The Soave, Twu and Boston–Mathias alpha functions in cubic equations of state. Part II. Modeling of thermodynamic properties of pure compounds

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ABSTRACT

Cubic equations of state (EoS) are commonly used for industrial applications, due to their simplicity in predicting pure compound and mixture thermodynamic properties in vapor and liquid phases. The accuracy of their predictions mainly depends on the choice of the attractive term $a(T)$ and numerous models were developed in literature for this purpose. Among them, the Soave and the Twu models have acquired a wide popularity, as well as the Boston–Mathias model commonly used for supercritical applications. However, most of the works concerned with the comparison of literature attractive terms only focuses on the representation of pure component saturation properties. In particular, the analysis of the respective influence of the EoS and the first and second derivatives of the alpha function on the modeling of enthalpies and heat capacities with respect to temperature and pressure, especially in the supercritical range, was never reported in literature. This is precisely the purpose of the present study.

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1. Introduction

Cubic equations of state (EoS) are commonly used for industrial applications, due to their simplicity in predicting pure compound and mixture thermodynamic properties in vapor and liquid phases. The accuracy of their predictions mainly depends on the choice of the attractive term $a(T)$ and numerous models were developed in literature for this purpose. Among them, the Soave [1] and the Twu et al. [2] models have acquired a wide popularity, as well as the Boston–Mathias [3] model commonly used for supercritical applications. However, most of the works concerned with the comparison of literature attractive terms [4,5] only focuses on the representation of pure component saturation properties, mainly vapor pressures and liquid heat capacities [6]. In particular, the analysis of the respective influence of the EoS and the first and second derivatives of the alpha function on the modeling of enthalpies and heat capacities with respect to temperature and pressure, especially in the supercritical range, was never reported in literature.

In the part I of this study [7], a theoretical analysis of the Soave, Twu and Boston–Mathias alpha functions associated with the Redlich–Kwong equation [8] was performed in a wide range of reduced temperatures; special attention was paid to the behaviour of the first and second derivatives, h_α and C_α, appearing, respectively in the expressions of the enthalpy and the constant-pressure heat capacity. For the Soave function, it was shown that, not only the well-known abnormal minimum of the alpha function occurs at high temperatures, always beyond the current domain of industrial applications, but also the h_α and C_α terms present consistent monotonous variations with increasing temperatures. Depending on the individual sets of L, M and N parameters, the Twu alpha function may or not present inflexion points leading to zero values of the second derivative C_α; but, for all the investigated sets of parameters, the first derivative h_α always presents inflexion points, providing inconsistent extrema of the C_α function for subcritical and supercritical conditions. Concerning the generalized Twu and Boston models, the different sets of parameters used below and above the critical temperature always allow continuous variations of the α function and its first derivative at the critical point; regarding the second derivative, both models lead to abnormal extrema of the C_α function for supercritical conditions and produce an inconsistent breakpoint at the critical temperature. However, in the case of the Twu model, the C_α function remains continuous at the critical point, whereas the Boston model exhibits a real strong discontinuity.

This second part deals with the modeling of saturation data and liquid enthalpies and heat capacities under pressure. An analysis of the influence of the various attractive terms with respect to

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temperature and pressure is performed for individual compounds, including hydrocarbons and polar substances.

2. Correlation of derived thermodynamic properties from the Redlich–Kwong equation

The calculation of thermodynamic properties of pure compounds is performed by using the Soave [1], Twu et al. [2] and Boston–Mathias [3] alpha functions associated with the Redlich–Kwong [8] EoS. In this framework, fugacity coefficients, required for the modeling of phase equilibria, and enthalpies and constant-pressure heat capacities are derived from the knowledge of the residual Helmholtz-free energy A^{res}:

$$
A^{\mathrm{res}} = A(T, V, n) - A^{\mathrm{ideal}}(T, V, n)
$$
$$
= -nRT \int_{\infty}^{V} (z-1) \frac{dV}{V}, \quad z = \frac{PV}{nRT} = \frac{Pv}{RT} \tag{1}
$$

where A and A^{ideal} are respectively the Helmholtz-free energies of n moles of the real fluid and of the ideal gas at temperature T and for the total volume V; z is the compressibility factor of the real fluid, expressed for the Redlich–Kwong EoS as:

$$
z = \frac{1}{1-\eta} - \frac{a(T)}{bRT} \frac{\eta}{(1+\eta)}, \quad \eta = \frac{b}{v} \tag{2}
$$

$a(T)$ and b are respectively the attractive term and the covolume defined from the alpha function $\alpha(T)$ and the critical properties according to:

$$
a(T) = a_c \alpha(T), \quad a_c = 0.42748023 \frac{R^2 T_c^2}{P_c}, \quad b = 0.08664035 \frac{RT_c}{P_c} \tag{3}
$$

From (Eqs. (1) and (2)), the expression of the residual Helmholtz-free energy A^{res} resulting from the use of the Redlich–Kwong equation is:

$$
\frac{A^{\mathrm{res}}}{nRT} = -Ln(1-\eta) - \frac{a(T)}{bRT} Ln(1+\eta) \tag{4}
$$

The derivative of A^{res} with respect to the mole number n provides the logarithm of the fugacity coefficient φ:

$$
\ln \varphi = -\ln z + \left(\frac{\partial (A^{\mathrm{res}}/RT)}{\partial n} \right)_{T,V}
$$
$$
= z - 1 - Ln\, z - Ln(1-\eta) - \frac{a(T)}{bRT} Ln(1+\eta) \tag{5}
$$

while the derivatives with respect to temperature lead successively to the molar residual enthalpy h^{res}:

$$
h^{\mathrm{res}} = h(T, V, n) - h^{\mathrm{ideal}}(T) = RT(z-1) + \left(\frac{\partial (A^{\mathrm{res}}/nT)}{\partial (1/T)} \right)_{V,n}
$$
$$
= RT(z-1) - \frac{1}{b} \left(\frac{d(a/T)}{d(1/T)} \right) Ln(1+\eta) \tag{6}
$$

and to the molar residual constant-pressure heat capacity C_P^{res}:

$$
C_P^{\mathrm{res}} = C_P(T, V, n) - C_P^{\mathrm{ideal}}(T) = - \left[T \left(\frac{\partial P}{\partial V} \right)^{-1} \left(\frac{\partial P}{\partial T} \right)^2 + R \right]
$$
$$
+ \frac{\partial}{\partial T} \left(\frac{\partial (A^{\mathrm{res}}/nT)}{\partial (1/T)} \right)_{V,n} \tag{7}
$$
$$
= - \left[T \left(\frac{\partial P}{\partial V} \right)^{-1} \left(\frac{\partial P}{\partial T} \right)^2 + R \right] - \frac{1}{b} \left[\frac{d}{dT} \left(\frac{d(a/T)}{d(1/T)} \right) \right] Ln(1+\eta)
$$

Hence, the modeling of thermodynamic properties, such as fugacity coefficients (Eq. (5)), enthalpies (Eq. (6)) or heat capacities (Eq. (7)), with respect to temperature and pressure, depends on the influence of the attractive functions weighted by $Ln(1+\eta)$, where η is the compacity (Eq. (2)) computed by means of the EoS.

The derivatives of the attractive term $a(T)$ occurring in the expressions of the residual enthalpy (Eq. (6)) and heat capacity (Eq. (7)) were defined as:

$$
h_a = \frac{d(a/T)}{d(1/T)}, \quad C_a = \frac{d}{dT} \left(\frac{d(a/T)}{d(1/T)} \right) = \frac{dh_a}{dT} \tag{8}
$$

They are correlated with the derivatives h_α and C_α of the alpha function $\alpha(T_r)$ analyzed in the first part of this study [7], as follows:

$$
h_a = a_c h_\alpha, \quad h_\alpha = \frac{d(\alpha/T_r)}{d(1/T_r)} \tag{9}
$$

$$
C_a = \frac{a_c}{T_c} C_\alpha, \quad C_\alpha = \frac{dh_\alpha}{dT_r} = -T_r \frac{d^2\alpha}{dT_r^2} \tag{10}
$$

The different literature alpha models considered in this work were divided into the following categories:

- The generalized versions, which only depend on the acentric factor ω; the corresponding expressions for the Soave (ω), Twu (ω) and Boston–Mathias (ω) functions are given in Table 1; for

Table 1
The Soave, Twu and Boston–Mathias alpha functions.

Soave	Twu	Boston-Mathias
$\alpha(T_r) = \left[1 + m\left(1 - T_r^\gamma\right) \right]^2,\ \gamma = 0.5$	$\alpha(T_r) = T_r^\delta\, exp\left[L\left(1 - T_r^\gamma\right)\right]$	For $T_r \leq 1$: α from Soave
	$\delta = N(M-1), \quad \gamma = NM$	For $T_r > 1$: $\alpha(T_r) = exp\left[c\left(1 - T_r^d\right)\right]$
• Soave(ω):	• Twu(ω):	• Boston-Mathias(ω):
$m = 0.480 + 1.574\omega - 0.176\omega^2$	$\alpha = \alpha^{(0)} + \omega\left(\alpha^{(1)} - \alpha^{(0)}\right)$	$d = 1 + m/2,\quad c = m/d$
	generalized L,M, N parameters (table 2)	with:
		$m = 0.480 + 1.574\omega - 0.176\omega^2$
• Soave(m):	• Twu(LMN):	
Individual component parameters (table 3)	Individual component parameters (table 3)	

Table 2
The generalized Twu (ω) parameters for subcritical and supercritical conditions.

Alpha parameters	$T_r \leq 1$		$T_r > 1$	
	$\alpha^{(0)}$	$\alpha^{(1)}$	$\alpha^{(0)}$	$\alpha^{(1)}$
L	0.141599	0.500315	0.441411	0.032580
M	0.919422	0.799457	6.500018	1.289098
N	2.496441	3.291790	−0.200000	−8.000000

the Twu et al. [9] model the generalized L, M and N parameters for subcritical and supercritical conditions are reported in Table 2.

- The Soave (m) and Twu (LMN) alpha terms, which make use of specific parameters estimated for individual components.

3. Results and discussion

The list of compounds studied in this work is reported in Table 3 together with the values of T_c, P_c and ω taken from Reid et al. [10]. The values of the L, M and N parameters are those reported by Twu et al. [9,11]; the m parameters were determined in this work by correlating experimental saturation pressure data by means of the Soave equation. The curves obtained for the attractive functions a/bRT, h_a/b and C_a/b (Eqs. (3) and (8)) with the different alpha models are illustrated in Figs. 1–3 for three selected compounds: methane and hexane, as representative of light and intermediate hydrocarbons, and methanol as a polar compound.

The first part of this study is devoted to the influence of the alpha functions on the modeling of subcritical properties, such as saturation pressures, vaporization enthalpies and saturated liquid heat capacities. It should be noticed that, in this domain, the Boston–Mathias (ω) model reduces to the Soave (ω) model, so that only four models were considered. The second part concerns the modeling of supercritical properties under pressure, namely residual enthalpies and heat capacities.

3.1. Saturation properties

Deviations between saturation pressures, enthalpies of vaporization and saturated liquid heat capacities obtained experimentally and calculated with the different alpha functions associated with the Redlich–Kwong EoS are reported, respectively in Tables 4–6. Results presented for the various hydrocarbons and polar compounds show that:

- For saturation pressures (Table 4), the Soave (ω) and Twu (ω) attractive functions lead to the same global deviations, with better results observed for light hydrocarbons with the Twu model and comparable deviations for polar compounds. Obviously, the versions with individual sets of m and L, M and N parameters provide more accurate estimations; the Twu (LMN) model is the most satisfactory, especially for polar components.

As illustrated in Fig. 1, all models lead to quite similar a/bRT curves in the subcritical region and since, at moderate pressures,
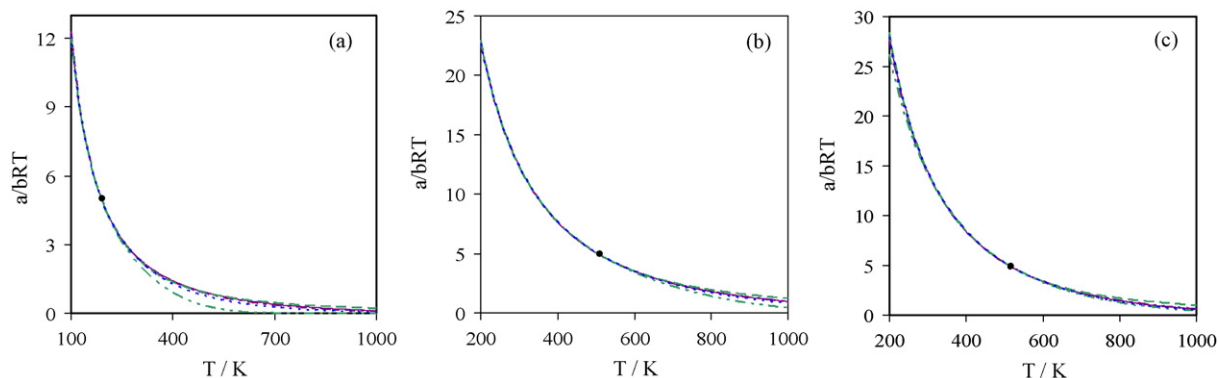
Table 3
Pure component parameters together with the m and L, M, N parameters used with the Soave (m) and Twu (LMN) functions for individual compounds.

Components	T_c (K)	P_c (bar)	ω	Individual component parameters				
				m	L	M	N	Ref
Methane	190.40	46.0	0.011	0.5036	0.106750	0.920161	3.09674	[9]
Pentane	469.70	33.7	0.251	0.8568	0.305259	0.835681	2.08969	[9]
Pentane	469.70	33.7	0.251		0.379229	0.841706	1.82331	[11]
Hexane	507.50	30.1	0.299	0.9298	0.128223	0.893666	4.88241	[9]
Hexane	507.50	30.1	0.299		0.158080	0.872819	3.84418	[11]
Heptane	540.30	27.4	0.349	1.0027	0.206521	0.852664	3.32097	[9]
Heptane	540.30	27.4	0.349		0.340339	0.844963	2.38332	[11]
Decane	617.70	21.2	0.489	1.2053	0.316547	0.828468	2.90395	[9]
Eicosane	767.00	11.1	0.907	1.7390	1.949590	1.180080	0.78281	[9]
Cyclohexane	553.50	40.7	0.212	0.8045	0.151079	0.865944	3.17613	[9]
Cyclohexane	553.50	40.7	0.212		0.245880	0.845046	2.25895	[11]
Benzene	562.20	48.9	0.212	0.8032	0.106109	0.890646	4.31730	[9]
Benzene	562.20	48.9	0.212		0.163664	0.860016	2.98498	[11]
Acetone	508.10	47.0	0.304	0.9304	0.479844	0.870627	1.79010	[11]
Methanol	512.60	80.9	0.556	1.2767	0.690551	0.911298	1.96941	[11]
Ethanol	513.90	61.4	0.644	1.4044	1.076460	0.964661	1.35369	[11]
Water	647.30	221.2	0.344	0.9542	0.413297	0.874988	2.19435	[11]

Fig. 1. Variations of the attractive term a/bRT with respect to temperature for (a) methane, (b) hexane and (c) methanol using the generalized models: (———) Soave (ω); (— — —) Twu (ω); (▪ ▪ ▪ ▪) Boston–Mathias (ω) and the versions with individual parameters: (—▪—▪—) Soave (m); (—·—·—) Twu (LMN); critical points are indicated by ●.
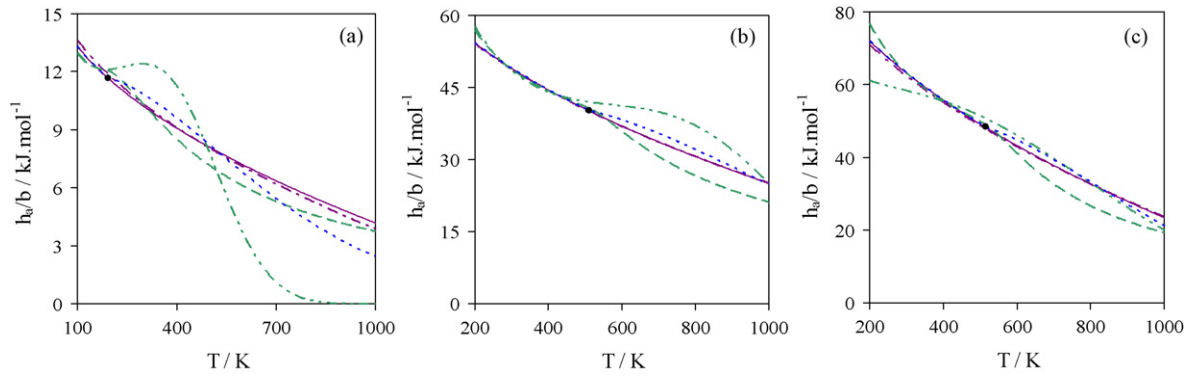
Fig. 2. Variations of the attractive term h_a/b with respect to temperature for (a) methane, (b) hexane and (c) methanol using the generalized models: (——) Soave (ω); (— —) Twu (ω); (■ ■ ■) Boston–Mathias (ω) and the versions with individual parameters: (—·—) Soave (m); (—··—) Twu (LMN); critical points are indicated by ●.
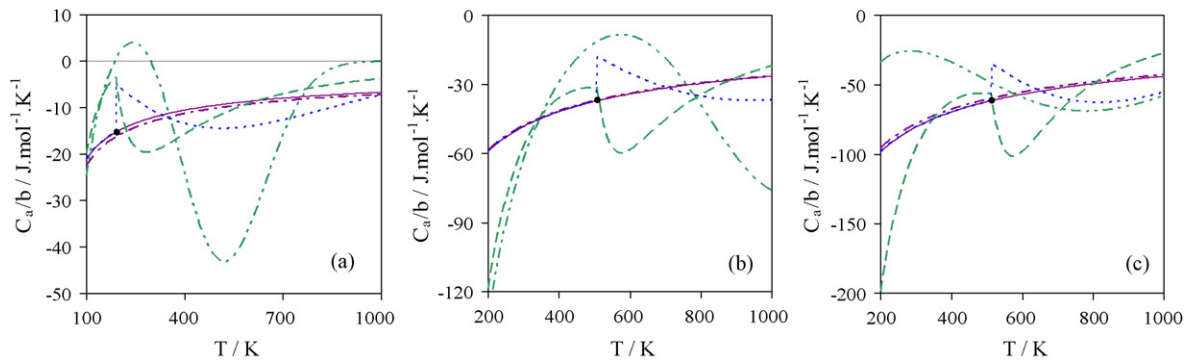

Fig. 3. Variations of the attractive term C_a/b with respect to temperature for (a) methane, (b) hexane and (c) methanol using the generalized models: (——) Soave (ω); (— —) Twu (ω); (■ ■ ■) Boston–Mathias (ω) and the versions with individual parameters: (—·—) Soave (m); (—··—) Twu (LMN); critical points are indicated by ●.

the factor $Ln(1+\eta)$ has a small variation according to pressure, they must provide rather similar estimations of saturation pressures. However, as can be observed in Fig. 1c for methanol, the Twu (LMN) model leads to a slightly different curve; this behaviour is in agreement with the deviation of 0.10% reported in Table 4 for this model instead of values superior to 4% with the other functions.

- Concerning the enthalpies of vaporization (Table 5), the generalized Soave (ω) and Twu (ω) models and the Soave (m) version give similar results for all components, with global deviations between 2.30 and 2.89%. The Twu (LMN) model still provides the best results with a global deviation of 1.46%.

This result is illustrated in Figs. 4 and 5 for methane, hexane and methanol; for each component, the residual enthalpies h^{res}

Table 4
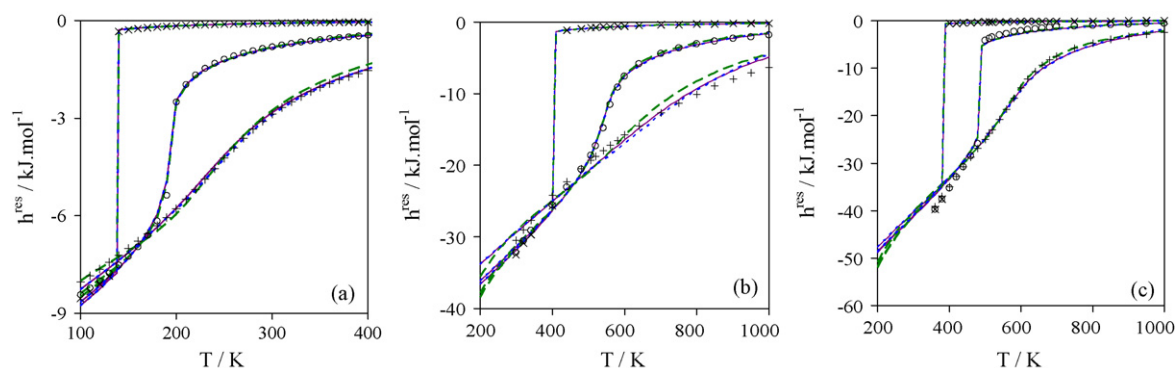Absolute percent deviations $D(P^{sat})$% on saturation pressures obtained with the various models.

Components	Data Ref.	T_{min} (K)–T_{max} (K)	N_p	Generalized models		Individual component parameters		
				Soave (ω)	Twu (ω)	Soave (m)	Twu (LMN)	Ref.
Methane	[12]	120–188	35	1.34	0.80	1.19	0.67	[9]
Pentane	[13,14]	208–310	22	1.82	0.75	0.49	2.02	[9]
Pentane	[13,14]	208–310	22				0.51	[11]
Hexane	[14,15]	286–342	24	1.19	0.10	0.22	0.52	[9]
Hexane	[14,15]	286–342	24				0.50	[11]
Heptane	[14,16]	299–372	40	1.15	0.25	0.37	0.50	[9]
Heptane	[14,16]	299–372	40				0.56	[11]
Decane	[14,17–20]	244–490	94	1.15	1.76	0.84	1.41	[9]
Eicosane	[18,20]	342–626	44	7.57	8.65	1.69	2.85	[9]
Cyclohexane	[14,21,22]	291–355	38	0.57	1.38	0.47	0.93	[9]
Cyclohexane	[14,21,22]	291–355	38				0.75	[11]
Benzene	[14,19,23,24]	286–383	86	0.98	0.99	0.65	0.37	[9]
Benzene	[14,19,23,24]	286–383	86				0.66	[11]
Acetone	[25–27]	241–351	48	2.76	2.04	1.87	0.37	[11]
Methanol	[28]	288–357	20	5.57	4.96	3.93	0.10	[11]
Ethanol	[28–31]	273–370	66	3.39	3.02	2.60	0.67	[11]
Water	[34,35]	273–643	89	14.36	14.43	4.18	0.41	[11]
Global			606	4.05	4.00	1.67	0.80	

$D(P^{sat}) \% = \frac{1}{N_p} \sum_i \left| \frac{P^{sat}_{exp} - P^{sat}_{cal}}{P^{sat}_{exp}} \right|_i$, N_p: number of experimental points.

Table 5
Absolute percent deviations $D(\Delta H^{vap})\%$ on vaporization enthalpies obtained with the various models.

Models	Data	T_{min} (K)–T_{max} (K)	$N_{\Delta H}$	Generalized		Individual component parameters		
				Soave (ω)	Twu (ω)	Soave (m)	Twu (LMN)	Ref
Methane	[33]	112–185	8	4.46	2.77	4.77	2.68	[9]
Pentane	[33]	260–428	24	1.68	1.16	1.18	1.65	[9]
Pentane	[33]	260–428	24				1.17	[11]
Hexane	[33,34]	183–493	54	2.01	1.99	1.68	2.33	[9]
Hexane	[33,34]	183–493	54				1.94	[11]
Heptane	[33]	298–371	9	1.21	0.77	0.85	0.52	[9]
Heptane	[33]	298–371	9				0.44	[11]
Decane	[33]	298–444	11	1.53	1.75	1.49	0.84	[9]
Eicosane	[34]	310–616	2	2.92	3.11	2.99	4.03	[9]
Cyclohexane	[33]	292–422	32	0.82	0.94	0.82	0.43	[9]
Cyclohexane	[33]	292–422	32				0.59	[11]
Benzene	[33]	293–478	50	1.00	0.98	0.95	0.54	[9]
Benzene	[33]	293–478	50				0.59	[11]
Acetone	[33]	293–345	8	5.53	4.97	4.86	4.10	[11]
Methanol	[33]	298–477	27	8.67	8.31	7.11	3.73	[11]
Ethanol	[33]	298–469	18	4.19	3.87	3.21	2.02	[11]
Water	[34]	273–633	25	5.11	5.69	2.66	2.09	[11]
Global			268	2.89	2.78	2.30	1.46	

$$D(\Delta H^{vap})\% = \frac{1}{N_{\Delta H}} \sum_i \left| \frac{\Delta H^{vap}_{exp} - \Delta H^{vap}_{cal}}{\Delta H^{vap}_{exp}} \right|_i, \quad N_{\Delta H}: \text{ number of experimental points.}$$

Fig. 4. Variations of the residual enthalpy h^{res} with respect to temperature for (a) methane, (b) hexane and (c) methanol using the generalized models: (——) Soave (ω); (— — —) Twu (ω); (▪ ▪ ▪) and Boston–Mathias (ω). Experimental data from literature [12,37,44] are reported at: (×) 5 bar, (○) 50 bar and (+) 250 bar (except for methane, 200 bar).

Table 6
Absolute percent deviations $D(C^{sat}_{pL})\%$ on saturated liquid heat capacities obtained with the various models.

Models	Data	T_{min} (K)–T_{max} (K)	N_{Cp}	Generalized		Individual component parameters		
				Soave (ω)	Twu (ω)	Soave (m)	Twu (LMN)	Ref.
Methane	[32]	115–187	9	28.29	31.00	28.40	30.03	[9]
Pentane	[36]	149–303	24	5.65	12.18	5.81	6.15	[9]
Pentane	[36]	149–303	24				1.38	[11]
Hexane	[37]	340–480	6	7.48	6.48	7.33	5.33	[9]
Hexane	[37]	340–480	6				5.35	[11]
Heptane	[38]	360–500	6	5.67	4.87	5.54	4.11	[9]
Heptane	[38]	360–500	6				1.38	[11]
Decane	[39,40]	247–460	41	5.48	14.03	5.44	12.08	[9]
Eicosane	[40]	320–400	9	2.83	4.46	3.16	7.01	[9]
Cyclohexane	[41]	340–540	8	12.73	12.07	12.68	12.70	[9]
Cyclohexane	[41]	340–540	8				12.68	[11]
Benzene	[40,42]	281–490	28	4.48	2.02	4.54	4.24	[9]
Benzene	[40,42]	281–490	28				2.12	[11]
Acetone	[43]	320–440	6	3.08	1.74	2.74	4.40	[11]
Methanol	[44]	360–480	7	16.88	14.17	15.44	13.39	[11]
Ethanol	[43]	360–500	7	21.16	19.23	20.37	17.56	[11]
Water	[35]	283–623	19	23.86	29.74	20.11	12.60	[11]
Global			170	9.91	13.04	9.42	8.14	

$$D(C^{sat}_{pL})\% = \frac{1}{N_{Cp}} \sum_i \left| \frac{C^{sat}_{pL,exp} - C^{sat}_{pL,cal}}{C^{sat}_{pL,exp}} \right|_i, \quad N_{Cp}: \text{ number of experimental points.}$$
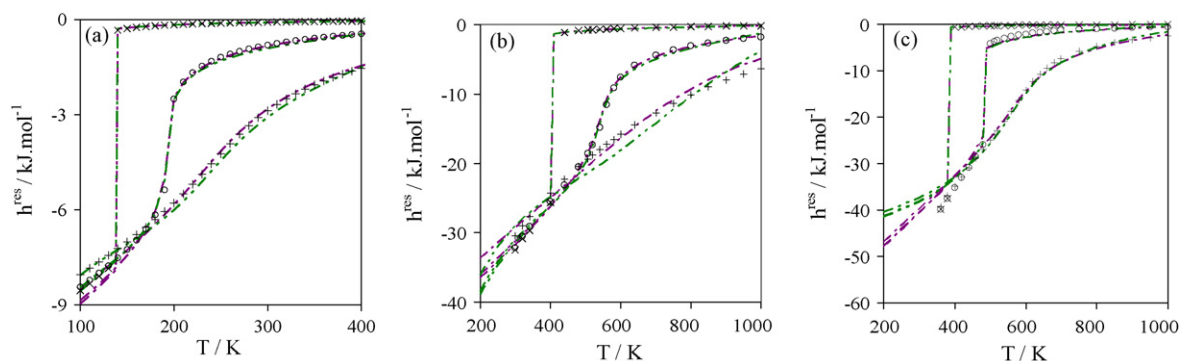
Fig. 5. Variations of the residual enthalpy h^{res} with respect to temperature for (a) methane, (b) hexane and (c) methanol using the models with individual parameters: (—·—) Soave (m) and (—···—) Twu (LMN). Experimental data from literature [12,37,44] are reported at: (×) 5 bar, (○) 50 bar and (+) 250 bar (except for methane, 200 bar).
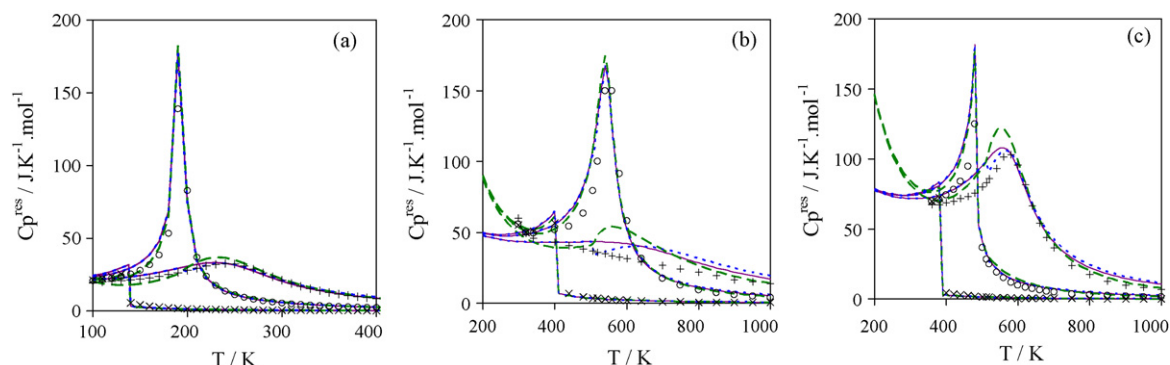

Fig. 6. Variations of the residual constant-pressure heat capacity C_P^{res} with respect to temperature for (a) methane, (b) hexane and (c) methanol using the generalized models: (——) Soave (ω); (——) Twu (ω) and (····) Boston–Mathias (ω). Experimental data from literature [12,37,44] are reported at: (×) 5 bar, (○) 50 bar and (+) 250 bar (except for methane, 200 bar).

(Eq. (6)) calculated at various pressures from the Soave (ω), Twu (ω), Soave (m) and Twu (LMN) models are plotted with respect to temperature and compared with literature data. At the subcritical pressure, $P^\circ = 5$ bar, these curves allow both locating the boiling temperature and the order of magnitude of the corresponding enthalpies of vaporization ΔH^{vap}. We can observe, especially in Figs. 4c and 5c for methanol, that the Twu (LMN) model exhibits a different behaviour, which is in agreement with the deviations on the enthalpies of vaporization reported in Table 5 for this component: 3.73% with the Twu (LMN) model, instead of more than 7% with the other models.

It must also be noticed, especially in Fig. 5c, that at the sub-critical pressure, the largest deviations between the different models are observed at temperatures much below the corresponding boiling point; in particular, in that domain, the Soave and Twu curves show visible different variations with respect to temperature. These behaviours can be explained by recalling that the calculation of residual enthalpies h^{res} depends on both the attractive term a/bRT and the first derivative h_a/b; and as is shown in Fig. 2, and more specially in Fig. 2c for methanol, the Soave and Twu models lead to different curves at the lowest temperatures.
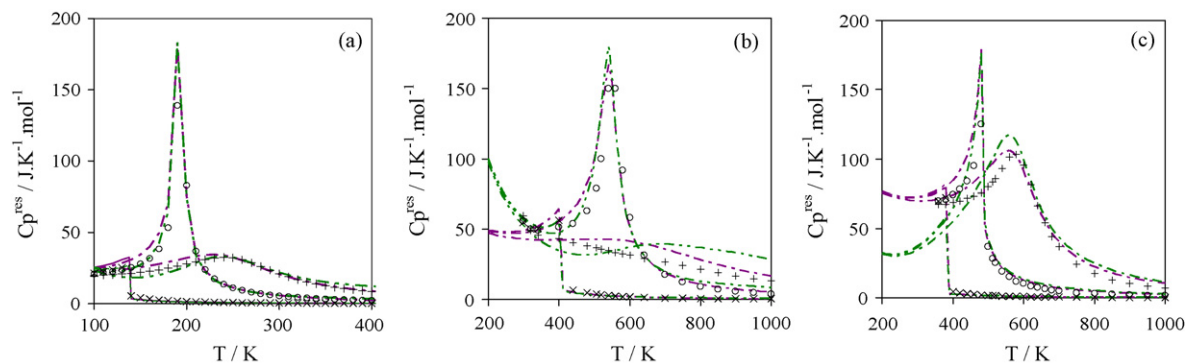

Fig. 7. Variations of the residual constant-pressure heat capacity C_P^{res} with respect to temperature for (a) methane, (b) hexane and (c) methanol using the models with individual parameters: (—·—) Soave (m) and (—···—) Twu (LMN). Experimental data from literature [12,37,44] are reported at: (×) 5 bar, (○) 50 bar and (+) 250 bar (except for methane, 200 bar).

- Concerning the saturated liquid heat capacities, Table 6 shows that, contrary to results for saturation pressures and enthalpies of vaporization, comparable estimations of C_{pL}^{sat} are obtained with the different models; in particular, the Twu (LMN) model with three specific parameters no longer provides smaller deviations for polar compounds.

The similar results observed on saturated heat capacities appear in complete disagreement with the wide variety of C_a/b and C_P^{res} (Eq. (7)) curves plotted in Figs. 3, 6 and 7. However, this apparent discrepancy can be explained as follows:

- At saturation conditions, for instance at 380 K for $P^\circ = 5$ bar for methanol, Figs. 6c and 7c show that the residual liquid heat capacities estimated from the Soave and Twu models are between 82 and 59 J K^{-1} mol^{-1}; with an experimental value of C_{pL}^{res} about 72 J K^{-1} mol^{-1} the two models lead to average deviations $D(C_{pL}^{res})\%$ between 14 and 18%. Since, at this temperature, the ideal heat capacity C_p^{ideal} of methanol is 53 J K^{-1} mol^{-1}, the corresponding average deviations $D(C_{pL}^{sat})\%$ are about 8–10%, which is in agreement with the order of magnitude of results reported in Table 6.
- But, if at the same pressure $P^\circ = 5$ bar, we consider the variations of residual heat capacities at temperatures much below the saturation conditions, for instance at 200 K, the C_{pL}^{res} values obtained with the different models are completely different, since they range (Figs. 6c and 7c) between 32 and 150 J K^{-1} mol^{-1}; thus, with experimental values of C_{pL}^{res} and C_p^{ideal}, respectively about

62 and 38 J K^{-1} mol^{-1} at this temperature, the deviations $D(C_{pL})\%$ obtained with the two models are scattered between 30 and 90%.

Hence, two different models, such as the Soave and Twu functions, which exhibit completely different behaviours with respect to pressure and temperature, may provide similar estimations of saturation properties. For this reason, as was already mentioned in a previous study [7], we maintain that a comparison between attractive terms $a(T)$ only based on saturation properties is a meaningless test of the capabilities of the considered models.

However, the representation of saturation properties still remains a crucial objective for chemical engineering processes. As was pointed out previously (Tables 4 and 5), the Twu (LMN) model with three adjustable parameters provides highly superior calculations of P^{sat} and ΔH^{vap} for polar compounds. Nevertheless, the Soave model can be improved in the same way by using only two adjustable parameters, γ and m, in the $\alpha(T_r)$ function (Table 1); this model called Soave (γ, m) is compared with the Soave (m) and Twu (LMN) equations in Fig. 8 for methanol.

3.2. Residual properties under pressure

This section deals with the modeling of supercritical properties under pressure, namely residual enthalpies and constant-pressure heat capacities. In that part, the Boston–Mathias (ω) function differs from the Soave (ω) equation, so that five models are considered. The
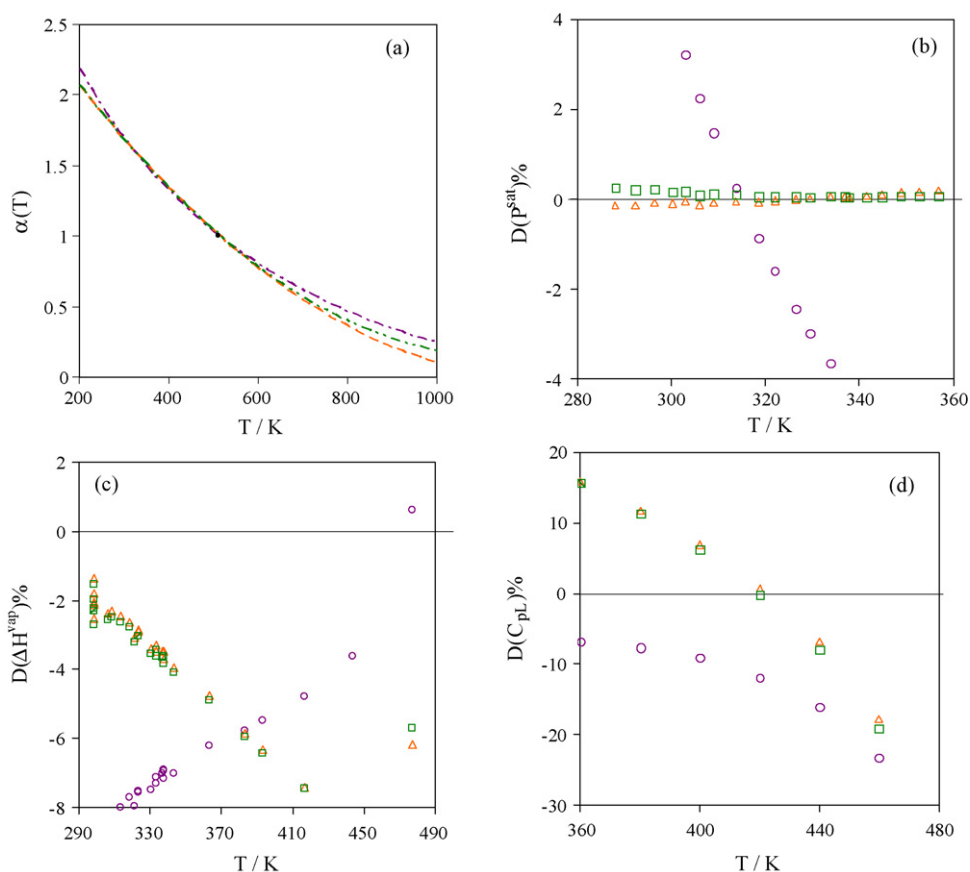

Fig. 8. Influence of specific parameters on the modeling of methanol properties: (━ · ━) (○) Soave ($m = 1.2767$); (━ ━) (△) Soave ($\gamma = 1$, $m = 0.7157$) and (━ ·· ━) (□) Twu (LMN) together with experimental data [28,33,44]. (a) Alpha function $\alpha(T)$, (b) saturation pressure deviations $D(P^{sat})\%$, (c) vaporization enthalpy deviations $D(\Delta H^{vap})\%$ and (d) saturated liquid heat capacity deviations $D(C_{pL}^{sat})\%$.

variations of h^{res} and C_P^{res} in a wide temperature range are illustrated in Figs. 4–7 for three different pressures.

- The calculation of the residual enthalpies h^{res}, illustrated in Figs. 4 and 5, mainly depends on the behaviour of the h_a/b curves given in Fig. 2 for the various models. As can be observed, and as was already pointed out in part I of this study [7], the Soave (ω) and Soave (m) functions present consistent monotonous variations with increasing temperatures; on the contrary, the Twu (ω), Twu (LMN) and Boston–Mathias (ω) models introduce inconsistent inflexion points at supercritical conditions. The effect of these undesirable accidents is particularly visible for hexane in Figs. 4b and 5b at the highest pressure and, to a lesser extent, for the two other components. Indeed, at this pressure, the factor $Ln(1 + \eta)$ in (Eq. (6)) has its maximum value; its rapid decrease with decreasing pressures (about one third at $P° = 50$ bar) weakens the influence of the inflexion points at lower pressures. In a general way, the various models allow satisfactory predictions of residual enthalpies; the worst results are obtained with the Twu (ω) and Twu (LMN) models.
- The estimation of residual constant-pressure heat capacities C_P^{res} mainly relies on the behaviour of the attractive functions C_a/b presented in Fig. 3. As previously analyzed [7], the inflexion points introduced by the Twu (ω), Twu (LMN) and Boston–Mathias (ω) models in the h_a/b function are responsible for the inconsistent extrema observed in the C_a/b curves (Fig. 3); in addition, for the Twu (ω) and Boston–Mathias (ω) models, the use of different sets of parameters below and above the critical temperature leads to unrealistic breakpoints at the critical point; consequently, at high pressures and in a wide temperature range around the critical point, the behaviour of these two models is totally unsatisfactory. Even if, in a general way, the constant-pressure heat capacity predictions are rather poor, the Soave (ω) and Soave (m) versions appear to provide the most consistent results.

4. Conclusion

The objective of this work was to check the influence of the Soave, Twu et al. and Boston–Mathias alpha functions on the modeling of pure compound thermodynamic properties by means of the Redlich–Kwong equation of state. For this purpose, the generalized versions of these models, which depend only on the knowledge of the acentric factor, were compared with the versions requiring individual sets of parameters determined from experimental data.

As was evidenced in this work, a consistent comparison between attractive functions cannot rely only on the analysis of saturation conditions. For this purpose, the study of predicted saturated properties was coupled with the analysis of residual enthalpies h^{res} and constant-pressure heat capacities C_P^{res}; indeed, as was already discussed [7], these functions evidence the strengths and weaknesses of the alpha functions and their derivatives with respect to temperature; moreover, at supercritical temperatures, the range of high pressures reinforces the influence of the first and second derivatives h_a/b and C_a/b on the behaviour of the residual properties. For saturation conditions, almost similar predictions of saturation pressures, enthalpies of vaporization and liquid heat capacities were provided by all the generalized alpha functions; better results were obtained for polar compounds with the Twu et al. model, but using the three L, M, N parameters fitted on experimental data; however, it was also shown that similar results could be obtained with the Soave model by fitting only two individual parameters. At supercritical conditions under high pressures, the various models give satisfactory predictions of residual enthalpies and rather poor estimations of heat capacities. For all these properties, the Soave model, even in its

generalized version, leads, in the range of industrial applications, to the most consistent behaviour of the attractive terms with respect to temperature and pressure. In particular, it avoids the undesirable and unrealistic inflexion points and breakpoints presented by the Twu et al. and Boston–Mathias models; as it was demonstrated previously [7], these defects are inherent to the complexity of the corresponding alpha functions and the change of modeling introduced by the generalized models at the critical point.

For its simplicity and the consistency of its predictions with respect to temperature, there is no objective reason to reject the Soave model. All trials to avoid the abnormal extrema of the Soave alpha function, even if occurring far beyond the range of practical applications, always led to more and more complex expressions which revealed, at the end, to have more defaults than the original equation.

List of symbols

a	attractive term
A	Helmholtz-free energy
b	covolume
c, d	parameters of the Boston–Mathias alpha function
C_p	constant-pressure heat capacity
C_a	second derivative of the attractive term occurring in the heat capacity
C_α	second derivative of the alpha term occurring in the heat capacity
h	enthalpy
h_a	first derivative of the attractive term occurring in the enthalpy
h_α	first derivative of the alpha term occurring in the enthalpy
L, M, N	parameters of the Twu alpha function
m	parameter of the Soave alpha function
n	mole number
N	number of experimental data
P	pressure
R	ideal gas constant
T	absolute temperature
V	volume
ν	molar volume
z	compressibility factor

Greek letters

α	alpha function
η	compacity
φ	fugacity coefficient
ω	acentric factor

Superscript

ideal	ideal gas property
res	residual property
sat	saturation property
vap	vaporization property

Subscript

c	critical property
r	reduced property

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