

Thermodynamic property calculations with the universal mixing rule for EoS/ G^E models: Results with the Peng–Robinson EoS and a UNIFAC model

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Abstract

The universal mixing rule (UMR), which incorporates an activity coefficient model in a cubic equation of state (EoS), and is applicable to all type of system asymmetries up to solvent/polymer ones, has been recently developed in our laboratory [Voutsas et al., *Ind. Eng. Chem. Res.* 43 (2004) 6238]. The original UNIFAC model with temperature-independent interaction parameters was used in the original publication, which leads, however, to unsatisfactory VLE predictions at high temperatures and poor heats of mixing predictions. In this study the UMR is applied by coupling the translated and modified Peng–Robinson (t-mPR) EoS with an original UNIFAC-type model that utilizes linearly temperature-dependent interaction parameters, eliminating, thus, the aforementioned weaknesses. The performance of the resulting EoS/ G^E model, referred to as UMR-PRU, utilizing the available UNIFAC interaction parameters, as well as some parameters developed here for gas involving pairs, is evaluated in the prediction and, when necessary, correlation/prediction, of various thermodynamic properties, i.e. VLE, LLE, VLLE, SGE and heats of mixing. The results indicate that the new model represents a unique, simple and reliable tool for thermodynamic property calculations for systems of various degrees of non-ideality and asymmetry, including polymer solutions.

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Keywords: Equation of state; Mixing rule; Peng–Robinson; UNIFAC; Asymmetric system; Thermodynamic properties

1. Introduction

The corresponding author considers John Prausnitz as the Grandfather of Chemical Engineering Thermodynamics, this is how he refers to him to his students, the man that led the way towards rendering Thermodynamics a useful tool for Engineers. He demonstrated the importance of developing a clear understanding of the physics of the problem we are dealing with and then connecting it with the theory. He emphasized the need for predictive models, and his influence on the corresponding author in this aspect is apparent in this manuscript. “I feel, however, that his most important influence on me – and I am certain on others – comes from his personality: mild, supportive but also constructively critical and encouraging, friendly and considerate. Perhaps he is not just the Grandfather of Chemical Engineering Thermodynamics”.

The combination of EoS, mainly cubic ones, with excess Gibbs free energy (G^E) models, that originated with the pio-

Abbreviations: cC6, cyclohexane; EoS, equation of state; FH, Flory–Huggins; IPs, interaction parameters in UNIFAC model; LCVM, linear combination of the Vidal and Michelsen mixing rules; LDPE, low-density polyethylene; LLE, liquid–liquid equilibrium; MHV1, modified Huron–Vidal mixing rule, 1st order; MHV2, modified Huron–Vidal mixing rule, 2nd order; nC_x , n -alkane with x carbon atoms; NP, number of data points; PMMA, poly(methyl methacrylate); PS, polystyrene; PSRK, predictive Soave–Redlich–Kwong mixing rule; SCCO₂, supercritical carbon dioxide; SGE, solid–gas equilibrium; SG, Staverman–Gugenheim; SRK, Soave–Redlich–Kwong EoS; t-mPR, translated and modified Peng–Robinson EoS; UMR, universal mixing rule; UMR-PRU, universal mixing rule applied to the t-mPR EoS and UNIFAC model; VLE, vapor–liquid equilibrium; VLLE, vapor–liquid–liquid equilibrium; VTPR, volume-translated Peng–Robinson EoS

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neering work of the late Vidal [1], represents a major development in the field of chemical engineering thermodynamics for it expanded the successful performance of cubic EoS in the field of the non-polar systems to that of polar ones. His work, followed by the Huron and Vidal model [2] who coupled the SRK EoS with the NRTL model at infinite reference pressure, has initiated a series of studies on EoS/ G^E mixing rules [3]. An important step in the field was the development of the zero reference pressure EoS/ G^E models and the use of UNIFAC as the G^E model, promoting the predictive abilities of the EoS/ G^E models. The first models of this category were proposed by Michelsen (MHV1 and MHV2) [4–6], followed by the work of Holderbaum and Gmehling [7], who developed the PSRK model. The MHV2 and PSRK models provided successful prediction of VLE for a wide range of compounds, but their applicability is limited to systems of low asymmetry as shown in Fig. 1. The LCVm mixing rule developed in our laboratory [8], which is a linear combination of the Huron–Vidal and Michelsen MHV1 mixing rules, overcomes this limitation of the MHV2 and PSRK models, as also shown in Fig. 1. Despite its successful results [9–12] the LCVm model involves an inconsistency, since by coupling a zero reference pressure mixing rule (MHV1) with an infinite reference pressure one (Huron–Vidal) has no specified reference pressure. Furthermore, LCVm and, of course, MHV2 and PSRK fail to describe the phase equilibria in solvent/polymer type asymmetries.

In the last few years, many studies have been focused on the improvement of the existing EoS/ G^E models so as to expand their applicability to more complex systems, such as those containing compounds that are highly polar or differ significantly in size (e.g. polymer/solvent systems) without losing their versatility and simplicity. Recently, Gmehling and co-workers [13] proposed the VTPR EoS/ G^E model, which combines a volume-translated PR EoS with UNIFAC. In VTPR the two Flory–Huggins (FH) type combinatorial terms coming from the EoS and the UNIFAC model, as well as the Staverman–Guggenheim (SG) part of the UNIFAC combina-

torial term have been eliminated. Additionally, on an empirical basis VTPR incorporates different exponents in the combining rule for the cross co-volume parameter of the EoS depending on the system studied: for systems that do not involve polymers the exponent was set equal to 0.75 [13], while for solvent/polymer systems it was set equal to 0.5 [14]. This empirical approach introduces, however, some uncertainties in the application of the model. For example, not a single exponent can be defined for mixtures containing two solvents and a polymer. Furthermore, there is a difficulty in choosing between the two exponents for some systems containing a polymer-like molecule, e.g. propane/hexacontane.

In the first part of our ongoing study towards an EoS/ G^E model applicable to a wide range of system asymmetries and non-idealities, the universal mixing rule (UMR) for EoS/ G^E models was developed [15]. The application of UMR, coupling the translated and modified Peng–Robinson EoS (t-mPR EoS [16]) with the original UNIFAC model that utilizes temperature-independent interaction parameters [17], demonstrated that it provides very satisfactory VLE and LLE predictions for both non-polar and polar systems and for a wide range of system asymmetries, even for solvent/polymer systems. The use, however, of UNIFAC with temperature-independent group interaction parameters (IPs) leads to unsatisfactory VLE predictions at high temperatures and poor heats of mixing predictions.

In the second part of this study, presented here, we apply the UMR mixing rules again to the t-mPR EoS but we couple it with the original UNIFAC-type model proposed by Hansen et al. [18], which utilizes linearly temperature-dependent group IPs eliminating the aforementioned weaknesses. The available in that work values of the interaction parameters will be used, while additional ones for some gas involving pairs, which are not of course available in the paper of Hansen et al., will be evaluated.

The performance of the resulting new EoS/ G^E model, referred to hereafter as UMR-PRU, is evaluated in the prediction: (a) of both low and high pressure vapor–liquid equilibria, including the very important gas containing systems, liquid–liquid and solid–gas equilibria, in binary and multi-component systems of various degrees of system non-ideality and asymmetry up to those observed in polymer/solvent systems and (b) of heats of mixing. Finally, the ability of the model to become a correlative/predictive tool of a difficult case, such as the three-phase equilibria in water/alkane systems, where straight prediction leads to unsatisfactory results, is evaluated.

2. The universal mixing rule

The UMR proposed by Voutsas et al. [15] uses the following mixing rules for the parameter $\alpha = a/bRT$ (a is the attractive term parameter of the EoS) and the co-volume parameter (b) of the EoS:

$$\alpha = \frac{1}{A} \frac{G_{AC}^{E,SG} + G_{AC}^{E,res}}{RT} + \sum_i x_i \alpha_i \quad (1)$$

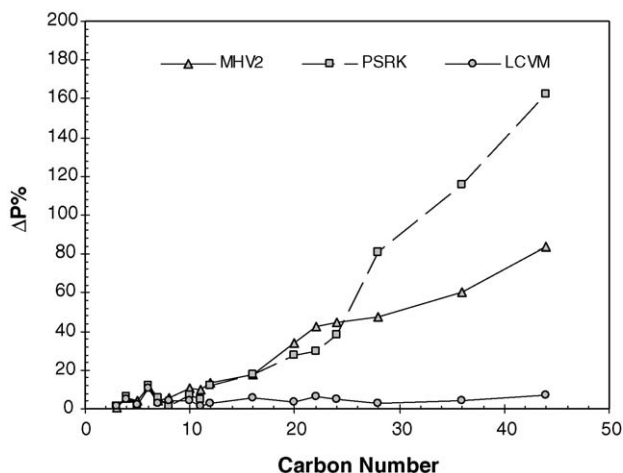


Fig. 1. VLE prediction results for C_2H_6/n -alkane systems with the MHV2, PSRK and LCVm models [8].

$$\frac{G_{AC}^{E,SG}}{RT} = 5 \sum_i x_i q_i \ln \frac{Q_i}{F_i}, \quad \frac{G_{AC}^{E,res}}{RT} = \sum_i x_i v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \quad (2)$$

$$F_i = \frac{r_i}{\sum_j x_j r_j}, \quad Q_i = \frac{q_i}{\sum_j x_j q_j} \quad (3)$$

and

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = \left(\frac{b_i^{1/2} + b_j^{1/2}}{2} \right)^2 \quad (4)$$

A in Eq. (1) is a constant that depends on the cubic EoS used, $A = -0.53$ for the t-mPR EoS. $G_{AC}^{E,SG}$ and $G_{AC}^{E,res}$ in Eq. (2) are the Staverman–Guggenheim term of the combinatorial part and the residual part of the excess Gibbs free energy (G^E), respectively, obtained from the UNIFAC activity coefficient model. In this study the UNIFAC model that utilizes linear temperature-dependent group interaction parameters [18] has been used. The Ψ function used in this model is the following:

$$\Psi_{nm} = \exp \left[-\frac{A_{nm} + B_{nm}(T - 298.15)}{T} \right] \quad (5)$$

3. The t-mPR EoS

The t-mPR EoS [16] employed in this study is:

$$P = \frac{RT}{(V + t - b)} - \frac{a}{(V + t)(V + t + b) + b(V + t - b)} \quad (6)$$

$$a = 0.45724 \frac{(RT_c)^2}{P_c} \alpha(T_r) \quad (7)$$

$$b = 0.0778 \frac{RT_c}{P_c} \quad (8)$$

where T_c and P_c are the pure compound critical temperature and pressure, respectively, and T_r is the reduced temperature (T/T_c). The translation t can be determined using either the experimental molar volume at a single temperature, e.g. at $T_r = 0.7$ [19], or through the generalized expression as a function of T_r proposed by Magoulas and Tassios [16] that leads to very satisfactory saturated liquid volume predictions.

For non-polar compounds, the $\alpha(T_r)$ function is related to the acentric factor, ω , as follows:

$$\alpha(T_r) = [1 + m(1 - \sqrt{T_r})]^2 \quad (9)$$

$$m = 0.384401 + 1.52276\omega - 0.213808\omega^2 + 0.034616\omega^3 - 0.001976\omega^4 \quad (10)$$

For polar compounds, the Mathias–Copeman expression [20] is used:

$$\alpha(T_r) = [1 + c_1(1 - \sqrt{T_r}) + c_2(1 - \sqrt{T_r})^2 + c_3(1 - \sqrt{T_r})^3]^2, \quad \text{if } T_r \leq 1 \quad (11)$$

$$\alpha(T_r) = [1 + c_1(1 - \sqrt{T_r})]^2, \quad \text{if } T_r > 1 \quad (12)$$

where the values of c_1 , c_2 and c_3 are determined by fitting pure compound vapor pressure data.

Experimental T_c , P_c and ω values were taken from the DIPPR data base [21] for all compounds involved in this study except from n -alkanes with number of carbon atoms (N_c) greater than 20. For n -alkanes with $N_c \leq 40$ these data were taken from Magoulas and Tassios [16], and for n -alkanes with $N_c > 40$ from Constantinou and Gani [22], according to the suggestions of Kontogeorgis and Tassios [23]. Finally, Mathias–Copeman parameters were taken from the literature [8–10,24].

4. New UNIFAC interaction parameters for gases with the UMR-PR model

The UNIFAC model used here is that of Hansen et al. [18] where linearly T-dependent IPs for a variety of pair groups are presented. No gas molecules are of course included, which are considered for the UMR-PRU model as separate groups like in all EoS/ G^E models. T_c , P_c and ω values as well as the UNIFAC r and q parameters for the two gases: methane (CH_4) and carbon dioxide (CO_2), examined in this study are given in Table 1. Linearly temperature-dependent group interaction parameters in the UNIFAC Ψ function (Eq. (5)) were also adopted for these pairs.

The group interaction parameters were determined by fitting isothermal VLE experimental data for CH_4 and CO_2 with alkanes and aromatic hydrocarbons and they are presented in Table 2. The objective function (F) used to this purpose is the following:

$$F = \sum_{i=1}^{\text{NP}} \left(100 \left| \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right| + 100 |y_i^{\text{exp}} - y_i^{\text{calc}}| \right) \quad (13)$$

where P is the bubble point pressure, y is the vapor phase mole fraction and NP is the number of data points.

Very satisfactory results are obtained for all systems asymmetries as indicated by the typical ones shown in Fig. 2.

Table 1
Gas parameters used in the UMR-PRU model

Gas	T_c (K)	P_c (bar)	ω	r	q
Methane	190.55	45.99	0.0110	1.1290	1.124
Carbon dioxide	304.19	73.82	0.2276	1.2960	1.261

Table 2
UNIFAC group-interaction parameters, A_{nm} and B_{nm} , for the UMR-PRU model

n	m	A_{nm} (K)	B_{nm}	A_{mn} (K)	B_{mn}
CO_2	CH_2	17.55	−0.0170	131.66	−1.0219
CO_2	ACH	−82.93	−1.1597	218.98	0.7783
CO_2	ACCH ₂	−76.83	−2.3820	459.89	2.9678
CH_4	CH_2	535.56	1.6457	−269.67	−1.1985
CH_4	ACH	113.38	1.8316	−47.51	1.3870
CH_4	ACCH ₂	168.68	1.8835	−129.83	1.2868

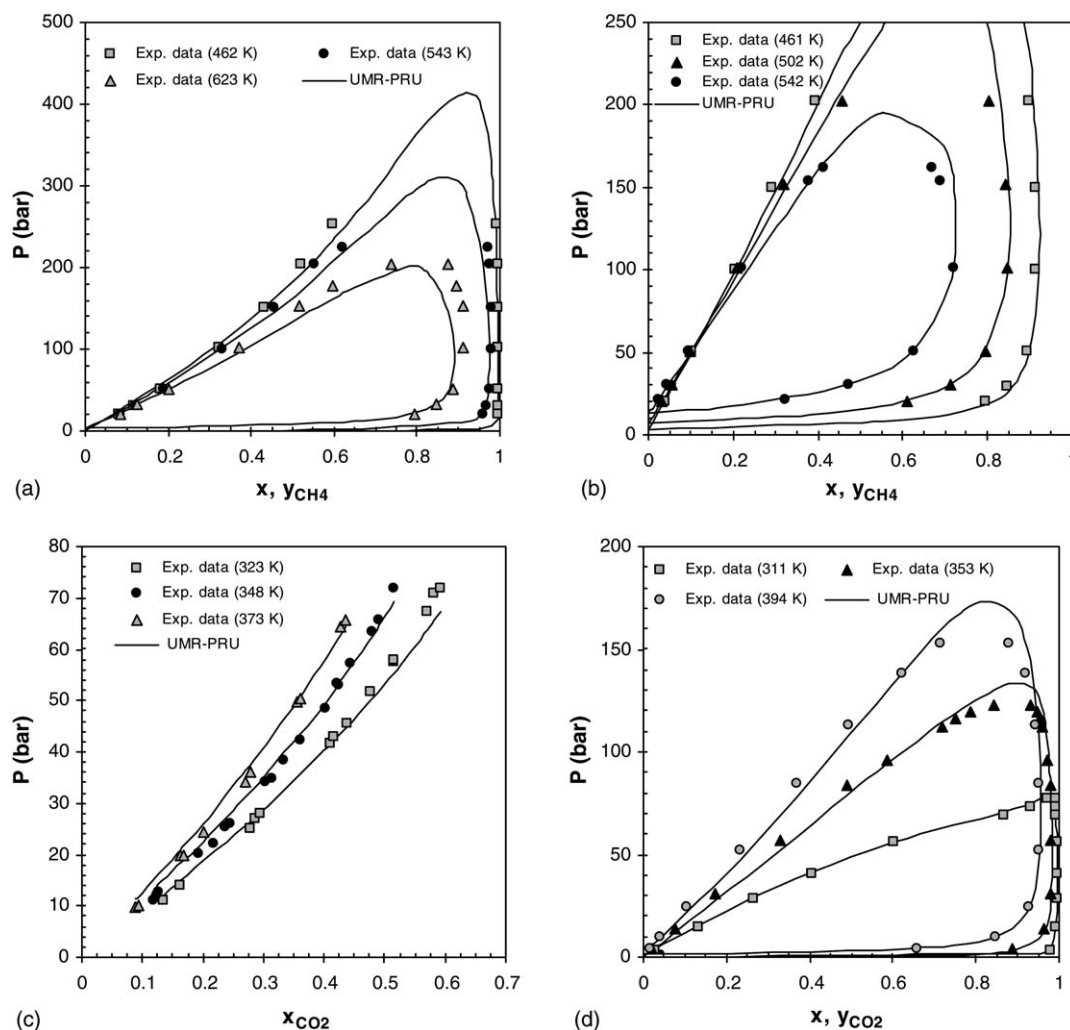


Fig. 2. P - x - y diagrams with the UMR-PR model for the binary mixtures: (a) $\text{CH}_4/n\text{C}_{16}$ [25], (b) CH_4/m -xylene [26], (c) $\text{CO}_2/n\text{C}_{22}$ [27] and (d) CO_2 /toluene [28]. Note that the experimental data for the $\text{CH}_4/n\text{C}_{16}$ were not used in the parameter evaluation of the model.

5. Results

5.1. VLE predictions for binary systems

Prediction of VLE in alkane/alkane athermal systems provides a very good test for the new model performance since no interaction parameters are used for these systems, i.e. the residual Gibbs free energy of the UNIFAC model is equal to zero. VLE predictions for propane/alkane binaries are presented in Table 3 and graphically in Fig. 3 for the $\text{C}_3/n\text{-C}_{60}$ system. The very satisfactory results demonstrate the success of the pro-

Table 3
VLE prediction results for propane/ n -alkane systems with the UMR-PRU model and zero UNIFAC group interaction parameters

System	Reference	T -range (K)	P -range (bar)	NP	$\Delta P\%$	$\Delta y \times 100$
$\text{C}_3/n\text{C}_8$	[29]	329–543	6.9–58.9	86	2.3	16.8
$\text{C}_3/n\text{C}_{10}$	[30]	278–511	1.7–70.9	55	6.5	0.9
$\text{C}_3/n\text{C}_{20}$	[31]	279–359	4.0–32.5	166	7.1	0.0
$\text{C}_3/n\text{C}_{34}$	[32]	319–428	10.5–95.2	79	5.0	0.0
$\text{C}_3/n\text{C}_{60}$	[33]	352–431	13.4–129.4	60	9.9	1.4

posed model for this large range of system asymmetries. Note that among the most popular EoS/ G^E models only LCVM gives good results at highly asymmetric systems, while MHV2 and PSRK models completely fail as shown in Fig. 1 for the case of the ethane/alkane binary systems.

For polar systems the existing UNIFAC group interaction parameters [18] have been utilized. Results for binary systems at low and high pressures are presented in Tables 4 and 5, respectively, while P - x - y diagrams for the systems water/acetone and water/ethanol at high temperatures and pressures are shown in Fig. 4. The UMR-PRU model gives very good results even at the very high temperatures and pressures involved. As it was expected, the use of UNIFAC T -dependent IPs with the UMR-PRU model gives much better results than those obtained using the T -independent IPs of the original UNIFAC model [17].

5.2. VLE predictions for multi-component systems

Results for multi-component systems that contain methane and carbon dioxide using the UMR-PRU model and the IPs of Table 2 are listed in Tables 6 and 7, while some typical ones are

Table 4
VLE results with the UMR-PRU model for binary polar systems at low pressures

System	Reference	<i>T</i> (K)	<i>P</i> -range (bar)	NP	UMR-PRU (T-independent)		UMR-PRU (T-dependent)	
					$\Delta P\%$	$\Delta y \times 100$	$\Delta P\%$	$\Delta y \times 100$
Acetone/CHCl ₃	[34]	298	0.26–0.3	31	0.8	0.9	1.6	0.9
	[35]	308	0.37–0.44	31	0.6	0.4	0.4	0.3
	[34]	323	0.68–0.79	31	0.8	1.4	0.6	1.4
Benzene/methyl acetate	[36]	303	0.18–0.35	16	1.6	0.3	0.7	0.5
	[36]	313	0.28–0.53	9	2.4	0.4	2.0	0.3
	[37]	323	0.39–0.78	17	1.3	0.2	1.3	0.2
Ethanol/ <i>n</i> -butane	[38]	299	0.08–2.54	24	3.1	–	2.8	–
	[38]	324	0.30–5.04	24	4.0	–	4.5	–
Methanol/water	[39]	298	0.06–0.15	10	0.8	0.4	2.1	0.7
Ethanol/water	[39]	348	0.62–0.88	9	5.9	2.1	5.5	2.5

Table 5
VLE results with the UMR-PRU model for binary polar systems at high pressures

System	Reference	<i>T</i> (K)	<i>P</i> -range (bar)	NP	UMR-PRU (T-independent)		UMR-PRU (T-dependent)	
					$\Delta P\%$	$\Delta y \times 100$	$\Delta P\%$	$\Delta y \times 100$
Acetone/methanol	[40]	373	3.5–4.0	14	5.0	1.3	4.2	1.2
	[40]	423	11.6–14.3	15	3.1	1.8	1.2	1.8
	[40]	473	29.5–39.8	10	5.5	3.3	2.6	3.2
Methanol/benzene	[41]	373	3.1–4.2	10	8.1	2.9	4.5	1.3
	[41]	413	6.7–11.8	10	11.8	3.6	5.5	1.3
	[41]	453	13.2–27.3	10	13.8	4.1	5.6	1.3
	[41]	493	22.6–57.6	10	7.3	5.8	3.3	4.2
Methanol/water	[40]	373	1.0–3.4	16	2.3	0.9	2.3	1.2
	[40]	423	5.1–13.7	14	1.8	1.5	1.6	1.2
	[40]	473	16.3–39.4	15	1.5	0.9	2.7	0.9
	[40]	523	46.9–85.1	12	1.0	1.2	5.1	1.7
Ethanol/water	[42]	423	5.6–9.9	17	7.7	2.3	1.9	1.1
	[42]	473	17.9–29.5	17	8.8	3.5	2.0	1.7
	[42]	523	40.8–71.7	15	10.0	2.7	1.5	1.1
	[42]	548	61.4–98.6	11	6.0	3.1	1.1	1.3
	[42]	573	88.5–125.5	7	6.6	2.0	0.6	0.7
	[42]	598	124.0–157.0	6	5.8	1.7	1.2	0.6
	[42]	623	170.6–189.7	3	2.0	0.4	0.3	0.1
<i>i</i> -Propanol/water	[42]	423	5.2–8.6	19	10.3	3.5	4.1	2.7
	[42]	473	18.5–28.1	18	11.7	4.6	3.9	2.9
	[42]	523	43.1–66.2	13	9.8	4.1	4.0	2.5
	[42]	548	69.0–93.1	17	8.5	4.3	3.5	2.1
	[42]	573	88.9–123.5	5	5.1	2.0	2.4	1.3
Acetone/water	[40]	423	5.0–12.0	17	4.9	2.5	0.9	0.6
	[40]	473	16.0–30.3	25	6.9	2.3	0.9	0.5
	[40]	523	40.4–67.6	13	4.7	1.5	1.5	0.5
Ethanol/ <i>n</i> -butane	[39]	344	0.8–8.8	24	4.3	–	5.7	–

Table 6
VLE prediction results for multi-component systems containing methane with the UMR-PRU model

System	Reference	<i>T</i> -range (K)	<i>P</i> -range (bar)	NP	$\Delta P\%$	$\Delta y_1 \times 100$	$\Delta y_2 \times 100$
CH ₄ (1)/C ₃ (2)/ <i>n</i> C ₁₀	[43]	311	27.6–275.7	17	1.7	0.8	0.4
CH ₄ (1)/ <i>n</i> C ₁₀ (2)/ <i>n</i> C ₁₈ / <i>n</i> C ₃₀	[44]	312–422	137.0–161.0	12	5.6	0.5	0.6
CH ₄ (1)/ <i>n</i> C ₁₀ (2)/ <i>n</i> C ₁₈ up to <i>n</i> C ₂₇ (12 compounds)	[44]	294–424	125.0–156.5	14	3.6	0.5	0.6
CH ₄ (1)/ <i>n</i> C ₁₀ (2)/ <i>n</i> C ₂₀ up to <i>n</i> C ₃₀ (13 compounds)	[44]	291–423	122.0–155.0	14	2.2	0.5	0.6
CH ₄ (1)/ <i>n</i> C ₁₀ (2)/ <i>n</i> C ₁₈ up to <i>n</i> C ₃₀ (15 compounds)	[44]	297–423	126.0–158.8	14	4.2	0.5	0.6

Table 7

VLE prediction results for CO₂ multi-component systems with the UMR-PRU model

System	Reference	T (K)	P-range (bar)	NP	$\Delta P\%$	$\Delta y_1 \times 100$	$\Delta y_2 \times 100$
CO ₂ (1)/ <i>n</i> C ₄ (2) up to <i>n</i> C ₁₃ , cC ₆ – <i>n</i> C ₇ cC ₆ toluene– <i>n</i> C ₅ Ben ^a	[45]	323	71.2–85.1	5	7.8	0.3	0.0
CO ₂ / <i>n</i> C ₄ / <i>n</i> C ₁₀	[46]	344	90.3–114.5	13	1.5	0.9	1.7

^a CO₂, *n*-butane (*n*C₄), *n*-pentane (*n*C₅), *n*-hexane (*n*C₆), *n*-heptane (*n*C₇), *n*-octane (*n*C₈), *n*-nonane (*n*C₉), *n*-decane (*n*C₁₀), *n*-undecane (*n*C₁₁), *n*-dodecane (*n*C₁₂), *n*-tridecane (*n*C₁₃), cyclohexane (cC₆), methylcyclohexane, ethylcyclohexane, propylcyclohexane, butylcyclohexane, pentylcyclohexane, hexylcyclohexane, heptylcyclohexane, toluene, ethylbenzene, propylbenzene, butylbenzene and pentylbenzene.

shown graphically in Fig. 5. The quality of the obtained results is very gratifying, especially in the case of the 24-component system of Table 7, demonstrating the excellent predictive capabilities of the new model.

Very successful predictions are also obtained for polar systems with the UMR-PRU model using again the existing UNIFAC parameters [18], as suggested by the results presented in Table 8.

5.3. Liquid–liquid equilibrium (LLE) predictions

It is well-known that UNIFAC with parameters determined from VLE data does not provide satisfactory LLE predictions [50]. In our previous publication [15], the UMR mixing rules coupled with the UNIFAC-LLE [51], which is a UNIFAC model especially developed for LLE calculations, have been successfully applied for the prediction of low pressure LLE, yielding, as expected, similar results to those obtained with the UNIFAC-LLE model.

5.4. Vapor–liquid–liquid equilibrium (VLLE) calculations

EoS/UNIFAC models fail to predict VLE and LLE in water/alkane systems, due to the poor performance of UNIFAC

in this kind of systems [52,53]. To demonstrate the flexibility of the UMR-PRU model, we chose the very difficult case of the VLLE of alkane/water systems and, instead of straight prediction, we proceed to correlate the LLE data and predict the vapor phase compositions. The UMR-PRU model was coupled here with the UNIQUAC model, while quadratic T-dependent IPs were used in order to describe quantitatively the minimum in the alkane solubility in the aqueous phase observed for the

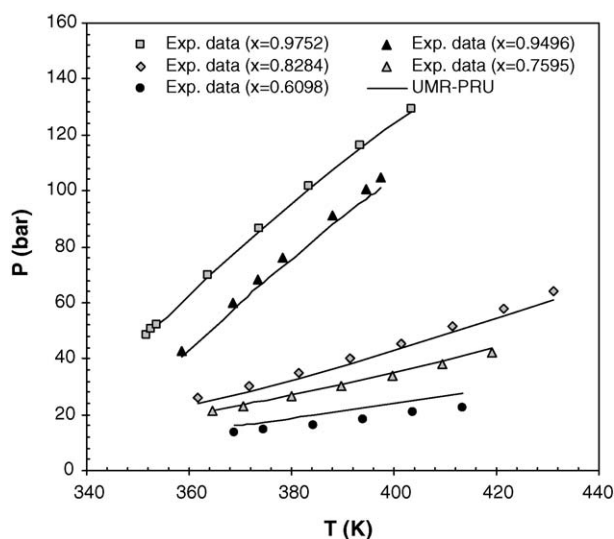


Fig. 3. VLE prediction results for the C₃H₈/*n*C₆₀ system with the UMR-PRU model using zero UNIFAC interaction parameters.

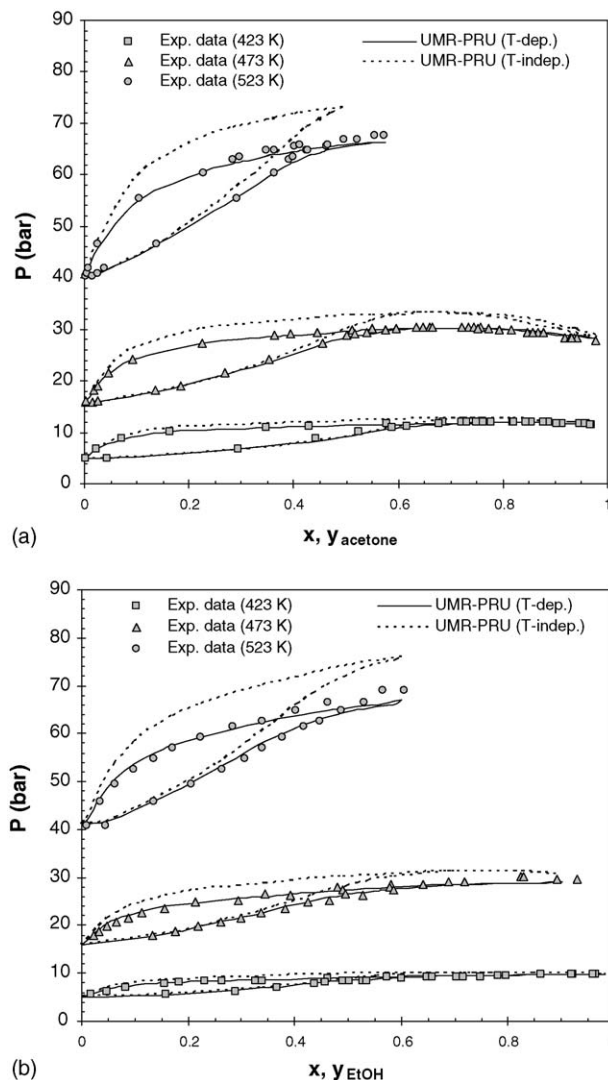


Fig. 4. VLE predictions with the UMR-PRU model for the systems: (a) water/acetone and (b) water/ethanol.

Table 8
VLE results with the UMR-PRU model for ternary polar systems

System	Reference	<i>T</i> (K)	<i>P</i> -range (bar)	NP	UMR-PRU (T-independent)			UMR-PRU (T-dependent)		
					$\Delta P\%$	$\Delta y_1 \times 100$	$\Delta y_2 \times 100$	$\Delta P\%$	$\Delta y_1 \times 100$	$\Delta y_2 \times 100$
Acetone(1), methanol(2), water(3)	[40]	373	1.2–3.9	51	2.6	1.7	2.0	1.9	1.8	2.8
Pentane(1), methanol(2), acetone(3)	[47]	373	5.4–8.2	36	3.2	2.0	1.9	1.4	1.6	1.9
Acetone(1), CHCl ₃ (2), methanol(3)	[48]	323	0.6–0.9	150	2.4	0.8	0.7	4.4	1.1	1.1
Benzene(1), cyclohexane(2), <i>i</i> -propanol(3)	[49]	≈344	1.013	70	3.6	0.8	1.0	1.8	0.6	0.7

Table 9
Parameters of solid compounds: critical data, acentric factor, antoine parameters^a and solid volume [56]

Compound	<i>T_c</i> (K)	<i>P_c</i> (bar)	ω	<i>A</i>	<i>B</i>	<i>C</i>	<i>V^s</i> (cm ³ /mol) ^b
Anthracene	873.1	34.05	0.494	10.080	3741.9	219.18	142.50
Biphenyl	773.0	33.38	0.364	8.9750	2374.6	190.78	134.65
Phenanthrene	890.0	32.50	0.429	6.7403	1842.4	148.62	153.10

^a Antoine equation: $\log P^{\text{sub}} (\text{mmHg}) = A - B/(C + \vartheta (^{\circ}\text{C}))$.

^b Solid volume *V^s* is assumed to be pressure-independent and constant within the temperature range examined.

Table 10
VLE results with the UMR-PRU model for some binary polymer/solvent systems

System	Reference	<i>T</i> (K)	<i>P</i> -range (bar)	NP	UMR-PRU (T-independent)	UMR-PRU (T-dependent)
					$\Delta P\%$	$\Delta P\%$
Benzene/PS (63000)	[61]	288	0.2–0.5	8	3.1	3.2
	[61]	303	0.1–0.2	7	3.4	3.5
	[61]	333	0.3–0.5	7	0.4	1.4
Butanone/PMMA (19770)	[61]	322	0.1–0.6	8	3.1	3.5
<i>n</i> -Hexane/dendrimer A4 (8870)	[62]	338	0.1–0.9	9	6.3	7.4
Chloroform/dendrimer A4 (8870)	[62]	323	0.1–0.7	11	11.4	6.6
LDPE (76000)/3-pentanol	[63]	423	0.8–2.8	6	12.4	9.6
	[63]	473	1.4–8.3	5	11.8	11.0
LDPE (76000)/pentanone	[63]	425	0.8–3.4	6	13.2	9.6
	[63]	477	1.6–9.4	6	12.8	9.0
LDPE (76000)/ <i>n</i> -pentane	[63]	424	2.5–15.0	6	8.5	8.5
	[63]	474	2.6–30.6	6	9.2	9.2
LDPE (76000)/ <i>c</i> -pentane	[63]	426	1.8–10.1	6	10.6	10.6
	[63]	474	2.7–22.4	6	10.8	10.8
LDPE (76000)/1-pentene	[63]	424	1.6–16.5	5	6.9	7.4
	[63]	474	4.2–32.7	5	6.0	6.0
LDPE (76000)/propylacetate	[63]	426	0.9–3.8	5	13.1	13.4
	[63]	474	1.6–10.4	5	15.2	12.4
LDPE (76000)/isopropylamine	[63]	427	4.3–20.0	5	2.8	5.5
	[63]	475	4.6–38.4	5	9.3	7.6

large temperature range involved. Very satisfactory results are obtained as indicated in Fig. 6, which presents the cases of the propane/water and *n*-butane/water systems.

5.5. Solid–gas equilibrium predictions

By utilizing the IPs presented in Table 2, which were obtained by fitting only VLE data, the UMR-PRU model was applied in the prediction of solid solubilities in supercritical CO₂ (SCCO₂).

The solubility of a solid compound, *y*₂, in SCCO₂ is calculated through the following expression:

$$y_2 = \frac{P_2^{\text{sub}}(\text{PE})_2}{\phi_2^{\text{v}} P} \quad (14)$$

where P_2^{sub} is the sublimation pressure, (PE)₂ the Poynting effect, ϕ_2^{v} the fugacity coefficient of the solid in the vapor phase and *P* is the total pressure. The Poynting effect is calculated

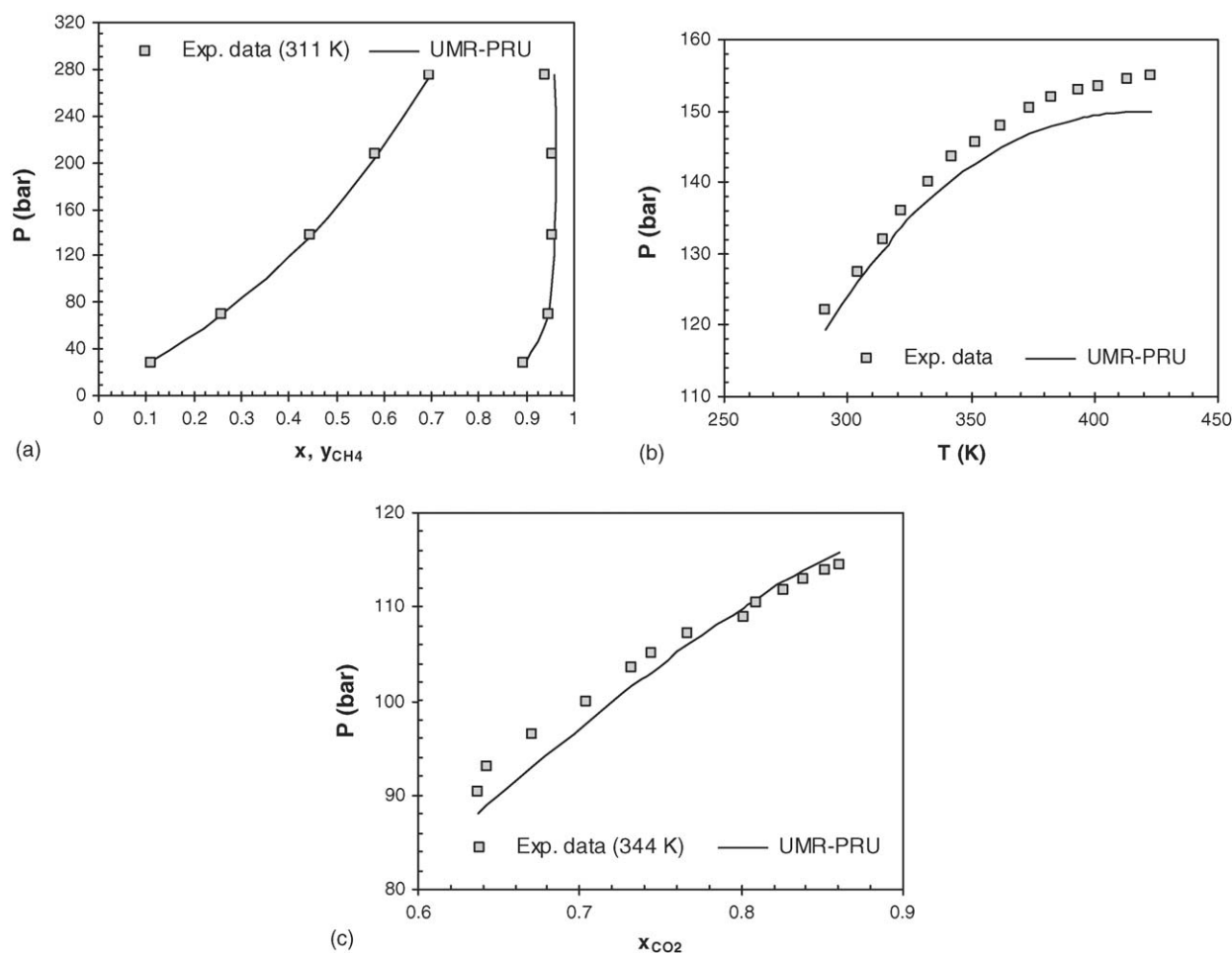


Fig. 5. VLE prediction results with the UMR-PRU model for the systems: (a) $CH_4/C_3/nC_{10}$, (b) $CH_4/nC_{10}/nC_{20}-nC_{30}$ ($x_{CH_4}=0.437$, $x_{nC_{10}}=0.461$) and (c) $CO_2/nC_4/nC_{10}$.

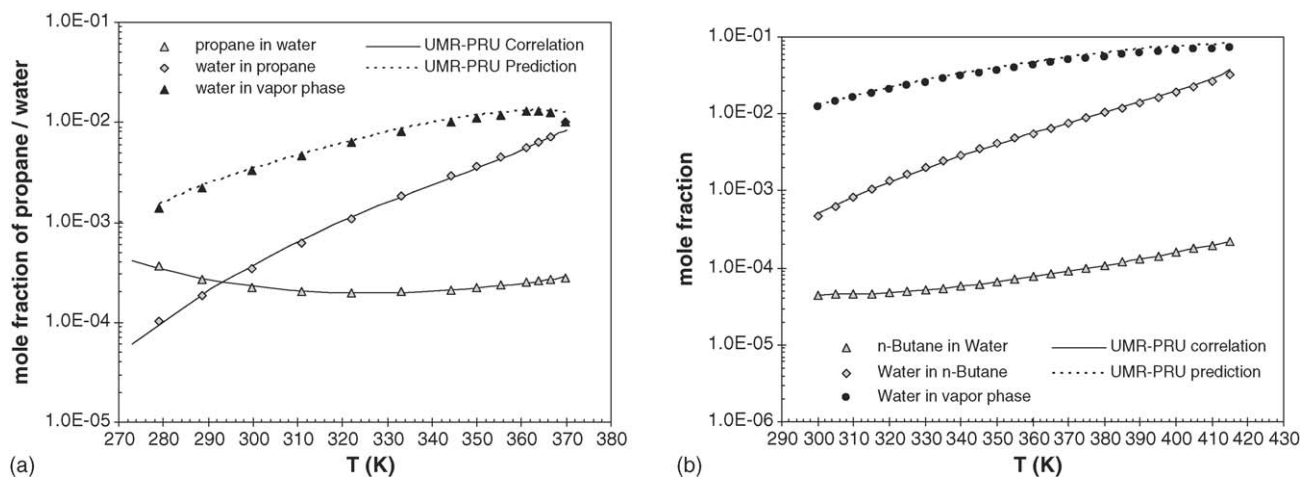


Fig. 6. VLLE calculations with the UMR-PRU model for the systems: (a) propane/water [54] and (b) n -butane/water [55]. Correlation of the liquid phase experimental data and prediction of the vapor phase compositions.

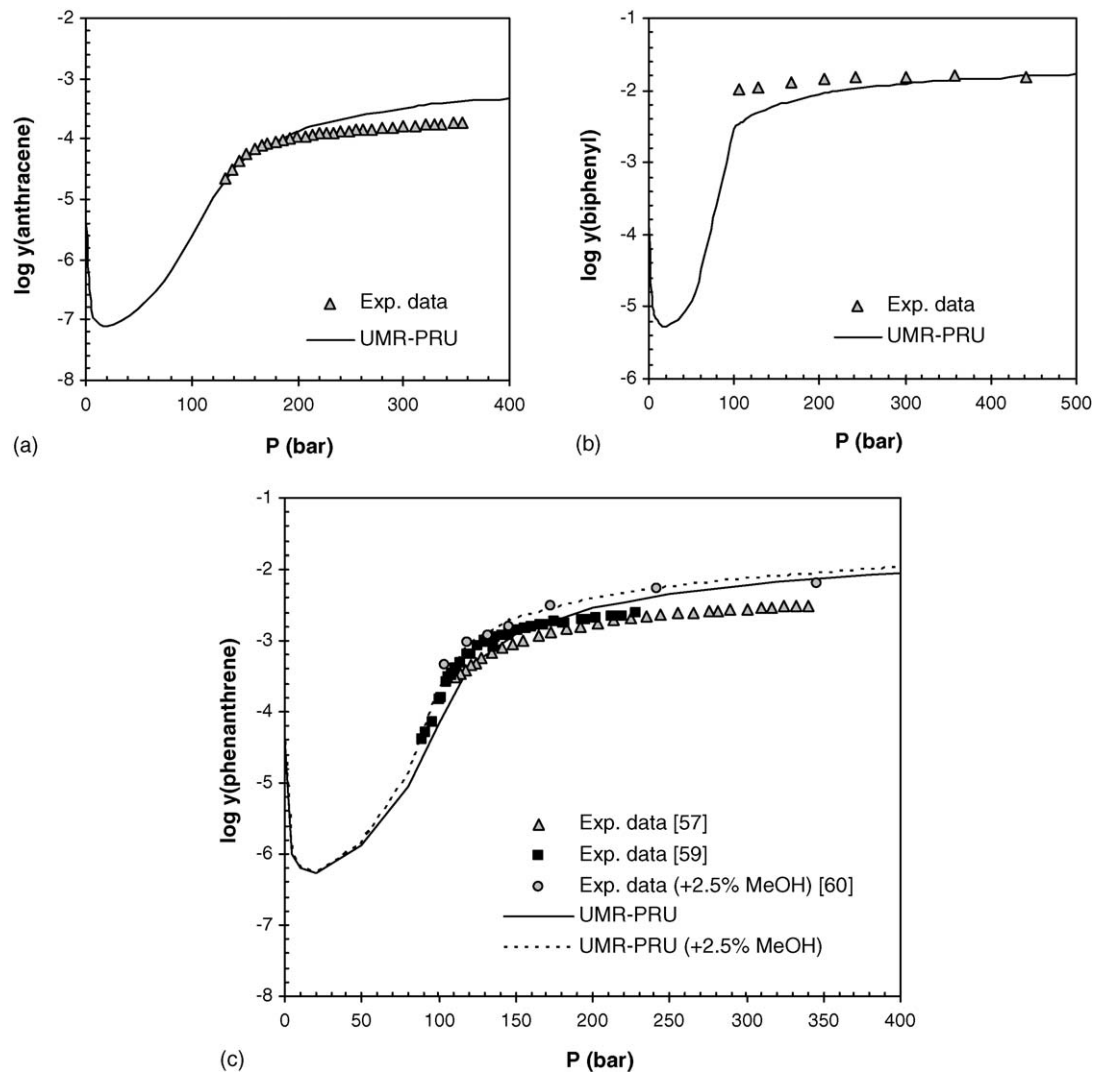


Fig. 7. Solubility of: (a) anthracene (333 K) [57], (b) biphenyl (309 K) [58] and (c) phenanthrene (323 K) [57,59,60], in carbon dioxide with the UMR-PRU model.

through the following equation:

$$(PE)_2 = \exp \left[\frac{V_2^s (P - P_2^{sub})}{RT} \right]$$

(15)

where V_2^s is the molar volume of the solid compound. The critical properties and the acentric factors, the Antoine parameters used for the estimation of solid vapor pressures, and the molar volumes of the compounds involved in this study are presented in Table 9.

Table 11
 H^E results with the UMR-PRU model for some binary systems

System	Reference	T-range (K)	P (bar)	NP	ΔH^E (%)	
					UMR-PRU (T-independent)	UMR-PRU (T-dependent)
Acetone/trichloromethane	[65]	323–343	1	15	12.8	7.9
Acetone/ <i>n</i> -heptane	[66]	283–363	4	91	18.6	9.3
Butanone/ <i>n</i> -hexadecane	[67,68]	298	1	9	19.5	6.9
Propanol-1/ <i>n</i> -nonane	[69]	298	1.7	8	45.5	7.3
Benzene/ <i>n</i> -octane	[70]	323	1	8	55.9	8.6
Benzene/ <i>n</i> -decane	[70]	323	1	8	54.2	7.5
Benzene/ <i>n</i> -hexadecane	[70]	323	1	8	50.9	5.7

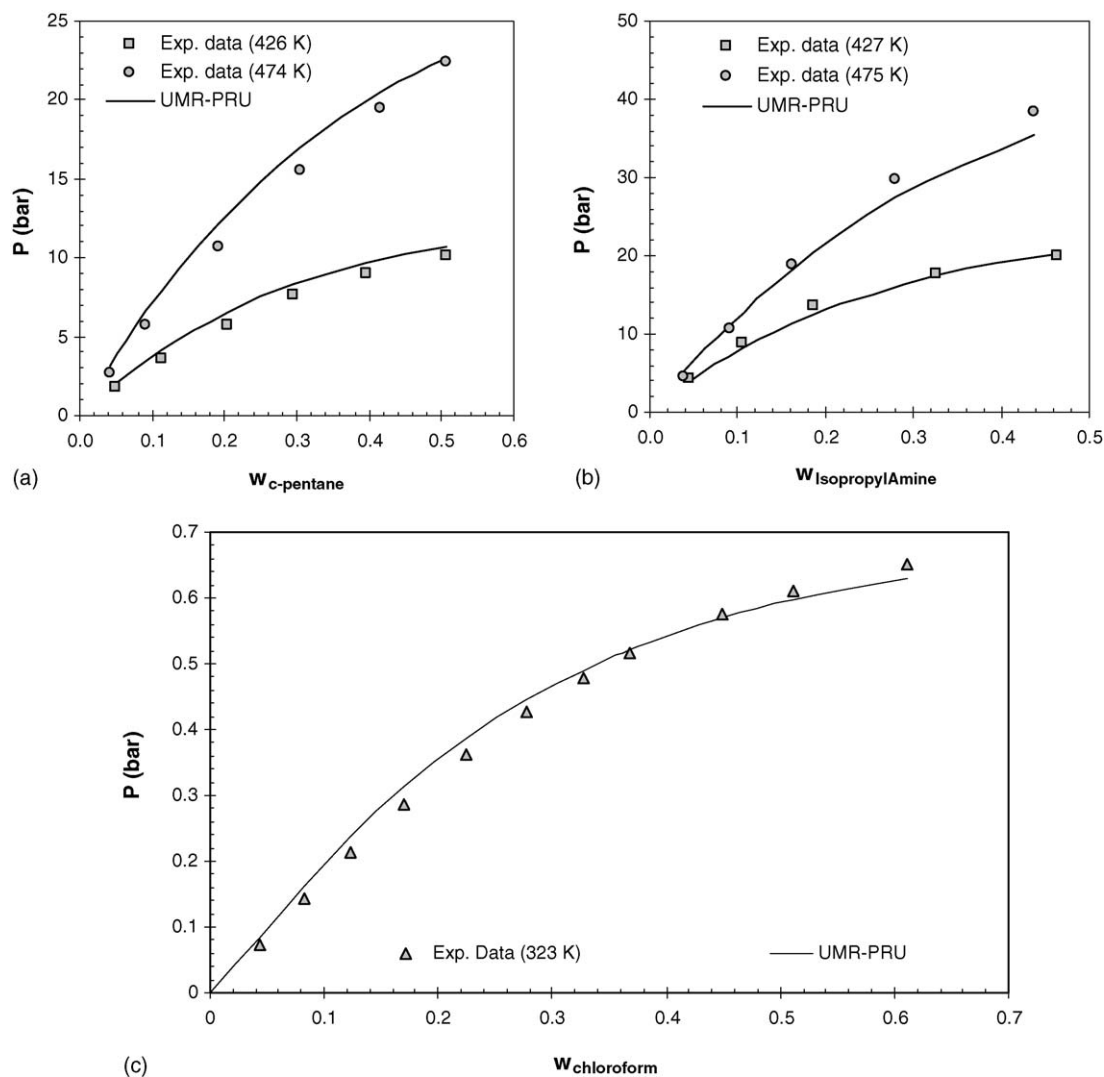


Fig. 8. VLE prediction results with the UMR-PRU model for polymer/solvent systems: (a) LDPE/c-pentane, (b) LDPE/isopropylamine and (c) chloroform/dendrimer A4.

Typical solid solubility predictions in SCCO_2 are shown in Fig. 7a and b, while Fig. 7c shows also the effect of adding a co-solvent (methanol) in the solubility of phenanthrene in SCCO_2 . Satisfactory results are obtained in all cases examined including the prediction of the co-solvent effect.

5.6. VLE predictions in polymer/solvent systems

The UMR-PRU model gives very satisfactory predictions for polymer/solvent vapor–liquid equilibrium at low and higher pressures, as indicated by the results presented in Table 10 and the typical ones shown graphically in Fig. 8. The attractive and co-volume parameters of the PR EoS for the polymers were obtained from Louli and Tassios [64]. An exception was the A4 dendrimer for which those parameters are not available, and they were calculated with the method of Louli and Tassios using the dendrimer densities given in the paper where the VLE data are presented [62].

5.7. Heat of mixing predictions

Available UNIFAC IPs can be utilized in the UMR-PRU model for the prediction of heats of mixing (H^E):

$$H^E = \left[\frac{\partial(G^E/T)}{\partial(1/T)} \right]_{T,x} \quad (16)$$

H^E predictions are presented in Table 11 and typical ones graphically in Fig. 9. Notice the successful results obtained in all case and, especially, for the $\text{CO}_2/\text{C}_2\text{H}_6$ system, where C_2H_6 was considered as a molecule that consists of two CH_3 groups, utilizing thus the CO_2/CH_2 parameters of Table 2, which were determined by fitting VLE data only. Also, the use of UMR-PRU model with T-dependent UNIFAC IPs leads, as it was expected, to much better results than those obtained with T-independent ones.

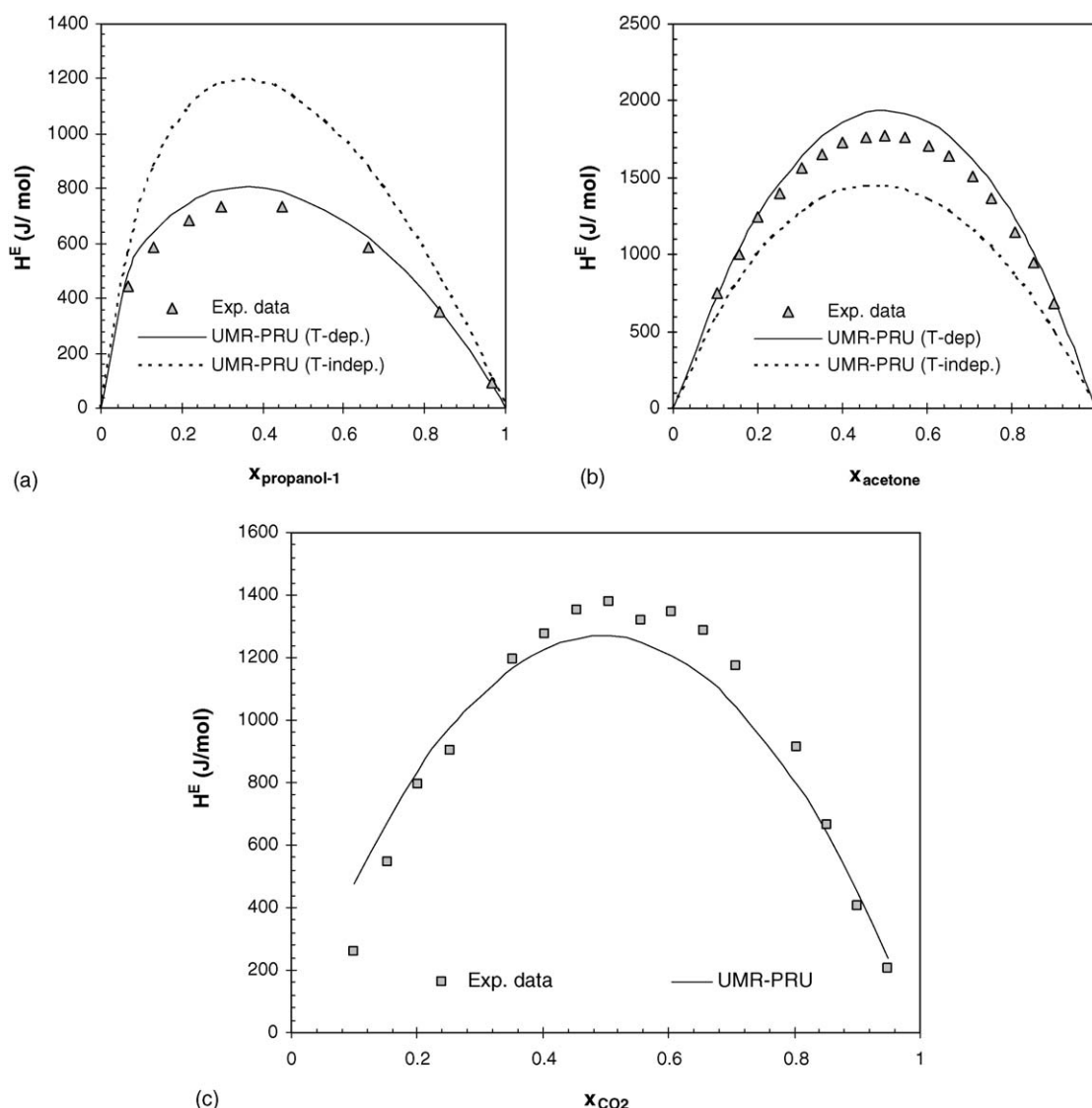


Fig. 9. Heat of mixing predictions with the UMR-PRU model for the systems: (a) 1-propanol/*n*-nonane (298 K), (b) acetone/*n*-heptane (323 K) and (c) CO₂/C₂H₆ (272 K, 110 bar) [71].

6. Discussion and conclusions

The new proposed EoS/ G^E model (UMR-PRU) has two basic advantages over the other well-known in the literature EoS/ G^E models. Firstly, it is applicable to the whole range of system asymmetries, up to polymer/solvent systems, as demonstrated with the results presented here, especially those where no IPs are used, e.g. the C₃H₈/alkane systems (Table 3 and Fig. 3) and the LDPE/*c*-pentane system (Fig. 8c). On the other hand, MHV2 and PSRK are applicable only to low asymmetries, LCVm is not applicable to polymer/solvent systems, while the use of different combining rules for the cross co-volume parameter of the EoS in the recently proposed VTPR model leads to some uncertainties in its application to certain types of systems such as, for example, polymer solutions where more than one solvent is involved.

Secondly, the UMR-PRU model provides satisfactory predictions of various thermodynamic properties (VLE, LLE, SGE and ΔH_m) in systems of various degrees of non-ideality utilizing

the existing linearly T-dependent UNIFAC IPs of Hansen et al., without need of their reevaluation, as is the case with the VTPR model.

Exceptions are, obviously, the cases of: (a) LLE predictions where the combination of the UMR mixing rules with the UNIFAC-LLE is proposed and (b) gas involving systems, since parameters of gas involving pairs are not, available in the UNIFAC model. Actually, some of them have been evaluated in this work.

Finally, the performance of the model in the VLLE of the water/alkane binaries (Fig. 6) indicates that it has the flexibility to be a successful correlative/predictive tool in the cases of complex systems where straight prediction does not provide satisfactory results.

In conclusion, it is demonstrated that the UMR-PRU EoS/ G^E model represents a unique, simple and reliable tool for the calculation of thermodynamic properties for systems of various degrees of non-ideality and asymmetry, up to those observed in

polymer/solvent systems. Following the successful performance of the model, we intend in ensuing publications to evaluate IPs for more gas involving pairs, so as to expand the range of the systems that the model is applicable to.

List of symbols

α	attractive parameter of a cubic EoS ($\text{bar cm}^6/\text{mol}^2$)
b	co-volume parameter of a cubic EoS (cm^3/mol)
c_1, c_2, c_3	pure compound parameters as defined in Mathias–Copeman expression
G	Gibbs free energy
H	enthalpy
P	pressure (bar)
$\Delta P\%$	average absolute error in pressure
	$\left(\Delta P\% = 100 \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} \left \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right \right)$
q	van der Waals area parameter
R	universal ideal gas constant ($= 83.14 \text{ bar cm}^3/(\text{mol K})$)
r	van der Waals volume parameter
t	translation in volume
T	absolute temperature (K)
V	molar volume (cm^3/mol)
w	weight fraction
x	mole fraction in liquid phase
y	mole fraction in vapor phase
Δy	average absolute error in vapor phase concentration
	$\left(\Delta y = \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} y_i^{\text{exp}} - y_i^{\text{calc}} \right)$

Greek symbols

Γ_k	residual activity coefficient of group k in a solution
v_k^i	number of groups of kind k in molecule i
ω	acentric factor

Superscripts

calc.	calculated value
exp.	experimental value
E	excess property
res	residual term
s	solid
SG	Staverman–Guggenheim contribution
sub	sublimation

Subscripts

AC	activity coefficient model
c	critical property
$i(j)$	component in a mixture
ij	cross parameter (defined by the combining rules)
m	mixing
r	reduced property

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