model

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

$$a = \sum_{i=1}^c \sum_{j=1}^c x_i x_j \sqrt{a_i a_j} (1 - K_{ij}), \quad b = \sum_{i=1}^c x_i b_i \quad (\text{A4.1}) \\ K_{ij} = k_{ij} - (k_{ij} - k_{ji}) \left(\frac{x_i}{x_i + x_j} \right)^{C_{ij}}, \quad k_{ij} = k_{Aij} + \frac{k_{Bij}}{T} + \frac{k_{Cij}}{T^2}.$$

D.1. Literature interaction parameters between water (1) and hydrocarbon (2)

Component (2)	$k_{A_{12}}$ $k_{A_{21}}$	$k_{B_{12}}$ $k_{B_{21}}$	$k_{C_{12}}$ $k_{C_{21}}$	C_{12} C_{21}	Component (2)	$k_{A_{12}}$ $k_{A_{21}}$	$k_{B_{12}}$ $k_{B_{21}}$	$k_{C_{12}}$ $k_{C_{21}}$	C_{12} C_{21}
Methane	0.1171	131.7	0	0.7606	Pentane	-0.0673	506.46	-91,416.3	1
	1.7921	-1167.81	161,363	1.2235		0.8464	-523.23	58,701.5	1
Hexane	3.0148	-1563.34	239,464	1	Heptane	0.0543	116.05	0	1
	0.3637	-220.69	7732.16	1		0.2021	-147.93	0	1
Octane	1.5598	-678.67	107,107	1	Decane	1.7079	-762.62	117,618	1
	0.5075	-368.75	36,169.4	1		0.6501	-548.67	73,399.5	1
2-Methylbutane	0.6948	-52.54	0	1	Cyclohexane	0.9392	-142.47	0	1
	0.2844	-164.52	0	1		0.8769	-498.18	57,812.9	1
Methylcyclohexane	0.4446	5.63	0	2.6918	Benzene	0.3828	-26.73	0	1.6441
	0.7096	-397.57	37,533.1	0.4867		0.3018	-168.12	10,011.8	0.295
Toluene	0.5716	-76.82	0	1	Ethylbenzene	0.5016	-56.36	0	1
	0.215	-114.68	0	1		0.1764	-106.53	0	1
<i>o</i> -Xylene	0.4457	-41.78	0	1	<i>m</i> -Xylene	0.4849	-53.26	0	1
	0.096	-80.03	0	1		0.1221	-93.23	0	1
<i>p</i> -Xylene	0.3027	0	0	1					
	-0.2008	0	0	1					

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

Component (2)	$k_{A_{12}}$ $k_{A_{21}}$	$k_{B_{12}}$ $k_{B_{21}}$	$k_{C_{12}}$ $k_{C_{21}}$	C_{12} C_{21}	Component (2)	$k_{A_{12}}$ $k_{A_{21}}$	$k_{B_{12}}$ $k_{B_{21}}$	$k_{C_{12}}$ $k_{C_{21}}$	C_{12} C_{21}
Alcane	0.5	0	0	1	Naphthene	0.445	0	0	1
	-0.06	0	0	1		-0.06	0	0	1
Aromatic	0.315	0	0	1					
	-0.06	0	0	1					

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