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A generalized reference state at constant volume for the prediction of phase equilibria from low pressure model parameters: Application to size-asymmetric systems and to the Wong–Sandler mixing rule

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This paper describes an EoS/ G^E approach based on cubic equations of state making reference to low pressure G^E models derived from the lattice fluid theory of Guggenheim. The proposed method does not present the theoretical problems encountered with the literature reference states (infinite pressure of Huron–Vidal, zero pressure of Michelsen and constant packing fraction of Pénélox), namely the description of the alpha function with combinatorial terms derived from both the excess Gibbs energy model and the EoS. The main advantage of the proposed method is to successfully account for the size-asymmetry of mixture components and to improve the results obtained with the Wong–Sandler mixing rule. Comparisons are performed with the MHV1, LCVm and the original Wong–Sandler approach at infinite pressure.

Keywords:

Reference state
Cubic equation of state
Excess Gibbs energy models
Wong–Sandler mixing rule
Size-asymmetric systems
Vapor–liquid equilibria

1. Introduction

The EoS/ G^E model approach, mainly developed for cubic equations of state, originates from the works of Vidal (1978) and represents a major development for chemical engineering thermodynamics. For a given reference state, this formalism assumes the equality of the excess properties estimated from the EoS and from a low pressure G^E model, which, in principle, should provide more physically meaningful EoS parameters. This approach was then completed by the works of Huron and Vidal (1979), with the infinite pressure reference, of Mollerup (1986), Heidemann and Kokal (1990) and Michelsen (1990), with the zero pressure reference, and of Pénélox et al. (1989), with the constant packing fraction reference. More complex mixing rules were also developed, such as: MHV2 (Modified Huron–Vidal 2nd order; Dahl and Michelsen, 1990), Wong–Sandler (Wong and Sandler, 1992) or LCVm (Linear Combination of Vidal and Michelsen mixing rules; Boukouvalas et al., 1994). From the original works, a great number of papers were devoted to the application of reference states in the formulation of mixing rules to be used with cubic EoS (Soave et al., 1994; Tochigi et al., 1994; Heidemann, 1996; Twu et al., 1998).

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Among all these reference states, the infinite pressure, and the MHV1 approaches have been most widely used, either to develop completely predictive models or to allow the prediction of high pressure equilibria from low pressure parameters determined without an EoS. However, it was shown by Kontogeorgis and Vlamos (2000) that they raise, as all the other literature reference states, the following problem: contrary to the theory, the α^M function defined as the difference between the alpha function $\alpha = a/bRT$ of the mixture and the sum $\sum x_i \alpha_i$ of the pure components depend, not only on the residual part of the excess Gibbs energy model, but also on combinatorial contributions. In practice, predictive equations of state based on the zero pressure reference state (VTPR (Ahlers and Gmehling, 2002), UMR–PRU (Vousta et al., 2006)), on the constant packing fraction (PPR78 (Jaubert and Mutelet, 2004)) or on the generalized reference state at constant volume (NRTL-PR (Neau et al., 2010b)) avoid this inconsistency since they assume that the Flory–Huggins term of the G^E model is equal to that of the EoS. However, the problem still remains unsolved when using low pressure models with parameters determined without an EoS.

To overcome this difficulty, a generalized reference state at constant volume (GRS-CV) was proposed (Escandell et al., 2011). In the present paper, the mixing rule is associated with the Peng–Robinson EoS and applied to the modeling of VLE for mixtures containing hydrocarbons and polar or associating compounds, such as water and alcohols. Using the UNIFAC model, we focus on

the ability of this mixing rule to represent highly size-asymmetric systems and multicomponent mixtures; results thus obtained are compared to those provided by the MHV1 and LCVM reference states. The influence of excess Gibbs energy models depending or not on combinatorial terms is also discussed with respect to the choice of reference states (MHV1, infinite pressure and GRS-CV). Finally, the GRS-CV approach is applied to the Wong–Sandler mixing rule.

2. The generalized reference state at constant volume

The compressibility factor Z of a cubic EoS can be expressed as

$$Z = \frac{1}{1-\eta} - \frac{\alpha\eta}{(1+e_1\eta)(1+e_2\eta)} \quad \text{with: } \alpha = a/bRT, \quad \eta = b/v \quad (1)$$

where a and b are the attractive term and the co-volume, respectively, η and v are the packing fraction and the molar volume at a given temperature T , respectively; e_1 and e_2 characterize the cubic equation of state according to

$$\begin{aligned} e_1 = 0, \quad e_2 = 1 & \text{ for the Redlich–Kwong EoS (Redlich and Kwong, 1949),} \\ e_1 = 1 + \sqrt{2}, \quad e_2 = 1 - \sqrt{2} & \text{ for the Peng–Robinson EoS (Peng and Robinson, 1976).} \end{aligned}$$

The proposed method is based on the EoS/ G^E approach. The attractive term a in Eq. (1) 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

$$A^{EV}(T, V^0, n)_{EoS} / nRT = A^{EV}(T, x) / nRT \approx g^E(T, x) / RT \quad (2)$$

where g^E is the molar excess Gibbs energy at constant pressure.

The excess Helmholtz energy at constant volume A^{EV} is estimated from the equation of state according to

$$A^{EV}(T, V^0, n)_{EoS} = A^{res}(T, V^0, n) - \sum_i A_i^{res}(T, V_i^0, n_i) + RT \sum_i n_i \ln \frac{V_i^0}{V^0} \quad (3)$$

with: $V^0 = \sum_i V_i^0$, where V_i^0 is the total volume of component i , and n_i its mole number.

In the case of cubic EoS (Eq. (1)) the above equation becomes

$$\begin{aligned} A^{EV}(T, V^0, n)_{EoS} / nRT = & - \sum_i x_i \ln \left(\frac{1-\eta^0}{1-\eta_i^0} \right) - \alpha C(\eta^0) \\ & + \sum_i x_i \alpha_i C(\eta_i^0) + \sum_i x_i \ln \frac{V_i^0}{V^0} \end{aligned} \quad (4)$$

where

$$C(\eta^0) = \frac{1}{(e_1 - e_2)} \ln \left(\frac{1 + e_1 \eta^0}{1 + e_2 \eta^0} \right), \quad C(\eta_i^0) = \frac{1}{(e_1 - e_2)} \ln \left(\frac{1 + e_1 \eta_i^0}{1 + e_2 \eta_i^0} \right) \quad (5)$$

so that

$$g^E / RT = - \sum_i x_i \ln \left(\frac{1-\eta^0}{1-\eta_i^0} \right) - \alpha C(\eta^0) + \sum_i x_i \alpha_i C(\eta_i^0) + \sum_i x_i \ln \frac{V_i^0}{V^0} \quad (6)$$

2.1. Application to the literature reference states

The above equation allows us to deduce the literature zero pressure, infinite pressure and constant packing fraction reference states. Values of the reference constants C indicated in the following equations correspond to the Peng–Robinson EoS.

- Zero pressure reference state (Michelsen, 1990). The original MHV1 (Modified Huron–Vidal 1st order) mixing rule proposed

by Michelsen can be obtained from Eq. (6) as follows: to eliminate volumes in the right hand side, packing fractions in the reference state ($\eta^0 = nb/V^0$ and $\eta_i^0 = nb_i/V_i^0$) are assumed to be equal; the functions $C(\eta^0) = C(\eta_i^0)$ are then fixed as a constant value C , so that

$$g^E / RT = C \left[-\alpha + \sum_i x_i \alpha_i \right] + \sum_i x_i \ln \frac{b_i}{b}, \quad C = 0.53 \quad (7)$$

leading to the α^M function:

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = -\frac{1}{C} \left[\frac{g^E}{RT} - \sum_i x_i \ln \frac{b_i}{b} \right] \quad (8)$$

- Infinite pressure reference state (Huron and Vidal, 1979). At infinite pressure, P_∞ , the packing fractions η^0 and η_i^0 tend to 1, so that, according to Eq. (1)

$$\begin{aligned} \left(\frac{V_i^0}{V^0} \right) \left(\frac{1-\eta_i^0}{1-\eta^0} \right) & \rightarrow 1 \\ \text{since at } P_\infty: & \begin{cases} P_\infty V_i^0 ((1-\eta_i^0)/nRT) = Z_{i,P_\infty}^0 (1-\eta_i^0) \rightarrow 1 \\ P_\infty V^0 ((1-\eta^0)/nRT) = Z_{P_\infty}^0 (1-\eta^0) \rightarrow 1 \end{cases} \end{aligned} \quad (9)$$

Finally, using the same value for the reference constants, $C(\eta^0) = C(\eta_i^0) = C$, we obtain

$$g^E / RT = C \left[-\alpha + \sum_i x_i \alpha_i \right], \quad C = 0.623 \quad (10)$$

and

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = -\frac{1}{C} \left[\frac{g^E}{RT} \right] \quad (11)$$

- Constant packing fraction (Péneloux et al., 1989). It is based on the same hypothesis as the zero pressure reference state (Eq. (8)), but using for the excess Gibbs energy the following expression derived from the lattice fluid theory of Guggenheim (1952)

$$g^E = g^{E,comb} + g^{E,res} \quad (12)$$

where, $g^{E,comb}$ and $g^{E,res}$ are, respectively, the combinatorial and residual terms; $g^{E,comb}$ is then expressed with a Flory–Huggins term in which the volume factors are estimated from the EoS co-volumes, so that Eq. (8) becomes

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = -\frac{1}{C} \left[\frac{g^{E,res}}{RT} \right], \quad C = 1.00 \quad (13)$$

As was shown by Kontogeorgis and Vlamos (2000), the α^M function (Eqs. (8) and (11)) should not depend on combinatorial contributions; therefore:

- only the residual term $g^{E,res}$ of the excess Gibbs energy should be used for Huron–Vidal type models (Eq. (11)).
- The predictive VTPR and UMR–PRU models based on the zero pressure (Eq. (8)) assume that the Flory–Huggins term of the UNIFAC model (Table 1) is equal to the combinatorial part of the α^M function. The same approximation is also made with the PPR78 equation (Jaubert and Mutelet, 2004) based on the constant packing fraction (Eq. (13)).

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

Table 1
Low pressure g^E models used in this study.

- **UNIFAC** (Hansen et al., 1991):

$$g_{UNIFAC}^E = RT \left[\sum_i x_i \ln \frac{r_i}{\sum_j x_j r_j} + (z/2) \sum_i x_i q_i \ln \frac{q_i r_i}{q \sum_j r_j} \right] + RT \sum_i x_i \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}), \quad z = 10$$

with : $v_k^{(i)}$: number of group k in molecule i

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right]$$

$$\theta_m = \frac{q_m X_m}{\sum_n q_n X_n}, \quad X_m = \frac{\sum_j v_{mj} x_j}{\sum_n \sum_j v_{nj} x_j}$$

$$\psi_{nm} = \exp(-\Delta u_{nm}/RT), \quad \Delta u_{nm} = a_{nm} + b_{nm}T + c_{nm}T^2$$

- **Original NRTL** (Renon and Prausnitz, 1968):

$$g_{NRTL}^E = \sum_i x_i \frac{\sum_j x_j G_{ji} \Gamma_{ji}}{\sum_i x_i G_{ii}}, \quad G_{ji} = \exp(-\alpha_0 \Gamma_{ji}/RT), \quad \Gamma_{ji} \neq \Gamma_{ij}, \quad \alpha_0 = 0.2$$

- **Generalized NRTL** (Neau et al., 2010a):

$$g_{NRTL-gen}^E = RT \left[\sum_i x_i \ln \frac{r_i}{r} \right] + \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_i x_i q_i G_{ii}}$$

this purpose, the following generalized reference state at constant volume was developed.

2.2. Generalized reference state at constant volume

In this approach, we consider that:

- the reference volumes V_i^0 and V^0 in Eq. (6) can be expressed directly from the volume factors r_i and r , respectively, used with the g^E model and no more from the EoS co-volumes b_i and b .
- Then, to eliminate the volumes in Eq. (6), 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, the functions $C(\eta^0)$ and $C(\eta_i^0)$ are fixed at the same constant value, C , which leads to

$$g^E/RT = C \left[-\alpha + \sum_i x_i \alpha_i \right] + \sum_i x_i \ln \frac{r_i}{r}, \quad C = 0.56 \quad (14)$$

and to the following α^M function

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = -\frac{1}{C} \left[\frac{g^E}{RT} - \sum_i x_i \ln \frac{r_i}{r} \right] \quad (15)$$

The value $C=0.56$ for the Peng–Robinson equation was obtained by correlating the bubble points of the binary systems of Tables 3 and 4. However, in principle, other values could be chosen for the C parameter (for instance: 0.530 or 0.623 as in Eqs. (7) and (10)); this is why this mixing rule is referred to as a “generalized reference state”.

This new reference state calls the following remarks discussed in the next section:

- any kind of low pressure model can be used in Eq. (15). In the case of g^E models containing no combinatorial part, such as van Laar (Van Laar, 1914) and original NRTL (Renon and Prausnitz, 1968) models, the volume factors r_i are estimated from any classical UNIFAC group contribution method. In this work,

calculations with the NRTL model (Table 1) were performed using the r_i parameters from Fredenslund et al. (1975).

- The proposed EoS/ G^E approach can be associated with linear or quadratic expressions of the co-volumes or with the Wong and Sandler (1992) mixing rule.

3. Results and discussion

In this paper, the GRS-CV reference state (Eq. (15)) is associated with the Peng–Robinson EoS and low pressure g^E models for the prediction of liquid–vapor equilibria (VLE) for mixtures containing hydrocarbons and polar or associating compounds, such as water and alcohols. As outlined in the introduction, the discussion about reference states is meaningless for models whose parameters were determined using the EoS (VTPR, UMR–PRU, PPR78, NRTL-PR, ...); for each model, the use of different α^M functions would lead to similar results, but with different values of model parameters. Therefore, in this work devoted to the influence of reference states, only models, such as UNIFAC or NRTL, with parameters determined at low pressure without an EoS were investigated; consequently, systems containing supercritical compounds, like methane or carbon dioxide, were not studied.

Section 3.1 focuses on the ability of the proposed approach to represent highly size-asymmetric systems and multicomponent mixtures; for this purpose the UNIFAC model was used. Section 3.2 studies the influence of the choice of low pressure g^E models associated with the MHV1, infinite pressure and GRS-CV reference states. Finally, in Section 3.3, the GRS-CV approach is applied to the Wong–Sandler mixing rule.

3.1. VLE predictions from the GRS-CV associated with the UNIFAC model

The UNIFAC group contribution method proposed by Hansen et al. (1991) was associated with the Peng–Robinson Soave(γ, m) type function (Neau et al., 2009) using, for hydrocarbons and non associating compounds, $\gamma=0.5$ (Soave, 1972) and the m function of Robinson and Peng (1978). For propylene oxide, the three-membered ring molecular shape did not agree with the generalized m function, and a specific value was fitted to vapor pressures (Table 2); for associating compounds, the γ and m parameters were determined by correlating the vapor pressures of pure compounds (Table 2).

Values of T_c , P_c and ω were taken from Poling et al. (2004), except for long linear paraffins for which no experimental values are available; in this work we have considered the values suggested by Magoulas and Tassios (1990).

Tables 3–5 compare the results obtained from the GRS-CV (Eq. (15)) and the MHV1 (Eq. (8)) models. We have also considered the LCVM approach developed by Boukouvalas et al.

Table 2
Pure component critical parameters T_c , P_c and fitted γ and m values for the Soave(γ, m) function*.

Compounds	T_c/K	P_c/bar	γ	m
Propylene oxide	488.20	54.40	0.50	0.7481
Methanol	512.64	80.97	0.90	0.6969
Ethanol	513.78	61.48	0.60	1.0808
1-Propanol	536.78	51.75	0.20	2.9524
2-Propanol	508.30	47.62	0.30	2.0950
1-Butanol	562.00	45.00	0.15	3.8931
2-Butanol	536.05	41.79	0.15	3.7435
Water	647.13	220.55	0.65	0.6864
Chloroethane	460.35	52.41	0.35	0.9087

* $a = a_c[1 + m(1 - (T/T_c)^\gamma)]^2$

Table 3

Size-asymmetric systems. Number of experimental bubble points, temperature and pressure ranges and mean percent deviations on bubble point pressures. Comparison between the MHV1, LCVM, GRS-CV and mGRS-CV reference states associated with the UNIFAC model and the Peng–Robinson EoS.

Components		Np	T _{min} /K–T _{max} /K	P _{min} /bar–P _{max} /bar	ΔP%				Ref.
(1)	(2)				MHV1	LCVM	GRS-CV	mGRS-CV	
Ethane	-Pentane	74	278–444	0.3–68	1.8	3.4	2.1	2.1	[1]
	-Decane	128	278–511	3.9–117	8.0	7.9	3.0	2.7	[2,3]
	-Dodecane	50	298–373	3.8–56	11.3	9.6	3.8	3.6	[4]
	-Eicosane	72	290–450	2.3–163	33.8	8.5	9.7	9.8	[5]
	-Tetracosane	62	321–369	4.2–137	46.9	13.4	12.5	12.6	[6]
	-Octacosane	36	373–573	5.6–52	89.2	5.6	7.1	7.7	[7,8]
	-Hexatriacontane	21	373–573	3.7–48	140.1	3.7	6.5	6.6	[7,9]
Propane	-Tetratetracontane	15	373–423	3.9–31	201.3	5.4	10.4	9.9	[7]
	-Hexane	40	273–313	0.5–12	1.4	1.7	1.4	1.4	[10]
	-Decane	65	278–511	0.01–71	4.8	3.6	2.6	2.6	[2]
Cyclohexane	-Hexadecane	38	273–313	0.6–13	6.5	8.1	5.8	5.5	[10]
	-Hexane	65	298–343	0.1–1.0	1.3	1.2	1.0	1.0	[11–14]
	-Hexadecane	54	298–312	0.01–0.2	7.4	2.3	3.1	3.0	[15,16]
Benzene	-Eicosane	27	306–317	0.01–0.3	11.6	1.9	4.0	3.8	[17]
	-Hexane	97	293–463	0.1–15	2.2	1.7	1.7	1.7	[18–20]
	-Dodecane	61	298–353	0.03–0.9	6.7	3.0	2.9	2.9	[21,22]
	-Hexadecane	89	298–353	0.01–1.0	9.4	2.5	1.9	1.8	[16,23,24]
Mean value		994			19.2	5.0	4.1	4.0	

[1] Reamer et al., 1960; [2] Reamer and Sage, 1962; [3] Bufkin et al., 1986; [4] Legret et al., 1980; [5] Peters et al., 1987a; [6] Peters et al., 1987b; [7] Gasem et al., 1989; [8] Huang et al., 1988; [9] Tsai et al., 1987; [10] Ishida et al., 1975; [11] Martin and Youngs, 1980; [12] Ott et al., 1980; [13] Meixner and Lichtenthaler, 1979; [14] Susarev and Chen, 1963; [15] Gómez-Ibáñez and Shien, 1965; [16] Snow et al., 1986; [17] Gómez-Ibáñez and Wang, 1971; [18] Markuzin and Plekhotkin, 1962; [19] Saez et al., 1985; [20] Medani and Hasan, 1977; [21] Messow and Quitzsch, 1976; [22] Rubio et al., 1983; [23] Jain and Lark, 1973; [24] Messow et al., 1976.

Table 4

Binary polar and moderate asymmetric mixtures. Number of experimental bubble points, temperature and pressure ranges and mean percent deviations on bubble point pressures. Comparison between the MHV1, LCVM, GRS-CV and mGRS-CV reference states associated with the UNIFAC model and the Peng–Robinson EoS.

Components		Np	T _{min} /K–T _{max} /K	P _{min} /bar–P _{max} /bar	ΔP%				Ref.
(1)	(2)				MHV1	LCVM	GRS-CV	mGRS-CV	
Ethanol	-Pentane	32	373–500	4.2–57	1.9	3.5	4.1	4.1	[1,2]
	-Undecane	18	333–353	0.4–1.1	4.5	4.6	5.4	5.3	[3]
1-Propanol	-Benzene	153	298–533	0.03–49	3.3	2.5	2.4	2.4	[4–8]
	-Toluene	45	298–313	0.03–0.12	2.4	3.0	3.6	3.6	[9–11]
1-Butanol	-Butane	45	333–473	2.0–46	3.7	4.3	4.3	4.3	[12]
	-Octane	161	283–373	0.004–1.0	4.5	2.8	3.0	3.0	[13–15]
2-Propanol	-Hexane	62	303–328	0.1–0.9	6.9	4.8	4.7	4.7	[16,17]
2-Butanol	-Benzene	59	298–353	0.02–1.0	5.0	4.0	4.0	4.0	[18–21]
3-Methyl-2-butanone	-2-Methylbutane	13	333	0.3–2.7	5.3	4.2	3.9	3.9	[22]
	-2-Methyl-2-butene	13	333	0.3–2.0	5.4	4.6	4.4	4.4	[22]
	-Isopentadiene	13	333	0.3–2.3	2.8	2.5	2.5	2.5	[23]
Propylene oxide	-Tetrachloromethane	28	320	0.4–1.6	6.1	6.3	5.7	5.7	[24]
	-Methyl t-butyl ether	20	363	2.8–5.5	6.4	7.0	5.8	5.7	[25]
Chloroethane	-Diethyl ether	14	298–303	0.7–1.8	1.7	1.8	1.8	1.8	[26]
Water	-Methanol	57	373–523	1.0–85	2.0	1.7	2.9	2.9	[27]
	-Ethanol	54	423–573	5.6–107	5.0	1.7	2.4	2.5	[28]
	-2-Propanol	54	423–573	5.2–94	5.1	3.8	1.6	1.6	[28]
	-Acetone	71	373–523	1.1–63	7.0	3.2	3.9	3.9	[27]
Methanol	-Acetone	39	373–473	3.5–40	2.6	1.6	2.5	2.5	[27]
	-Benzene	40	373–493	3.1–58	5.4	3.5	6.1	6.1	[29]
	Mean value	991			4.4	3.2	3.4	3.4	

[1] Campbell et al., 1987; [2] Seo et al., 2000; [3] Schmelzer et al., 1983; [4] Hwang and Robinson, 1977; [5] Rhodes et al., 2001; [6] Kurihara et al., 1997; [7] Fu and Lu, 1966; [8] Skaates and Kay, 1964; [9] Gupta et al., 1996; [10] Maken et al., 1999; [11] Oracz and Kolasinska, 1987; [12] Deák et al., 1995; [13] Gierycz et al., 1988; [14] Gracia et al., 1992; [15] Hiaki et al., 1998; [16] Barraza and Edwards, 1981; [17] Berro et al., 1981; [18] Allen et al., 1939; [19] Brown et al., 1969; [20] Ruiz Echevarria, 1973; [21] Rodriguez et al., 1993; [22] Smirnov et al., 1976a; [23] Smirnov et al., 1976b; [24] Gutsche and Knapp, 1980; [25] Wilding et al., 1987; [26] Neimann and Demikhovskaya, 1949; [27] Griswold and Wong, 1952; [28] Barr–David and Dodge, 1959; [29] Butcher and Medani, 1968.

(1994) to improve the MHV1 predictions:

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = -\frac{1}{C} \left[\frac{g^E}{RT} - \delta \sum_i x_i \ln \frac{b_i}{b} \right], \quad C = 0.553, \quad \delta = 0.680 \quad (16)$$

in which the parameter values are those obtained by the authors with the original UNIFAC model (Hansen et al., 1991) associated with the Peng–Robinson EoS.

A similar approach, named mGRS-CV (modified GRS-CV), was also proposed:

$$\alpha^M = \alpha - \sum_i x_i \alpha_i = -\frac{1}{C} \left[\frac{g^E}{RT} - \delta \sum_i x_i \ln \frac{r_i}{r} \right], \quad C = 0.56, \quad \delta = 1.01 \quad (17)$$

where the parameter δ was fitted to the experimental bubble points of the studied size-asymmetric systems.

Table 5
Ternary polar and moderate asymmetric mixtures. Number of experimental bubble points, temperature and pressure ranges and mean percent deviations on bubble point pressures. Comparison between the MHV1, LCVm, GRS-CV and mGRS-CV reference states associated with the UNIFAC model and the Peng–Robinson EoS.

Components			Np	$T_{\min}/K-T_{\max}/K$	$P_{\min}/\text{bar}-P_{\max}/\text{bar}$	$\Delta P\%$				Ref.
(1)	(2)	(3)				MHV1	LCVM	GRS-CV	mGRS-CV	
Ethane	-Butane	-Heptane	56	339–394	31–79	3.5	3.9	3.4	3.4	[1]
Benzene	-Cyclohexane	-Methanol	19	311–328	0.5–1	4.3	2.2	4.9	5.0	[2]
		-2-Propanol	19	343–344	1	3.8	1.8	1.5	1.5	[3]
Water	-Methanol	-Ethanol	37	298	0.07–0.15	4.4	6.1	5.2	5.2	[4]
		-Acetone	106	373–523	1.2–82	4.2	3.8	4.9	4.8	[5]
Mean value			237			4.1	3.9	4.3	4.3	

[1] Mehra and Thodos, 1966; [2] Morachevskii and Komarova, 1957; [3] Nagata, 1964; [4] Hall et al., 1979; [5] Griswold and Wong, 1952.

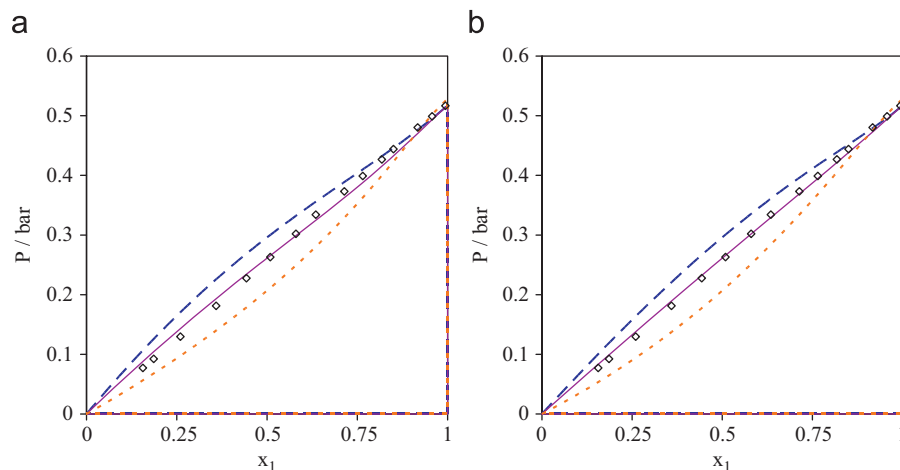


Fig. 1. Prediction of benzene(1)–hexadecane(2) system at $T=333\text{ K}$ using with the Peng–Robinson EoS parameters fitted to low pressure data without an EoS. Modeling with the (—) MHV1, (---) infinite pressure and (—) GRS-CV reference states. (\diamond) Experimental data from Messow et al., 1976. (a) Original NRTL model ($\Gamma_{12}=3801$, $\Gamma_{21}=-2790$ in J mol^{-1} (Neau et al., 2010a)); (b) Generalized NRTL model ($\Gamma_{12}=-930$, $\Gamma_{21}=1573$ in J mol^{-1} (Neau et al., 2010a)).

3.1.1. Size-asymmetric systems

In Table 3, the VLE for 17 size-asymmetric systems including ethane, propane, cyclohexane and benzene with long chain paraffins were studied at pressures up to 160 bar.

As was previously mentioned by several authors (Boukouvalas et al., 1994; Kontogeorgis and Folas, 2010), it can be observed that the MHV1 reference state provides poor results as the length of the paraffin chain increases, due to the combinatorial term based on the co-volumes (Eq. (8)). On the contrary, the proposed GRS-CV approach, which estimates the α^M combinatorial part from the volume factors of the Flory–Huggins term (Eq. (15)), correctly accounts for the chain length effect.

As could be expected, the two modified approaches, LCVm and mGRS-CV, yield comparable results; however, it must be noted that:

- the LCVm reference state provides a better description of ethane–paraffin mixtures, from octacosane to tetratetracontane;
- the mGRS-CV model, with a δ value close to unit, provides predictions similar to the GRS-CV equation. This result proves that, contrary to the MHV1 mixing rule, the original GRS-CV reference state needs no improvement.

3.1.2. Polar compounds and moderate asymmetric mixtures

The VLE for 20 binary and five ternary systems containing hydrocarbons and polar or associating compounds were studied at pressures up to 100 bar. Results obtained with the GRS-CV, mGRS-CV, MHV1 and LCVm reference states are reported in Tables 4 and 5.

These mixtures mainly contain alcohols or water and do not exhibit size-asymmetric effects. The combinatorial terms (Eqs. (8), (15)–(17)) have therefore a very small influence and the MHV1 approach provides satisfactory predictions as the three other models.

3.2. Influence of low pressure g^E models

The purpose of this part is to check the influence of other literature g^E models (such as the original and generalized NRTL equations given in Table 1), on VLE predictions using the GRS-CV, MHV1 and infinite pressure reference states associated with the Peng–Robinson EoS. All parameters considered in this section were estimated by correlating the low pressure data without an EoS.

Fig. 1 represents the prediction of the benzene–hexadecane system with parameters fitted from this system:

- for a given reference state, both the original (Fig. 1a) and generalized (Fig. 1b) NRTL models provide exactly the same VLE calculations. This result is in agreement with the previous work of Neau et al. (2010a) concerning the modeling of VLE without an EoS: once parameters are fitted to experimental data, identical results are obtained with excess Gibbs energy models depending or not on a combinatorial term (except the one parameter van Laar (1914) model).
- In comparison with the GRS-CV mixing rule, the MHV1 reference state provides less satisfactory predictions for this size-asymmetric system; the same observation was already

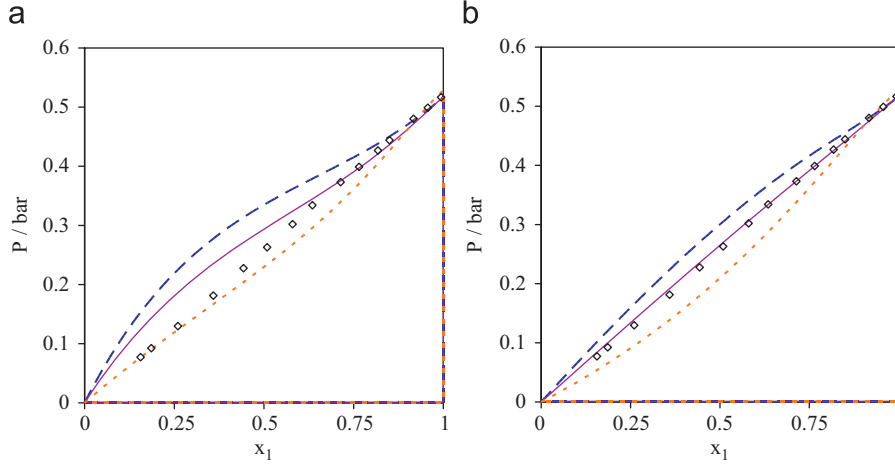


Fig. 2. Extrapolation towards benzene(1)–hexadecane(2) system at $T=333$ K using with the Peng–Robinson EoS parameters of benzene–hexane system fitted to low pressure data without an EoS. Modeling with the (—) MHV1, (---) infinite pressure and (—) GRS-CV reference states. (◇) Experimental data from Messow et al., 1976. (a) Original NRTL model ($\Gamma_{12}=2247$, $\Gamma_{21}=-540$ in J mol^{-1} (Neau et al., 2010a)); (b) Generalized NRTL model ($\Gamma_{12}=-493$, $\Gamma_{21}=1095$ in J mol^{-1} (Neau et al., 2010a)).

made using the UNIFAC model (Table 3). Due to the lack of combinatorial term in Eq. (11), the infinite pressure reference state leads, as was expected, to the worse calculations.

Fig. 2 illustrates the interest of using Gibbs energy models containing both a residual and a combinatorial term; for this purpose, the benzene–hexadecane system was predicted using the interaction parameters fitted from the benzene–hexane mixture. In the previous paper of Neau et al. (2010a) it was shown that only the generalized NRTL model provides physically meaningful Γ_{ji} values (Table 1), allowing extrapolation from hexane to hexadecane; in the same way, Fig. 2 shows that:

- For MHV1 and GRS-CV reference states, the use of a model containing both a residual and a combinatorial term (Fig. 2b) leads to more reliable predictions; the conclusion is less clear for the infinite pressure.
- Very satisfactory VLE extrapolations can only be obtained using the GRS-CV reference state (Fig. 2b).

3.3. Application to the Wong–Sandler mixing rule

The Wong–Sandler (WS) method (Wong and Sandler, 1992) is based on the EoS/ G^E approach associated with a co-volume b derived from the quadratic variation of the second virial coefficient, B , with respect to the mole fraction

$$B = b - \frac{a}{RT} = \sum_i \sum_j x_i x_j B_{ij}, \quad B_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (18)$$

The binary interaction parameters k_{ij} can be fitted to experimental data.

Using the infinite pressure (Eq. (11)) for estimating the α^M function, the authors derived, for the Peng–Robinson EoS, the following expression (WS_{ori}) of the co-volume

$$b = \frac{B}{1-\alpha} \quad \text{with} : \quad \alpha = \sum_i x_i \alpha_i + \alpha^M, \quad \alpha^M = -\frac{1}{C} \left[\frac{g^E}{RT} \right], \quad C = 0.623 \quad (19)$$

In the development of their model, Wong and Sandler needed to consider the infinite pressure P_∞ , since, only this reference state corresponds to an α^M function independent on the co-

volume b . The proposed GRS-CV reference state is also independent on the co-volume (Eq. (15)), so that it can easily be associated with the WS mixing rule, leading to the WS_{GRS-CV} equation

$$b = \frac{B}{1-\alpha} \quad \text{with} : \quad \alpha = \sum_i x_i \alpha_i + \alpha^M, \quad \alpha^M = -\frac{1}{C} \left[\frac{g^E}{RT} - \sum_i x_i \ln \frac{r_i}{r} \right], \quad C = 0.56 \quad (20)$$

The VLE for binary mixtures already studied by Wong and Sandler (1992) were considered for the comparison of the WS_{ori} and WS_{GRS-CV} approaches; calculations in Table 6 were performed with the UNIFAC g^E model (Hansen et al., 1991). Two methods were investigated:

- fitting k_{ij} parameters to experimental data: both mixing rules provide exactly the same satisfactory calculations for all mixtures and temperatures. However, the WS_{GRS-CV} technique leads to substantially smaller k_{ij} values, which suggests that the corresponding reference state is more consistent.
- Assuming a full prediction with $k_{ij}=0$: the WS_{ori} method yields poor predictions (except for the water–methanol and methanol–acetone systems, which were previously correlated with very small values of k_{ij}). Only the WS_{GRS-CV} mixing rule is able to provide satisfactory predictions for all the studied systems.

Compounds considered in Table 6 have quite similar sizes, so that the lack of a combinatorial term in the α^M function (Eq. (19)) cannot explain the poor predictions obtained with WS_{ori} using zero k_{ij} parameters; the influence of the C reference state parameter was therefore investigated. Fig. 3 compares, for all the mixtures of Table 4, the global deviations $\Delta P\%$ on bubble points obtained with the infinite pressure and GRS-CV approaches versus the C parameter value; it clearly shows that:

- results are strongly influenced by the reference parameter C ; the value 0.623 calculated by Huron and Vidal (1979) for the infinite pressure does not correspond to the minimum of the curve. Highly improved results could have been obtained in Table 6 using $C=0.53$, as for the zero pressure reference state.
- Nevertheless, the proposed GRS-CV reference state with $C=0.56$ will always provide more satisfactory predictions.

Table 6
Application to the Wong–Sandler mixing rule. Number of experimental bubble points, temperatures and mean percent deviations on bubble point pressures. Comparison between the original WS_{ori} and the proposed WS_{GRS-CV} approaches using fitted k_{ij} parameters (values indicated in parenthesis) or assuming a full prediction ($k_{ij}=0$). Calculations were performed with the UNIFAC model and the Peng–Robinson EoS.

Components		Np	T/K	$\Delta P\%$ (WS_{ori})			$\Delta P\%$ (WS_{GRS-CV})			
(1)	(2)			Fitted	(k_{ij})	$k_{ij}=0$	Fitted	(k_{ij})	$k_{ij}=0$	
Water	-Methanol	16	373	1.9	(0.07)	2.7	1.9	(0.01)	1.9	
		14	423	1.6	(0.07)	3.6	1.6	(0.01)	1.9	
		15	473	0.8	(0.07)	2.6	0.8	(0.01)	1.0	
	-Ethanol	12	523	2.7	(0.07)	1.2	2.2	(0.01)	1.7	
		17	423	2.2	(0.16)	8.9	1.8	(-0.06)	1.9	
		17	473	1.4	(0.16)	7.9	1.2	(-0.06)	2.6	
		10	523	2.3	(0.16)	5.7	1.6	(-0.06)	4.7	
		6	548	2.2	(0.16)	4.1	1.8	(-0.06)	4.4	
		4	573	1.3	(0.16)	2.6	1.4	(-0.06)	3.1	
	-2-Propanol	19	423	1.8	(0.29)	14.0	1.5	(-0.02)	0.9	
		18	473	0.8	(0.29)	13.0	0.8	(-0.02)	1.1	
		8	523	4.1	(0.29)	10.4	3.1	(-0.02)	4.4	
		7	548	4.1	(0.29)	9.9	3.1	(-0.02)	4.3	
		2	573	0.8	(0.29)	2.6	1.0	(-0.02)	1.1	
	-Acetone	22	373	1.8	(0.25)	12.3	1.8	(0.02)	2.1	
		17	423	0.8	(0.25)	8.6	1.0	(0.02)	1.4	
		25	473	1.2	(0.25)	7.3	1.0	(0.02)	1.1	
		7	523	1.2	(0.25)	7.2	0.6	(0.02)	1.0	
	Methanol	-Acetone	14	373	1.0	(0.06)	1.9	1.5	(-0.01)	1.9
			15	423	1.3	(0.06)	3.1	1.1	(-0.01)	0.8
10			473	2.1	(0.06)	3.3	2.1	(-0.01)	2.2	
-Benzene		10	373	1.6	(0.28)	14.7	0.7	(0.14)	7.0	
		10	413	0.7	(0.28)	13.1	0.8	(0.14)	6.2	
		10	453	1.3	(0.28)	10.6	1.3	(0.14)	4.8	
		10	493	2.8	(0.28)	8.8	1.2	(0.14)	4.3	
Mean value		315		1.7		7.6	1.4		2.4	

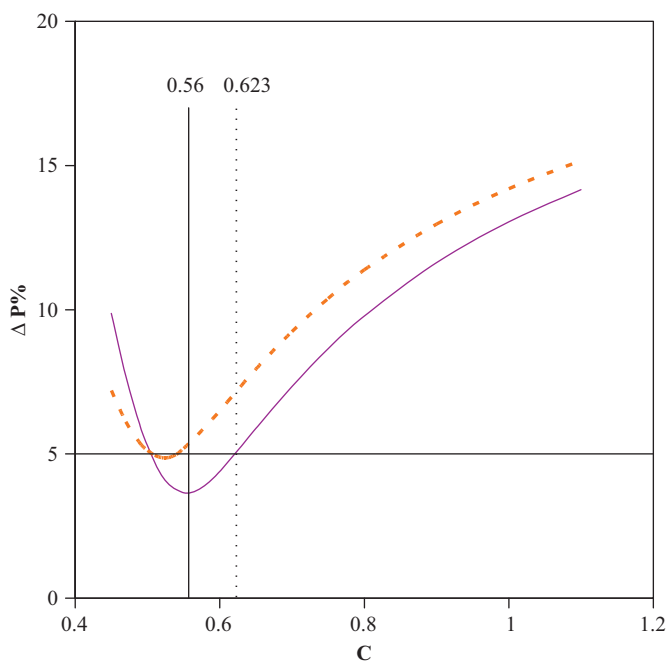


Fig. 3. Variation of the mean percent deviations $\Delta P\%$ on mixture bubble points calculated for polar-hydrocarbon systems of Table 4 with the UNIFAC model, versus the C reference state parameter: (---) infinite pressure and (—) GRS-CV reference states.

4. Conclusion

We proposed an alternative reference state, GRS-CV, based on the EoS/g^E approach. This mixing rule does not present the theoretical problems encountered with the literature reference

states, namely the simultaneous contributions, in the alpha function, of combinatorial terms derived from both the excess Gibbs energy model and the EoS. The attractive term a of the cubic EoS is estimated from the excess Helmholtz energy, A^{EV} , at constant volume; the reference volumes V^0 are expressed directly from the volume factors r of the g^E model and no more from the EoS co-volumes b . In this work, the proposed mixing rule was associated with the Peng–Robinson EoS and applied to the modeling of VLE for mixtures containing hydrocarbons and polar or associating compounds.

Highly size-asymmetric systems were predicted with the UNIFAC model. It was shown that the GRS-CV reference state successfully accounts for the chain length effect; contrary to the MHV1 approach, which was later improved according to the LCVM expression, the GRS-CV model does not need any further modification. The study of binary and ternary systems with polar and moderate size-asymmetric components was also performed with the UNIFAC model; all the considered reference states provide similar satisfactory predictions.

The use of excess Gibbs energy models depending or not on Flory–Huggins combinatorial terms was also studied with respect to the choice of reference states (MHV1, infinite pressure and GRS-CV). By considering the original and generalized NRTL models, it was observed that the GRS-CV always yields the best predictions.

It was underlined that the GRS-CV reference state can be associated with the Wong–Sandler mixing rule, since it does not depend on the co-volumes. We have shown that the proposed WS_{GRS-CV} mixing rule always allows very satisfactory predictions from low pressure parameters using zero k_{ij} values, which is not the case of the original WS method based on the infinite pressure.

On the whole, we have developed an alternative reference state which avoids the drawbacks of the other literature approaches. The proposed method improves the prediction of size-asymmetric systems, it can be associated with any kind of low pressure g^E model and appears to be a useful tool for VLE

calculations using the Wong–Sandler approach without fitting any k_{ij} parameter.

List of symbols

a	attractive term
A	Helmholtz free energy
b	co-volume
B	second virial coefficient
C	reference state parameter
g	molar Gibbs energy
G	Gibbs energy
k_{ij}	binary interaction parameter
m	parameter of the Soave function
n	mole number
P	pressure
q	molar surface area factor
Q_k	UNIFAC group surface area parameter
r	molar volume factor
R_k	UNIFAC group volume parameter
R	ideal gas constant
T	temperature
v	molar volume
V	volume
x	mole fraction
z	coordination number
Z	compressibility factor

Greek letters

α	alpha function
α_0	NRTL non randomness factor
γ	parameter of the Soave function
Γ_{ij}	NRTL binary interaction parameter
δ	LCVM and mGRS-CV correction parameters
Δu_{mn}	UNIFAC binary interaction parameter
η	packing fraction

Subscript

i	pure component property
∞	infinite pressure reference state

Superscript

0	property in the reference state
E	excess property at constant pressure
EV	excess property at constant volume
M	mixing property
comb	combinatorial property
res	residual property

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