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Development of a New Alpha Function for the Peng–Robinson Equation of State: Comparative Study of Alpha Function Models for Pure Gases (Natural Gas Components) and Water-Gas Systems

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Numerous modifications have been suggested for the temperature dependence of the attractive term of the Peng–Robinson equation of state (PR-EOS), through the alpha function. In this work, a new alpha function combining both exponential and polynomial forms is proposed. Pure-compound vapor pressures for different molecular species were fitted and compared using different alpha functions including the Mathias–Copeman and Trebble–Bishnoi alpha functions. The new alpha function allows significant improvements of pure compound vapor pressure predictions (about 1.2% absolute average percent deviations) for all the systems considered, starting from a reduced temperature of 0.4. In addition, a generalization of the classical Mathias–Copeman alpha function was proposed as a function of the acentric factor. These alpha functions were used for VLE calculations on water + various gases including gaseous hydrocarbons. A general procedure is presented to fit experimental VLE data. The corresponding thermodynamic approach is based on the Peng–Robinson equation of state with the above cited alpha functions. It includes the classical mixing rules for the vapor phase and a Henry's law approach to treat the aqueous phase.

KEY WORDS: alpha function; hydrocarbons; modeling; natural gas compounds; pure compound; water-gas mixtures.

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1. INTRODUCTION

The prediction of thermodynamic properties and particularly phase equilibrium of mixtures depends strongly on pure compound calculations. In fact, the accuracy of calculations is clearly not only dependent on the choice of an equation of state or mixing rules but also on sufficiently accurate representations of pure compound vapor pressures. The capacity to correlate phase equilibria is then directly related to the adequate choice of an alpha function.

Many alpha functions have been proposed to improve the precision of cubic equations of state via a more accurate prediction of pure compound vapor pressures. Some selected alpha functions are shown in Table I. Generally, the mathematical expressions of alpha functions are either polynomials of various order in reduced temperature or exponential functions or switching functions. It is well established that alpha functions do not always represent accurately supercritical behavior, and they could have a limited temperature utilization range. To improve their potential, different approaches have been developed: use of alpha functions with specific compound parameters or switching alpha functions.

Generalized alpha functions are preferably used because of their predictive ability through a reduced number of parameters. In this work, the capacity of three alpha functions have been compared: a new proposed form [this work], a generalized Trebble–Bishnoi (TB) alpha function from Daridon et al. [6], and a generalized Mathias–Copeman (MC) [5] alpha function [this work] for particular cases involving natural gas compounds, i.e., light hydrocarbons (methane, ethane, propane, butane, pentane), water, carbon dioxide, nitrogen, and hydrogen sulfide.

The vapor pressures of 22 pure compounds have been used to develop and generalize our new alpha function associated with the Peng–Robinson equation of state (PR EoS) [3]. Water-gas mixture calculations with these generalized alpha functions have been performed using the PR EoS, the classical mixing rules, and a Henry's law approach to estimate compositions in the aqueous phase.

2. THEORY

Up to now, a large number of equations of state have been proposed to predict thermodynamic properties of pure compounds and mixtures. In this work, the PR EoS [3] was selected because of its simplicity and its widespread utilization in chemical engineering. Moreover, this EoS gives better results for the VLE of polar mixtures than the Soave–Redlich–

Table I. Temperature Dependence of Alpha Functions and Generalization

Alpha Functions	Generalization	
Soave [1] $\alpha(T_R)=[1+m(1-T_R^{1/2})]^2$	For SRK Eos $m=0.480+1.574\omega-0.175\omega^2$	Soave [1]
	For SRK EoS $m=0.47830+1.6337\omega-0.3170\omega^2+0.760\omega^3$	Soave [2]
	For PR EoS $m=0.374640+1.542260\omega-0.26992\omega^2$	Peng and Robinson [3]
	$m=c_0+c_1(1+T_R^{0.5})(0.7-T_R)$ with $c_0=0.378893+1.4897153\omega-0.17131848\omega^2+0.0196554\omega^3$ and c_1 is an adjustable parameter	Stryjek and Vera [4]
	$m=0.480+1.574\omega-0.175\omega^2$	
Mathias and Copeman [5] $\alpha(T_R)=[1+c_1(1-T_R^{1/2})+c_2(1-T_R^{1/2})^2+c_3(1-T_R^{1/2})^3]^2$ if $T<T_c$ $\alpha(T_R)=[1+c_1(1-T_R^{1/2})]^2$ if $T>T_c$		
Trebble and Bishnoi [10] $\alpha(T_R)=\exp[m\times(1-T_r)]$	$m=0.418+1.58\omega-0.580\omega^2$ when $\omega<0.4$ $m=0.212+2.2\omega-0.831\omega^2$ when $\omega\geqslant 0.4$	Daridon et al. [6]
Twu et al. [7, 8] $\alpha(T_R)=\alpha^{(0)}(T_R)+\omega(\alpha^{(1)}(T_R)-\alpha^{(0)}(T_R))$ with $\alpha^{(i)}(T_R)=T_R^{N(M-1)}[\exp(L(1-T_R^{NM}))]$		Twu et al. [7, 8]

	$T_R\leqslant 1$		$T_R>1$	
Parameters	$\alpha^{(0)}(T_R)$	$\alpha^{(1)}(T_R)$	$\alpha^{(0)}(T_R)$	$\alpha^{(1)}(T_R)$
		For SRK Eos		
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
		For PR EoS		
L	0.125283	0.511614	0.401219	0.024955
M	0.911807	0.784054	4.963075	1.248088
N	1.948153	2.812522	−0.20000	−8.00000

Kwong equation of state [1] (SRK EoS) and provides reliable calculations of the molar liquid volume. Its formulation is

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

in which

$$b = 0.07780\,\frac{RT_\mathrm{c}}{P_\mathrm{c}} \tag{2}$$

and

$$a(T) = a_\mathrm{c}\alpha(T_r) \tag{3}$$

where

$$a_\mathrm{c} = 0.45724\,\frac{(RT_\mathrm{c})^2}{P_\mathrm{c}} \tag{4}$$

To have accurate representations of vapor pressures of pure compounds, a temperature dependence of the attractive term is imposed through alpha functions. These functions must satisfy some requirements:

- they must be finite and positive at all temperatures;
- they must be equal to 1 at the critical point;
- they must tend to zero when T tends to infinity;
- they must be continuous as are their first and second derivatives (for $T > 0$), to assure continuity in thermodynamic properties.

Different mathematical expressions satisfy these requirements. Historically, Redlich and Kwong [9] were the first to propose a temperature dependence of the attractive parameter through an alpha function,

$$\alpha(T) = \frac{1}{\sqrt{T}} \tag{5}$$

Classically, the alpha function expressions are exponential expressions or quadratic expressions.

The Trebble–Bishnoi (TB) [10] alpha function is one of the examples of exponential expressions selected in this study:

$$\alpha(T) = \exp\left[m\left(1-\frac{T}{T_\mathrm{c}}\right)\right] \tag{6}$$

Different quadratic forms have been proposed:

- the Soave alpha function with one adjustable parameter [1],

$$\alpha(T)=\left[1+m\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{7}$$

- the Mathias–Copeman (MC) alpha function with three adjustable parameters [5]

$$\alpha(T)=\left[1+c_1\left(1-\sqrt{\frac{T}{T_c}}\right)+c_2\left(1-\sqrt{\frac{T}{T_c}}\right)^2+c_3\left(1-\sqrt{\frac{T}{T_c}}\right)^3\right]^2$$
$$\text{if}\quad T<T_c \tag{8}$$

otherwise,

$$\alpha(T)=\left[1+c_1\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{9}$$

c_1, c_2, and c_3 are three adjustable parameters.

In this work, a combination, Eq. (10), of both mathematical expressions is proposed. The resulting new alpha function satisfies every requirement. This alpha function combines the advantages of the two alpha functions (TB and MC),

$$\alpha(T)=\exp\left[c_1\left(1-\frac{T}{T_c}\right)\right]\left[1+c_2\left(1-\sqrt{\frac{T}{T_c}}\right)^2+c_3\left(1-\sqrt{\frac{T}{T_c}}\right)^3\right]^2 \tag{10}$$

If $T>T_c$, an exponential form is chosen similar to the Trebble–Bishnoi expression, Eq. (6), and the single parameter m of this expression must conform with Eq. (11),

$$m=-\left(\frac{\partial\alpha}{\partial T_R}\right)_{T_R=1}=c_1 \tag{11}$$

$$\alpha(T)=\exp\left[c_1\left(1-\frac{T}{T_c}\right)\right] \tag{12}$$

3. PURE COMPOUND VAPOR PRESSURES

The quality of the representation using the various alpha functions has been tested on the vapor pressures of 22 selected compounds. The critical coordinates and the vapor pressure correlations necessary for the preceding step are taken from "The Properties of Gases and Liquids" [11] (Table II) and DIPPR® Version 11.0, respectively.

3.1. Mathias–Copeman Alpha Function

The three adjustable parameters, c_1, c_2, and c_3 of the MC alpha function were evaluated from a reduced temperature of 0.4 up to 1 using a modified Simplex algorithm [12] for the 22 selected compounds. The objective function is

$$F = \frac{100}{N} \sum_{1}^{N} \left(\frac{P_{\text{cor}} - P_{\text{cal}}}{P_{\text{cor}}} \right)^2 \tag{13}$$

where N is the number of generated data points using the correlation, N is typically between 50 and 100, P_{cor} is the calculated pressure from the DIPPR® correlation, and P_{cal} is the calculated pressure.

The adjusted parameter values for each compound are reported in Table II for both the SRK EoS and the PR EoS. For each equation of state, it appears that these three MC adjusted parameters of the 22 pure compounds can be correlated as a function of the acentric factor, Eqs. (14)–(19). The equations are as follows:

For the SRK EoS,

$$c_1 = -0.1094\omega^2 + 1.6054\omega + 0.5178 \tag{14}$$

$$c_2 = -0.4291\omega + 0.3279 \tag{15}$$

$$c_3 = 1.3506\omega + 0.4866 \tag{16}$$

For the PR EoS,

$$c_1 = 0.1316\omega^2 + 1.4031\omega + 0.3906 \tag{17}$$

$$c_2 = -1.3127\omega^2 + 0.3015\omega - 0.1213 \tag{18}$$

$$c_3 = 0.7661\omega + 0.3041 \tag{19}$$

This MC generalized alpha function associated with the SRK EoS represents pure compound vapor pressures with an overall AAD of 1.4% (0.4% bias) compared to 3.4% AAD (2.7% bias) with the classical generalized Soave alpha function [2] (Table III). Improvements of the MC alpha functions with respect to the Soave alpha function are generally significant for each of the 22 compounds.

Table II. Adjusted Mathias–Copeman Alpha Parameters for the SRK EoS and PR EoS from DIPPR® Correlations

Component	P_c (Pa) [11]	T_c (K) [11]	ω [11]	c_1 (SRK)	c_2 (SRK)	c_3 (SRK)	c_1 (PR)	c_2 (PR)	c_3 (PR)
Hydrogen	1296960	33.19	−0.2160	0.161	−0.225	−0.232	0.095	−0.275	−0.029
Methane	4600155	190.56	0.0110	0.549	−0.409	0.603	0.416	−0.173	0.348
Oxygen	50804356	154.58	0.0222	0.545	−0.235	0.292	0.413	−0.017	0.092
Nitrogen	3394388	126.20	0.0377	0.584	−0.396	0.736	0.448	−0.157	0.469
Ethylene	5041628	282.35	0.0865	0.652	−0.315	0.563	0.512	−0.087	0.349
Hydrogen sulfide	8936865	373.53	0.0942	0.641	−0.183	0.513	0.507	0.008	0.342
Ethane	4883865	305.32	0.0995	0.711	−0.573	0.894	0.531	−0.062	0.214
Propane	4245518	369.95	0.1523	0.775	−0.476	0.815	0.600	−0.006	0.174
Isobutane	3639594	408.80	0.1808	0.807	−0.432	0.910	0.652	−0.149	0.599
n-Butane	3799688	425.15	0.2002	0.823	−0.267	0.402	0.677	−0.081	0.299
Cyclohexane	4073002	553.58	0.2096	0.860	−0.566	1.375	0.684	−0.089	0.549
Benzene	4895001	562.05	0.2103	0.840	−0.389	0.917	0.701	−0.252	0.976
Carbon dioxyde	7377000	304.21	0.2236	0.867	−0.674	2.471	0.705	−0.315	1.890
Isopentane	3381003	460.43	0.2275	0.876	−0.386	0.660	0.724	−0.166	0.515
Pentane	3369056	469.70	0.2515	0.901	−0.305	0.542	0.763	−0.224	0.669
Ammonia	11287600	405.65	0.2526	0.916	−0.369	0.417	0.748	−0.025	0.001
Toluene	4107999	591.75	0.2640	0.923	−0.301	0.494	0.762	−0.042	0.271
Hexane	3014419	507.40	0.3013	1.005	−0.591	1.203	0.870	−0.588	1.504
Acetone	4701004	508.20	0.3065	0.993	−0.322	0.265	0.821	0.006	−0.090
Water	22055007	647.13	0.3449	1.095	−0.678	0.700	0.919	−0.332	0.317
Heptane	2740000	540.20	0.3495	1.036	−0.258	0.488	0.878	−0.031	0.302
Octane	2490001	568.70	0.3996	1.150	−0.587	1.096	0.958	−0.134	0.487

Table III. Comparison of Pure Component Vapor Pressures using the SRK EoS

	Generalized MC Alpha Function[a]		Generalized Soave Alpha Function [2]	
Component	Bias (%)	AAD (%)	Bias (%)	AAD (%)
Hydrogen	5.31	5.31	1.14	4.12
Methane	−0.23	0.33	−0.06	1.54
Oxygen	−1.51	1.51	1.06	2.07
Nitrogen	−0.12	0.26	0.81	1.43
Ethylene	−1.67	1.67	0.61	1.34
Hydrogen sulfide	−0.83	1.53	1.79	1.79
Ethane	−0.59	0.68	1.55	2.48
Propane	−0.64	0.76	2.1	2.55
Isobutane	−0.07	1.66	1.39	1.54
n-Butane	−0.27	0.47	0.52	1.76
Cyclohexane	−0.44	0.84	2.42	2.45
Benzene	−1.22	1.31	1.43	1.93
Carbon dioxyde	0.63	0.63	0.74	0.82
Isopentane	−0.07	0.32	3	3.58
Pentane	−0.02	0.31	3.4	3.92
Ammonia	1.92	1.92	3.24	3.62
Toluene	−0.2	0.41	1.46	2.35
Hexane	−0.22	0.96	2.62	3.72
Acetone	2.35	2.4	7.26	7.35
Water	4.3	5.22	9.16	9.8
Heptane	1.03	1.09	6.9	6.99
Octane	1.3	1.64	6.68	7.04
Overall	0.4	1.42	2.69	3.37

[a] This work, Eqs. (14)–(16).

If the PR EoS is used instead of the SRK EoS, the generalized MC alpha function represents pure compound vapor pressures with an overall AAD of 1.2% (0.5% bias) compared to 2.1% AAD (−1.2% bias) through the generalized PR alpha function [3] (Table IV). However this generalization leads to poor results especially for water for which c_1 is not well represented by the correlation, Fig. 1.

To get good representations especially for water, polar compounds, and natural gas compounds, the number of compounds has been reduced from 22 to 8; i.e., the previously adjusted (c_1, c_2, and c_3) MC parameters (see Table II) have been correlated to the acentric factor ω for only methane to pentane, water, hydrogen sulfide, and nitrogen, Fig. 2. The new corresponding relationships obtained for the PR EoS are the following:

Table IV. Comparison of Pure Component Vapor Pressures using the PR EoS

	Generalized PR Alpha Function [3]		Generalized MC Alpha Function[a]		Generalized New Alpha Function[b]	
Component	Bias (%)	AAD (%)	Bias (%)	AAD (%)	Bias (%)	AAD (%)
Hydrogen	0.77	3.73	3.01	3.01	1.23	1.23
Methane	−0.70	0.70	0.15	0.48	0.03	0.39
Oxygen	−1.77	1.77	0.14	0.46	−0.16	0.30
Nitrogen	−0.88	0.88	−0.30	0.30	−0.32	0.32
Ethylene	−2.26	2.26	−0.55	0.55	−0.48	0.48
Hydrogen sulfide	−1.14	1.54	−0.75	1.15	−0.65	1.02
Ethane	−1.41	1.41	0.26	0.66	0.36	0.72
Propane	−2.14	2.25	−0.22	0.53	−0.05	0.46
Isobutane	−3.83	3.96	−1.50	1.50	−1.38	1.40
n-Butane	−1.66	1.79	0.53	0.98	0.53	0.98
Cyclohexane	−1.52	1.72	−1.09	1.13	−1.04	1.08
Benzene	−0.71	1.19	−0.40	0.68	−0.34	0.57
Carbon dioxyde	0.69	0.69	0.57	0.57	0.51	0.51
Isopentane	−1.78	1.93	0.54	0.82	0.42	0.77
Pentane	−2.35	2.49	0.30	0.59	−0.05	0.32
Ammonia	0.70	0.70	1.34	1.36	1.23	1.31
Toluene	−1.92	2.11	0.25	0.51	−0.15	0.32
Hexane	−3.69	3.92	−0.83	1.38	−1.81	2.10
Acetone	1.22	1.22	3.15	3.15	2.39	2.39
Water	***3.30***	***4.28***	***5.27***	***6.00***	***4.07***	***4.95***
Heptane	−3.16	3.33	0.07	0.49	−1.87	2.11
Octane	−2.41	2.42	0.35	0.56	−2.22	2.44
Overall	−1.21	2.11	0.47	1.22	0.01	1.19

[a] This work, Eqs. (17)–(19).
[b] This work, Eqs. (23)–(25).

$$c_1 = 1.0113\omega^2 + 1.1538\omega + 0.4021 \tag{20}$$

$$c_2 = -7.7867\omega^2 + 2.2590\omega - 0.2011 \tag{21}$$

$$c_3 = 2.8127\omega^2 - 1.0040\omega + 0.3964 \tag{22}$$

This more specific generalized alpha function represents water vapor pressures with an AAD of 0.4% (0.3% bias) compared to 6% AAD (5.3% bias) with the first generalization, Eqs. (17)–(19). Vapor pressures of carbon dioxide (one of the gases often present in natural gas) were also calculated using this MC generalized alpha function and the results are not degraded, even though c_2 and c_3 are not well represented (see Fig. 2), because c_1 is the most sensitive parameter for the MC alpha function.

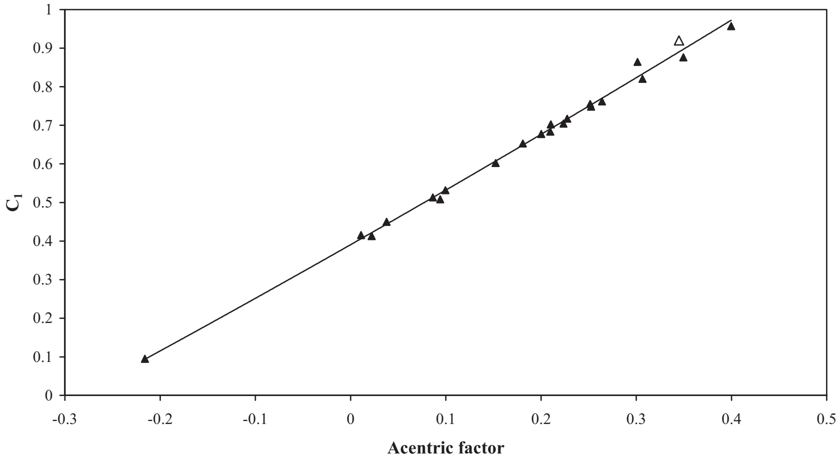

Fig. 1. Mathias–Copeman c_1 parameter as a function of the acentric factor for the PR EoS; (△) c_1 parameter for water.

3.2. New Proposed Alpha Function

The three adjustable parameters, c_1, c_2, and c_3 (Table V) for this new form (Eq. (10)) were evaluated following the procedure described in Section 3.1. They are also correlated as a function of the acentric factor for all the compounds:

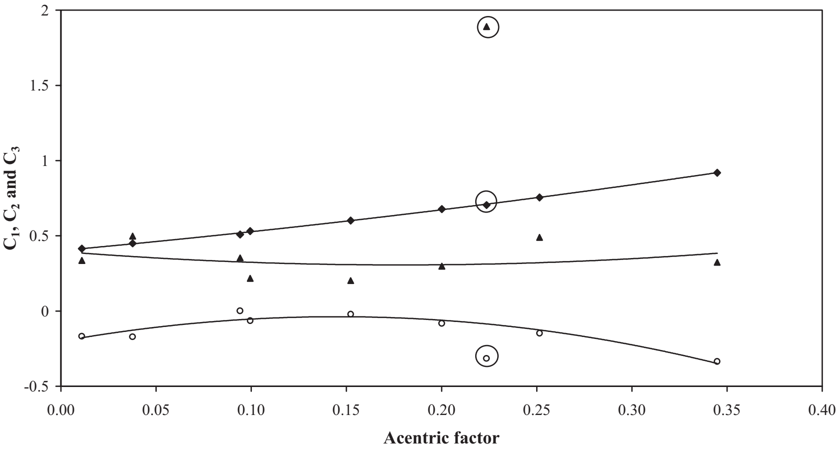

Fig. 2. Mathias–Copeman parameters as a function of the acentric factor for the PR EoS for selected components; (◆) c_1 parameter; (○) c_2 parameter; (▲) c_3 parameter. Circled points are the c_1, c_2, and c_3 parameters for carbon dioxide.

Table V. Adjusted New Alpha Function Parameters for the PR EoS from DIPPR® Correlations

Component	c_1	c_2	c_3	$F \times 10^4$
Hydrogen	0.09406	−0.22429	−0.02458	0.2
Methane	0.41667	−0.05156	0.38954	2.1
Oxygen	0.41325	0.10376	0.10971	3.0
Nitrogen	0.44950	−0.03278	0.49308	1.6
Ethylene	0.51014	0.06247	0.32052	1.8
Hydrogen sulfide	0.50694	0.14188	0.31438	0.9
Ethane	0.52539	0.11674	0.13968	7.6
Propane	0.59311	0.17042	0.10182	14.6
Isobutane	0.64121	0.07005	0.42647	11.6
n-Butane	0.67084	0.09474	0.23091	13.1
Cyclohexane	0.68259	0.04522	0.53089	2.0
Benzene	0.69709	−0.07749	0.86396	8.0
Carbon dioxyde	0.68583	0.17408	0.18239	2.0
Isopentane	0.71103	0.06958	0.29784	8.2
Pentane	0.74373	0.05868	0.35254	10.6
Ammonia	0.74852	0.07849	0.10073	0.5
Toluene	0.75554	0.11290	0.22419	10.2
Hexane	0.83968	−0.19125	0.93864	42.2
Acetone	0.82577	0.04252	0.15901	3.3
Water	0.91402	−0.23571	0.54115	3.2
Heptane	0.87206	0.08945	0.28459	9.7
Octane	0.94934	−0.00379	0.43788	15.8

$$c_1 = 0.1441\omega^2 + 1.3838\omega + 0.387 \tag{23}$$

$$c_2 = -2.5214\omega^2 + 0.6939\omega + 0.0325 \tag{24}$$

$$c_3 = 0.6225\omega + 0.2236 \tag{25}$$

This generalization leads to better results than the generalized PR alpha function [3] with the PR EoS (Table IV). The new alpha function represents pure compound vapor pressures with an overall AAD of 1.2% (0.01% bias) compared to 2.1% (−1.2% bias) with the generalized PR alpha function. However the water vapor pressures are degraded by this generalization as in the previous study of Section 3.1.

To get good representations especially for water, polar compounds, and natural gas compounds, the number of compounds has been reduced from 22 to 8; i.e., the previously adjusted (c_1, c_2, and c_3) parameters (see Table II) have been correlated to the acentric factor ω for only methane to pentane, water, hydrogen sulfide, carbon dioxide, and nitrogen. The new corresponding relationships obtained for the PR EoS are the following:

$$c_1 = 1.3569\omega^2 + 0.9957\omega + 0.4077 \tag{26}$$

$$c_2 = -11.2986\omega^2 + 3.5590\omega - 0.1146 \tag{27}$$

$$c_3 = 11.7802\omega^2 - 3.8901\omega + 0.5033 \tag{28}$$

This more specific generalized alpha function represents water vapor pressures with an AAD of 0.4% (0.02% bias) compared to 6% AAD (5.3% bias) with the first generalization (Eqs. (23)–(25)).

3.3. Comparisons

The comparison of results with the 22 compounds leads to the conclusion that the three different generalized alpha functions represent accurately the vapor pressures except those of the two polar compounds: water and ammonia. This is the reason why the MC and the new alpha functions were generalized using only the parameters obtained for methane to pentane, water, carbon dioxide, hydrogen sulfide, and nitrogen.

The pure compound vapor pressures of these selected compounds (Table VI) were calculated using both the generalized alpha function and the generalized Trebble–Bishnoi alpha function, Eq. (6). In the Trebble–Bishnoi alpha function, the m parameter was correlated to the acentric factor ω specifically for alkanes (up to C_{20}), water and carbon dioxide

Table VI. Comparison of Pure Component Vapor Pressures using the PR EoS

	TB Generalized Alpha Function [6]		Generalized MC Alpha Function		Generalized New Alpha Function	
Component	Bias (%)	AAD (%)	Bias (%)	AAD (%)	Bias (%)	AAD (%)
Nitrogen	1.19	1.72	−0.07	0.17	−0.08	0.19
Methane	1.27	1.55	0.12	0.24	0.15	0.22
Hydrogen sulfide	0.80	2.66	−0.25	0.69	−0.32	0.59
Ethane	−1.12	3.73	1.23	1.57	1.19	1.65
Propane	−2.60	5.05	0.56	0.93	0.59	1.15
Carbon dioxide	2.16	2.16	0.66	0.66	0.37	0.37
Water	***0.75***	***1.16***	***0.28***	***0.44***	***0.02***	***0.44***
Butane	−2.89	5.10	0.40	0.78	0.51	1.14
Pentane	−4.84	6.57	−1.68	1.75	−1.47	1.47
Overall	−0.59	3.30	0.14	0.80	0.11	0.80

by Daridon et al. [6]. The relationships obtained for the PR EoS are the following:

$$m = 0.418 + 1.58\omega - 0.580\omega^2 \qquad \text{when} \quad \omega < 0.4 \tag{29}$$

$$m = 0.212 + 2.2\omega - 0.831\omega^2 \qquad \text{when} \quad \omega \geqslant 0.4 \tag{30}$$

The new generalized alpha function represents pure compound vapor pressures with an overall AAD of 0.8% (0.1% bias) compared to 3.3% (−0.6% bias) with the generalized Trebble–Bishnoi alpha function. The results obtained with the generalized MC alpha function are similar, 0.8% AAD (0.1% bias).

4. VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

The above evaluation of the alpha functions is based only on pure compound vapor pressures. It is interesting to examine their influence on VLE calculations, particularly for water-gas systems that are closely related to hydrate formation.

4.1. Model Development

Six different water-gas systems were selected to be treated (Table VIII), some in the supercritical region to study the sensitivity of these alpha functions. An assymetric approach (γ-Φ) was selected to fit the selected experimental data involving the Henry's law approach for the aqueous phase and the PR-EoS for the vapor phase with the three described alpha functions and the classical mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{31}$$

$$\text{where} \quad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{32}$$

$$b = \sum_i x_i b_i \tag{33}$$

The fugacity coefficient in the vapor phase is calculated using the Peng–Robinson EoS. For the aqueous phase, a Henry's law approach is used for both compounds. As the gas is at infinite dilution, the asymmetric convention ($\gamma_{(2)} \to 1$ when $x_{(2)} \to 0$) is used to express the Henry's law,

Table VII. Sources of Vapor-Liquid Equilibrium Data for Water-Gas Mixtures

Component	Reference	$T_{\min}$ (K)	$T_{\max}$ (K)	$P_{\min}$ (MPa)	$P_{\max}$ (MPa)
Methane	Chapoy et al. (2003) [13]	283.08	318.12	1	34.5
	Althaus (1999) [14]	253.15	293.15	0.5	10
	Gillepsie and Wilson (1982) [15]	323.15	588.70	1.4	13.8
	Rigby and Prausnitz (1968) [16]	298.15	373.15	2.3	9.3
	Yarym-Agaev et al. (1985) [17]	298.15	338.15	2.5	12.5
	Yokoama et al. (1988) [18]	298.15	323.15	3	8
	Culberson and Mc Ketta (1951) [19]	310.93	310.93	5.2	35.7
	Kosyakov et al. (1982) [20]	273.16	283.16	1	10.1
Ethane	Chapoy et al. (2003) [21]	278.08	303.12	0.3	4.63
	Coan and King (1971) [22]	298.15	373.15	2.3	3.6
	Culberson and McKetta (1951) [19]	310.93	310.93	4.2	12
	Reamer et al. (1943) [23]	310.93	510.93	2.2	68.2
Propane	Klausutis (1968) [24]	310.93	310.93	0.545	1.31
	Kobayashi and Katz (1953) [25]	310.93	422.04	0.703	19.33
n-Butane	Brooks et al. (1951) [26]	310.93	377.59	7.27	68.36
	Reamer et al. (1952) [27]	310.93	510.93	0.14	68.95
Carbon dioxide	Takenouchi and Kennedy (1964) [28]	383.15	423.15	10	150
	Coan and King (1971) [22]	298.15	373.15	1.7	5.2
	Briones et al. (1987) [29]	323.15	323.15	6.8	17.7
	Nakayama et al. (1987) [30]	298.2	298.2	3.6	6.4
	Mueller (1983) [31]	373.15	413.15	0.3	3.2
	Wiebe and Gaddy (1941) [32]	298.15	348.15	0.1	70.9
	D'Souza et al. (1988) [33]	323.15	348.15	10	15.2
	Dohrn et al. (1993) [34]	323.15	323.15	10	30.1
	Sidorov et al. (1953) [35]	323.15	348.15	2.5	30.4
Nitrogen	Maslennikova et al. (1971) [36]	298.15	623.15	5.1	50.7
	Sidorov et al. (1953) [35]	373.15	373.15	5.1	40.5
	Ugrozov et al. (1996) [37]	310.15	310.15	1.4	13.8
Hydrogen sulfide	Burgess and Germann (1969) [38]	323.15	443.15	1.7	2.3
	Selleck et al. (1952) [39]	310.93	444.26	0.7	20.7

Eq. (34), while the symmetric convention ($\gamma_{(1)} \to 1$ when $x_{(1)} \to 1$) is used for water, Eq. (35).

$$f^{L}_{(2)}(P,T) = H^{L}_{(1)}(T)\, x_{(1)}(T) \exp\left(\left(\frac{v^{\infty}_{(1)}(T)}{RT}\right)(P - P^{\mathrm{sat}}_{(1)})\right) \quad \text{for the gas} \tag{34}$$

$$f^{L}_{(1)}(P,T) = \gamma^{L}_{(1)}\varphi^{\mathrm{sat}}_{(1)} P^{\mathrm{sat}}_{(1)} x_{(1)}(T) \exp\left(\left(\frac{v^{\mathrm{sat}}_{(1)}(T)}{RT}\right)(P - P^{\mathrm{sat}}_{(1)})\right) \quad \text{for water} \tag{35}$$

The partial molar volume of the gas at infinite dilution is based on the work of Lyckman et al. [40] reported by Heidmann and Prausnitz [41] in the form

$$\left(\frac{P_{\mathrm{c},i} v_i^{\infty}}{RT_{\mathrm{c},i}}\right) = 0.095 + 2.35\,\frac{TP_{\mathrm{c},i}}{cT_{\mathrm{c},i}} \tag{36}$$

with $P_{\mathrm{c},i}$ and $T_{\mathrm{c},i}$ the solute critical pressure and temperature and c the cohesive energy density of water,

$$c = \frac{\Delta U_w}{v_w^{\mathrm{sat}}} \qquad \text{with} \quad \Delta U_w = \Delta H_w - RT \tag{37}$$

with ΔU_w the energy of vaporization of water (at zero pressure).

For high temperatures, the following correction is used,

$$v_i^{\infty}(T) = [v_i^{\infty}(T)]_{\mathrm{Lyckman}} + \left(\frac{dv_w}{dT}\right)^{\mathrm{sat}} (T - 298.15) \tag{38}$$

The Henry's law constants are taken from the literature [42] and represented as a function of temperature using the correlation (Table VIII),

$$\log_{10}(H_{(1)(2)}(T)) = A + B/T + C\log_{10}(T) + DT \qquad (H \text{ in atm}) \tag{39}$$

The NRTL model [43] is used to calculate the water activity with $\tau_{1,2} = 3100$ and $\tau_{2,1} = 2800$ (these values were obtained by VLE data fitting) and $\alpha_{1,2} = 0.3$.

The experimental VLE data are fitted by means of in-house software, developed at Ecole des Mines de Paris. The binary parameter, $k_{i,j}$, is

Table VIII. Parameters for the Henry's Law Constant Correlation (Eq. (39))

Component	A	$B \times 10^{-3}$	c	$D \times 10^{3}$	$T_{\min}$ (K)	$T_{\max}$ (K)
Methane	146.8858	−5.76834	−51.9144	18.4936	273.15	360.95
Ethane	108.9263	−5.51363	−34.7413	0	275.15	323.15
Propane	2874.113	−85.67320	−1128.09	701.58	283.15	360.95
n-Butane	121.8305	−6.34244	−38.7599	0	273.15	349.15
Carbon Dioxide	69.4237	−3.79646	−21.6694	0.478857	273.15	353.15
Nitrogen	78.8622	−3.74498	−24.7981	0	273.15	353.15
Hydrogen Sulfide	10.8191	−1.51009	−39.93	−6.81842	273.15	353.15

adjusted directly to VLE data through a modified Simplex algorithm [12] using the objective function

$$F = \frac{100}{N} \sum_{i=1}^{N} \sqrt{\left(\frac{y_{i,\exp} - y_{i,\text{cal}}}{y_{i,\exp}}\right)^2} \tag{40}$$

where N is the number of data points, $y_{\exp}$ is the measured water mole fraction in the gas phase, and y_{cal} is the calculated water mole fraction in gas phase. The BIAS values on vapor phase mole fractions defined by Eq. (41) are listed in Tables IX to XV for each system,

$$\text{BIAS}\ Y = (100/N) \sum ((Y_{i,\exp} - Y_{i,\text{cal}})/Y_{i,\exp}) \tag{41}$$

4.2. Results

VLE data from the literature that are consistent with those used to define the parameters of the just generalized alpha functions are easily represented. Thus, this is a good tool to check for inconsistent data.

For the methane-water and propane-water systems, the three alpha functions give similar results. For the subcritical region of the ethane-water system, the three functions lead also to similar results. In the supercritical region, the objective function for each set of data is equivalent whatever the alpha function is, but the new alpha function leads to significantly smaller bias values. For the propane-water, the water-sulfur dioxide and the water-butane systems, a discontinuity of the k_{ij} binary interaction parameter vs. temperature is observed at the critical point of the gas (Fig. 3). For carbon dioxide and nitrogen, the different sets of isotherms are accurately represented.

5. CONCLUSION

Our new function with three parameters accurately represents the pure compound vapor pressures as does the Mathias–Copeman alpha function. Particularly in the case of water, this generalized alpha function improves the vapor pressure calculation abilities of the PR EoS. The mean absolute deviations (compounds studied either independently or together) are smaller than those with the other specific generalized functions (study performed on either a set of 8 or 22 compounds).

Vapor-liquid equilibrium calculations, carried out with our new alpha function for mixtures involving components that are either supercritical or not, give results that are in average better than those obtained through the

Table IX. Methane-Water System

		Alpha function type								
		Daridon et al. generalized			MC generalized			New alpha generalized		
Reference	T (K)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)
Chapoy et al. (2003) [13]	283.08	1.335	0.666	−1.560	1.316	0.790	5.38	1.308	0.793	5.42
	288.11	1.139	0.762	−0.534	1.107	0.924	5.56	1.098	0.930	5.55
	293.11	0.965	0.652	7.616	0.964	0.503	−0.23	0.957	0.506	−0.22
	298.11	0.760	0.561	4.946	0.780	0.575	2.41	0.776	0.594	2.51
	303.11	0.711	0.44	5.438	0.704	0.384	3.32	0.701	0.406	3.43
	308.12	0.625	0.18	2.096	0.626	0.146	1.04	0.624	0.152	1.16
	313.12	0.568	0.44	2.176	0.580	0.358	2.64	0.579	0.378	2.79
	318.12	0.555	0.56	2.570	0.563	0.492	2.04	0.562	0.508	2.16
Althaus (1999) [14]	283.15	0.535	0.020	−0.082	0.530	0.022	0.23	0.529	0.022	0.25
	288.15	0.535	0.002	−0.180	0.530	0.000	−0.03	0.529	0.000	0.03
	293.15	0.530	0.007	−0.118	0.006	0.013	−0.11	0.006	0.000	−0.08
Culberson and McKetta (1951) [19]	310.93	0.457	1.448	2.786	0.467	1.411	2.54	0.463	1.421	2.61
Rigby and Prausnitz (1968) [16]	298.15	0.457	0.005	0.145	0.543	0.0000	0.13	0.536	0.0001	0.16
	323.15	0.508	0.004	0.185	0.525	0.0002	0.005	0.519	0.0003	0.02
	348.15	0.475	0.012	0.330	0.527	0.0011	0.08	0.519	0.0021	0.12
	373.15	0.480	0.003	0.094	0.525	0.000	0.01	0.519	0.000	0.03
Gillespie and Wilson (1982) [15]	323.15	0.478	0.110	1.961	0.495	0.044	1.22	0.494	0.056	1.37
	348.15	0.532	0.068	1.537	0.559	0.012	0.60	0.555	0.018	0.76
	423.15	0.488	0.005	0.390	0.520	0.003	−0.28	0.517	0.001	−0.14
	477.59	0.353	0.013	−0.429	0.375	0.018	−0.52	0.379	0.015	−0.48
	533.15	0.603	0.005	−0.206	0.600	0.005	−0.20	0.593	0.004	−0.18
Yokoyama et al. (1988) [18]	298.15	0.513	0.023	0.386	0.521	0.020	0.38	0.517	0.022	0.37
	323.15	0.442	0.102	−0.591	0.473	0.138	−0.85	0.469	0.129	−0.78
Kosyakov et al. (1982) [20]	283.16	0.621	0.136	0.586	0.611	0.152	0.84	0.610	0.153	0.86
Yarym-Agaev et al. (1985) [17]	298.15	0.189	7.358	15.367	0.195	7.297	15.32	0.200	7.374	15.45
	313.15	0.443	0.166	0.045	0.457	0.175	−0.25	0.456	0.173	−0.19
	338.15	0.419	0.234	−0.492	0.448	0.286	−0.96	0.445	0.275	−0.89

Table X. Ethane-Water System

		Alpha function type								
		Daridon et al. generalized			MC generalized			New alpha generalized		
Reference	T (K)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)
Chapoy et al. (2003) [21]	278.08	0.135	0.006	0.194	0.024	0.019	0.35	0.026	0.019	0.38
	283.11	0.387	0.505	3.598	0.414	0.597	3.97	0.410	0.603	3.97
	288.11	0.608	1.042	4.659	0.601	1.097	4.82	0.600	1.109	4.85
	293.11	0.598	0.882	5.550	0.584	0.891	5.61	0.582	0.912	5.68
	298.11	0.499	1.767	6.888	0.477	1.723	6.76	0.475	1.750	6.85
	303.11	0.476	1.969	8.313	0.469	1.853	8.03	0.467	1.892	8.13
Coan and King (1971) [22]	298.15	0.482	0.074	0.499	0.486	0.071	0.47	0.483	0.073	0.46
	323.15	0.488	0.014	0.201	0.514	0.007	0.13	0.509	0.008	0.14
	348.15	0.478	0.044	0.485	0.523	0.024	0.32	0.476	0.004	−149.38
	373.15	0.430	0.009	0.156	0.485	0.003	0.07	0.476	0.004	0.08
Culberson and McKetta (1951) [19]	310.93	0.454	1.769	4.382	0.458	1.694	3.99	0.457	1.711	4.07
Reamer et al. (1943) [23]	310.93	0.468	1.376	1.710	0.470	1.370	1.71	0.470	1.372	1.72
	344.26	0.482	0.314	0.884	0.486	0.296	0.35	0.486	0.297	0.45
	410.93	0.482	0.177	−0.416	0.487	0.194	−0.55	0.486	0.186	−0.53
	444.26	0.470	0.091	−0.596	0.474	0.101	−0.69	0.473	0.093	−0.64
	477.59	0.442	0.034	−0.239	0.445	0.034	−0.21	0.444	0.032	−0.20
	510.93	0.397	0.039	0.323	0.401	0.038	−0.36	0.401	0.035	−0.30

Table XI. Propane-Water System

		Alpha function type								
		Daridon et al. generalized			MC generalized			New alpha generalized		
Reference	T (K)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)
Klausutis (1969) [24]	310.93	0.853	0.155	−0.173	0.897	0.168	−0.34	0.886	0.164	−0.32
Kobayashi and Katz (1953) [25]	310.93	0.510	9.187	11.960	0.525	8.739	12.94	0.524	8.750	12.98
	338.71	0.504	0.224	2.066	0.509	0.153	0.55	0.508	0.162	0.77
	360.93	0.505	0.180	1.164	0.511	0.155	0.10	0.510	0.155	0.27
	369.65	0.512	0.794	0.233	0.526	0.849	−0.30	0.525	0.838	−0.19
	383.15	0.514	1.107	−0.897	0.521	1.172	−1.51	0.520	1.160	−1.42
	399.82	0.518	0.197	−0.476	0.523	0.209	−0.83	0.522	0.204	−0.75
	422.04	0.522	0.146	−1.106	0.526	0.174	−1.33	0.525	0.165	−1.30

Table XII. *n*-Butane-Water System

		Alpha function type								
		Daridon et al. generalized			MC generalized			New alpha generalized		
Reference	T (K)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)
Brooks et al. (1951) [26]	310.93	0.461	8.513	8.250	0.463	8.535	18.78	0.463	8.531	8.287
	377.59	0.597	12.991	12.626	0.602	13.025	27.78	0.601	13.020	12.647
Reamer et al. (1952) [27]	310.93	0.414	0.004	0.203	0.585	7.3×10^{-5}	0.02	0.543	0.0005	0.061
	344.26	0.501	0.013	0.542	0.677	0.001	−0.13	0.650	0.001	0.003
	377.59	0.574	0.028	0.739	0.693	0.028	−0.66	0.673	0.023	−0.462
	410.93	0.596	0.023	1.009	0.646	0.004	−0.09	0.638	0.004	0.123
	444.26	0.521	1.355	−2.444	0.524	1.438	−1.41	0.524	1.415	−2.668
	477.59	0.478	0.089	−0.405	0.479	0.085	−0.42	0.478	0.082	−0.449
	510.93	0.425	0.392	−1.265	0.425	0.373	−0.84	0.424	0.365	−1.125

Table XIII. Carbon Dioxide-Water System

		Alpha function type								
		Daridon et al. generalized			MC generalized			New alpha generalized		
Reference	T (K)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)
Takenouchi and Kennedy (1964) [28]	383.15	−0.053	5.381	2.47	−0.044	5.885	2.71	−0.059	6.416	3.46
	423.15	−0.067	1.692	1.22	−0.030	1.387	0.71	−0.057	1.855	1.22
Coan and King (1971) [22]	298.15	0.001	0.046	0.38	0.007	0.043	−0.02	0.004	0.044	0.37
	323.15	0.149	0.042	0.64	0.182	0.020	−0.04	0.174	0.024	−0.11
	348.15	0.219	0.109	0.61	0.261	0.086	−0.23	0.254	0.089	0.46
	373.15	0.247	0.008	0.08	0.297	0.005	−0.04	0.289	0.005	0.05
Briones et al. (1987) [29]	323.15	0.182	0.030	0.05	0.188	0.030	−0.31	0.187	0.029	−0.26
Nakayama et al. (1987) [30]	298.2	0.187	1.324	2.36	0.188	1.310	2.35	0.187	1.317	2.38
Mueller (1983) [31]	373.15	0.734	0.253	−2.07	0.898	0.399	−2.77	0.872	0.373	−2.66
	393.15	0.499	0.040	−0.03	0.633	0.058	−0.60	0.611	0.053	−0.51
	413.15	0.011	0.032	0.96	0.142	0.008	0.31	0.119	0.011	0.43
Wiebe and Gaddy (1941) [32]	298.15	0.188	0.367	0.19	0.188	0.372	8.65	0.188	0.370	0.14
	304.19	0.189	0.306	−1.14	0.190	0.340	−0.28	0.189	0.328	−1.36
	323.15	0.186	0.286	−0.67	0.190	0.343	−0.88	0.189	0.329	−1.39
	348.15	0.194	8.526	−13.09	0.202	9.772	−0.71	0.200	9.558	−14.00
D’Souza et al. (1988) [33]	323.15	0.128	0.356	1.58	0.134	0.262	1.36	0.133	0.280	1.35
	348.15	0.225	0.287	4.05	0.237	0.355	−1.28	0.235	0.343	−1.24
Dohrn et al. (1993) [34]	323.15	0.173	1.555	4.00	0.178	1.374	3.66	0.177	1.411	3.75
Sidorov et al. (1953) [35]	323.15	0.179	0.298	2.53	0.186	0.216	−0.72	0.185	0.230	1.99
	348.15	0.194	0.201	−1.40	0.204	0.313	−0.64	0.202	0.292	−1.98

Table XIV. Nitrogen-Water System

		Alpha function type								
		Daridon et al. generalized			MC generalized			New alpha generalized		
Reference	T (K)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)
Maslennikova et al. (1971) [36]	298.15	0.492	0.508	−1.26	0.532	0.591	−1.35	0.511	0.508	−1.28
	323.15	0.380	0.416	1.22	0.410	0.382	0.58	0.395	0.416	0.94
	343.15	−0.137	0.443	1.59	−0.087	0.387	0.91	0.403	−0.055	1.17
	373.15	0.403	0.110	−0.63	0.443	0.172	−1.15	0.149	0.453	−1.00
	423.15	0.316	0.736	−3.24	0.359	0.885	−3.55	0.844	0.381	−3.48
	473.15	0.190	4.091	−7.89	0.273	4.152	−7.89	4.185	0.266	−8.03
	503.15	0.255	1.886	−6.48	0.285	1.911	−6.54	1.775	0.387	−6.33
	513.15	0.403	1.283	−4.99	0.337	1.396	−5.20	1.372	0.371	−5.12
	543.15	0.580	2.334	−6.21	0.583	2.295	−6.25	2.081	0.735	−6.01
	573.15	0.818	1.145	−4.43	0.805	1.111	−4.35	1.103	0.750	−4.33
	603.15	0.773	0.326	−2.78	0.749	0.319	−2.71	0.316	0.750	−2.71
	623.15	0.105	0.052	−1.40	−0.697	0.149	−1.85	0.123	−0.471	−1.73
Sidorov et al. (1953) [35]	373.15	0.433	0.008	−0.29	0.473	0.041	−0.78	0.028	0.481	−0.63
Ugrozov (1996) [37]	310.95	0.428	0.043	1.10	0.476	0.003	0.28	0.023	0.462	0.82

Table XV. Hydrogen Sulfide-Water System

		Alpha function type								
		Daridon et al. generalized			MC generalized			New alpha generalized		
Reference	T (K)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)	k_{ij}	F	BIAS (%)
Burgess and Germann (1969) [38]	323.15	−0.172	2.3	0.002	−0.127	3.9	−0.004	−0.138	−1381.4	−0.029
	343.15	−0.111	0.2	−0.011	−0.043	11.3	−0.052	−0.055	8.0	−0.018
	363.15	−0.064	1.4	0.002	0.022	4.6	−0.040	0.008	2.7	−0.035
	383.15	−0.019	8.8	0.046	0.080	0.8	−0.016	0.064	0.7	−0.011
	403.15	0.038	16.0	0.067	0.151	2.3	0.027	0.131	3.4	0.033
	423.15	0.121	12.0	0.042	0.254	3.8	0.012	0.226	4.1	−0.001
	443.15	0.286	7.1	−0.031	0.456	20.4	−0.071	0.412	15.7	−0.083
Selleck et al. (1952) [39]	310.93	−0.207	145.5	0.506	−0.179	38.5	0.191	−0.188	55.2	0.280
	344.26	−0.086	257.4	0.846	−0.057	37.3	−0.041	−0.063	40.7	0.124
	377.59	0.194	10939.6	3.250	0.177	13287.6	4.216	0.176	13559.7	4.337
	410.93	0.143	2416.6	2.567	0.151	1764.0	1.827	0.149	1897.3	−0.783
	444.26	0.130	117.2	−0.484	0.140	269.1	−0.935	0.138	213.8	−0.783

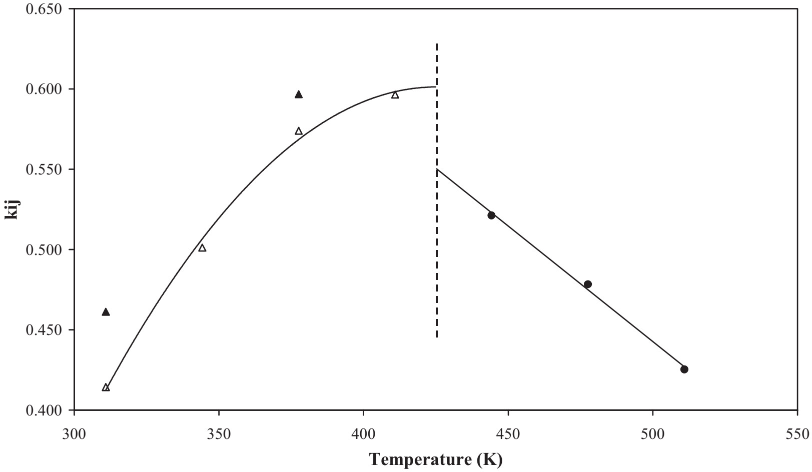

Fig. 3. Binary interaction parameters for the butane-water system; (●) supercritical parameters from Reamer et al. [27]; (△) subcritical parameters from Reamer et al. [27]; (▲) subcritical parameters from Brooks et al. [26].

Trebble–Bishnoi function generalized by Daridon et al. These results are much better than those with the generalized Mathias–Copeman function when supercritical components are involved. For all light hydrocarbons, the smallest BIAS value is obtained using our new generalized alpha function.

LIST OF SYMBOLS

a	Parameter of the equation of state, energy parameter ($\mathrm{Pa \cdot m^6 \cdot mol^{-2}}$)
b	Parameter of the equation of state, co-volume parameter ($\mathrm{m^3 \cdot mol^{-1}}$)
F	Objective function
H	Molar enthalpy ($\mathrm{J \cdot mol^{-1}}$)
P	Pressure (MPa)
R	Gas constant ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)
T	Temperature (K)
U	Energy of vaporization ($\mathrm{J \cdot mol^{-1}}$)
v	Molar volume ($\mathrm{m^3 \cdot mol^{-1}}$)
Z	Compressibility factor
x	Liquid mole fraction
y	Vapor mole fraction
k	Binary interaction parameter

Greek Letters

α_{ij}	NRTL model parameter
τ_{ij}	NRTL model binary interaction parameter ($J \cdot mol^{-1}$)
ω	Acentric factor

Superscript

E	Excess property
Ref	Reference property
L	Liquid state
V	Vapor state
Sat	Property at saturation
∞	Infinite dilution

Subscripts

c	Critical property
cal	Calculated property
exp	Experimental property
i, j	Molecular species
∞	Infinite pressure reference state
(1) or w	Water
(2)	Gas

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