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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 component and water – gas system.

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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 generalized alpha function is proposed quadratically proportional to the acentric factor. Pure-component vapor pressure for different molecular species were fitted and compared using three different alpha functions including Mathias-Copeman and Trebble-Bishnoi alpha functions. In addition the classical Mathias-Copeman alpha function was generalized to become a quadratic function of the acentric factor. The new alpha function leads to improved pure component vapor pressure predictions from a reduced temperature equals to 0.4 (about 1.2 % absolute average percentage deviations) for all the systems considered.

In addition, these alpha functions were used for VLE calculation for water- gas and hydrocarbon gas systems. A general procedure is presented to generate diverse experimental VLE data, the Peng-Robinson equation of state is used with the different alpha functions; the classical mixing rules for the vapor phase and a Henry's law approach to treat the aqueous phase.

*Keywords:* Alpha function, pure component, water – gas and gas hydrocarbon mixtures.

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## **Introduction**

At first prediction of thermodynamic properties and phase equilibrium of mixture is based on pure component calculation, the accuracy of the calculation is not only dependent on the choice of an equation of state or a mixing rule but also on a sufficiently accurate representation of pure component vapor pressure. The capacity to correlate the phase equilibria depends thus on the choice of an alpha function.

Many alpha functions have been proposed to improve the precision of cubic equation of state via a more accurate prediction in pure component vapor pressures. Some selected alpha functions are shown in table I. Generally the mathematical expression of alpha functions is in the form of polynomials of high order in either acentric factor or reduced temperature, exponential function, or switching function. The difficulty associated mainly with alpha functions are their incapacity to represent accurately supercritical behavior or their limiting temperature utilization range. To avoid these difficulties, different approaches have been developed in the literature: use of alpha functions with specific component parameter or switching alpha functions. Even if mathematical constraints are associated with the latest, particularly in the continuity of the function and its derivatives.

Generalized alpha functions are preferably used because of their ability of prediction and limitation of the number of parameters. In this work, the capacity of three different alpha functions have been compared: a new proposed form, a generalized Trebble-Bishnoi and a generalized Mathias-Copeman alpha function for the particular cases of natural gas compounds, light hydrocarbons, water, carbon dioxide....

The vapor pressure of 22 pure components were used to develop and generalize a new alpha function for the PR EoS. These functions have been also used to perform water-gas mixture calculations using the Peng-Robinson equation of state (PR EoS) and

the classical mixing rules and a Henry's law approach to estimate the composition in the aqueous phase.

## 1. Theory

A large number of equations of state has been proposed to predict thermodynamics properties of pure components and mixtures. In this work, the Peng-Robinson [3] equation of state (PR EoS) is selected because of its simplicity and its widespread utilization in chemical engineering. Moreover this EoS gives better results for VLE of polar mixtures than Soave-Redlich-Kwong (SRK) EoS [1] and provides reliable calculations of the molar liquid volume. Its formulation is:

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

in which :

$$b = 0.07780 \frac{RT_c}{P_c} \quad (2)$$

and

$$a(T) = a_c \alpha(T_r) \quad (3)$$

where

$$a_c = 0.45724 \frac{(RT_c)^2}{P_c} \quad (4)$$

To have an accurate representation of vapor pressures of pure components a temperature dependence of the attractive term through the alpha function is imposed. The alpha functions must verify some requirements:

- Must be finite and positive at all temperatures
- Must be equal to 1 at the critical point

- Must tend to zero when T tends to infinity
- Must belong to the C2 function group (for T>0) to assure continuity in thermodynamic properties

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

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

Classically, the alpha function forms are:

- Exponential form,

The Trebble-Bishnoi [10] alpha function is one of the example selected in this study

$$\alpha(T) = \exp \left[ m \times \left( 1 - \frac{T}{T_c} \right) \right] \quad (6)$$

- Quadratic form,

Different quadratic forms have been proposed:

- The Soave alpha function with one adjustable parameter [1].

$$\alpha = \left[ 1 + m \left( 1 - T_R^{1/2} \right) \right]^2 \quad (7)$$

- The Mathias-Copeman alpha function with three adjustable parameters [5].

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

If T>T<sub>C</sub>,

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

$c_1$ ,  $c_2$  and  $c_3$  are the three adjustable parameters

In addition in this work, a new alpha function is proposed, which is a combination of the both mathematical form. This alpha function verify every requirements.  $c_1$ ,  $c_2$  and  $c_3$  are the three adjustable parameters.

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

If  $T > T_c$ , an exponential form is chosen similar to the Treble Bishnoi expression (eq .6) and the single parameter  $m$  of this expression should verify eq. 11:

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

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

## 2. Pure Component Vapor Pressure

The predictive ability of alpha function is usually tested by comparing pure component vapor pressures. 22 components were selected to perform the comparison and the generalization of the alpha functions. All the critical coordinates and vapor pressure correlations are taken from “The properties of gases and liquids”[11].(table II)

### 2.1 Mathias – Copeman alpha function

$c_1$ ,  $c_2$  and  $c_3$ , the three adjustable parameters for Mathias-Copeman were evaluated from a reduced temperature equals to 0.4 up to 1 using a modified Simplex algorithm [12] for the 22 selected components. The objective function is:

$$F = \frac{100}{N} \sum_1^N \left( \frac{P_{exp} - P_{cal}}{P_{exp}} \right)^2 \quad (13)$$

where  $N$  is the number of data points,  $P_{exp}$  is the measured pressure, and  $P_{cal}$  is the calculated pressure.

The adjustable parameters for each compound are reported in Table II for the SRK EoS and for the PR EoS.

In the case of the SRK EoS, it appears that the three parameters can be quadratically correlated as a function of the acentric factor:

$$c_1 = -0.10935 \omega^2 + 1.60539 \omega + 0.51780 \quad (14)$$

$$c_2 = 0.32788 - 0.42909 \omega \quad (15)$$

$$c_3 = 0.48658 + 1.35060 \omega \quad (16)$$

This generalization of the MC for the SRK EoS leads to better results that for example the classical generalized Soave alpha function [2] (table III). The deviations obtained by the MC alpha function are in general smaller than those obtained with the classical Soave alpha function. The generalized alpha function predicts pure component vapor pressure with an overall AAD of 1.42 % compared to 3.37 % AAD with the classical Soave alpha function.

In the case of the PR EoS, the three parameters (table II) could also be generalized as a function of the acentric factor (eqs. 16, 17 and 18), however this generalization degrades the vapor pressure of some component including water, hydrogen, acetone

because the adjusted and calculated  $c_1$  parameter using the generalization differ strongly (figure 1). This is particularly true for water.

$$c_1 = 0.1316 \omega^2 + 1.4031 \omega + 0.3906 \quad (17)$$

$$c_2 = -1.3127 \omega^2 + 0.30151 \omega - 0.12133 \quad (18)$$

$$c_3 = 0.76606 \omega + 0.3041 \quad (19)$$

To obtain more accurate pure component vapor pressure, the three parameters were only correlated to the acentric factor  $\omega$  for light hydrocarbons, water and carbon dioxide, hydrogen sulfide and nitrogen (figure 2). The relationships obtained for the PR EoS are the following:

$$c_1 = 1.01127 \omega^2 + 1.15380 \omega + 0.40209 \quad (20)$$

$$c_2 = -7.7867 \omega^2 + 2.259 \omega - 0.2011 \quad (21)$$

$$c_3 = 2.8127 \omega^2 - 1.004 \omega + 0.3964 \quad (22)$$

## 2.2 The new proposed alpha function

$c_1$ ,  $c_2$  and  $c_3$ , the three adjustable parameters for this new form were evaluated following the same procedure as the study of Mathias Copeman function (table IV).

The three parameters are also quadratically correlated as a function of the acentric factor for the all components (figure 2):

$$c_1 = 0.14405 \omega^2 + 1.38375 \omega + 0.38790 \quad (23)$$

$$c_2 = -2.52144 \omega^2 + 0.69392 \omega + 0.03246 \quad (24)$$

$$c_3 = 0.22361 + 0.62252 \omega \quad (25)$$



This generalization leads also to better results than the classical generalized Soave alpha function (table V ). The deviations obtained by the new alpha function are in general smaller than those obtained with the classical Soave alpha function. The new alpha function predicts pure component vapor pressure with an overall AAD of 1.19% (0.01% BIAS) compared to 2.11% (-1.21 % BIAS) with the classical Soave alpha function. However the water vapor pressure is degraded by this generalization similarly to the Mathias Copeman study.

To obtain more accurate vapor pressure, the three parameters were also correlated to the acentric factor  $\omega$  for the same specific components. The relationships obtained for the PR EoS are the following:

$$c_1 = 1.3569 \omega^2 + 0.9957 \omega + 0.4077 \quad (26)$$

$$c_2 = -11.2986 \omega^2 + 3.5590 \omega - 0.1146 \quad (27)$$

$$c_3 = 11.7802 \omega^2 - 3.8901 \omega + 0.5033 \quad (28)$$

### 2.3 Comparison

The comparison of results with the 22 compounds leads to the conclusion that the three different generalized alpha functions represent accurately the vapor pressure except for the polar components, water and ammonia. That is why the MC and the new alpha functions were generalized using only the parameters obtained for light hydrocarbons, water and carbon dioxide, hydrogen sulfide and nitrogen.

The pure component vapor pressure of these selected compounds (table VI) were calculated using the both generalized alpha function as well as generalized Trebble-Bishnoi alpha function (eq.6). In the Trebble Bishnoi the  $m$  parameter was correlated to

the acentric factor  $\omega$  specifically for alkanes (up to C20), water and carbon dioxide by Daridon et al. [6]. The relationships obtained for the PR EoS are the following:

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

$$m = 0.212 + 2.2\omega - 0.831\omega^2 \quad \text{when } \omega \geq 0.4 \quad (30)$$

The new generalized alpha function predicts pure component vapor pressure with an overall AAD of 0.8 % (0.11% BIAS) compared to 3.3% (-0.59 % BIAS) with the generalized Trebble-Bishnoi alpha function. The results obtained with the generalized MC alpha function are similar, 0.8 % AAD (0.14% BIAS).

### 3 Vapor Liquid Equilibria Calculation

As the above evaluation of the alpha functions is based only on pure component vapor pressure, the sensitivity of these alpha functions is chosen to be studied in VLE calculation to test their consistently particularly for water – gas system.

#### 3.1 Model development

Six different water – gas systems were selected to be treated (table VIII), some were in the supercritical region to study the sensitivity of these alpha functions. A dissymmetric approach ( $\gamma - \Phi$ ) has been selected to fit the different selected experimental data involving the Henry's law approach for the aqueous phase and the PR-EoS for the vapor phase with the three different alpha functions and the classical quadratic mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (31)$$

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

$$b = \sum_i x_i b_i \quad (33)$$

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 ( $\gamma_{(2)} \rightarrow 1$  when  $x_{(2)} \rightarrow 0$ ) is used to express the Henry's law (Eq. 34) and a symmetric convention ( $\gamma_{(1)}$  when  $x_{(1)} \rightarrow 1$ ) in the case of water (Eq. 35).

$$f_{(2)}^L(P, T) = H_{(1)}^L(T) \times x_{(1)}(T) \times \exp\left(\frac{v_{(1)}^\infty(T)}{RT}(P - P_{(1)}^{sat})\right) \quad \text{for the gas} \quad (34)$$

$$f_{(1)}^L(P, T) = \gamma_{(1)}^L \times \phi_{(1)}^{sat} \times P_{(1)}^{sat} \times x_{(1)}(T) \times \exp\left(\frac{v_{(1)}^{sat}(T)}{RT}(P - P_{(1)}^{sat})\right) \quad \text{for water} \quad (35)$$

The partial molar volume of the gas at infinite dilution is based on the work of Lyckman et al. [41] reported by Heidmann and Prausnitz [42] in the following form:

$$\left(\frac{P_{c,i} \cdot v_i^\infty}{R \cdot T_{c,i}}\right) = 0.095 + 2.35 \cdot \frac{T \cdot P_{c,i}}{c \cdot T_{c,i}} \quad (36)$$

with  $P_{ci}$  et  $T_{ci}$ , solute critical pressure and temperature and  $c$  the cohesive energy density of water:

$$c = \frac{\Delta U_w}{v_w^{sat}} \quad \text{avec} \quad \Delta U_w = \Delta H_w - R \cdot T \quad (37)$$

with  $\Delta U_w$ , energy of water vaporization (to zero pressure)

For a better high temperature dependence the following correction is used:

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

The Henry's law constants for the different gas are taken from the literature [43] and are fitted using the correlation below (table VIII):

$$\log_{10}(H_{(1)(2)}(T)) = A + B/T + C \times \log_{10}(T) + D \times T \quad (H \text{ in atm}) \quad (39)$$

The NRTL model [44] is used to calculate the water activity with  $\tau_{1,2}=3100$  and  $\tau_{2,1}=2800$  and  $\alpha_{1,2} = 0,3$ .

The experimental VLE data are correlated by means of in-house software, developed by Ecole des Mines de Paris.

$k_{i,j}$ , is adjusted directly to VLE data through a modified Simplex algorithm [12] using the objective function:

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

where  $N$  is the number of data points,  $y_{exp}$  is the measured water mole fraction in gas phase and  $y_{cal}$  is the calculated water mole fraction in gas phase.

The BIAS values on vapor phase mole fractions defined by equation 41 are listed in tables IX to XV for each system:

$$BIAS = (100 / N) \sum \left( (Y_{i,exp} - Y_{i,cal}) / Y_{i,exp} \right) \quad (41)$$

### 3.2 Results

Depending of the quality of the experimental data, these specific generalized alpha functions with three parameters represent accurately the VLE calculation.

For the methane –water system (table IX), the three alpha function give close results. In the case of the ethane-water system, in the subcritical region the 3 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. However it could be noticed that the new alpha function leads to better bias. For propane- water system, the results are quite identical. For this system, the water- sulfur dioxide and the water-butane system , it could be noticed that, a discontinuity in the binary parameter is observed by the passage

from subcritical state to supercritical state (figure3). For carbon dioxide and nitrogen, the different sets of isotherms are accurately represented.

### **Conclusion.**

As Mathias-Copeman, this new alpha function with three parameters represents accurately the pure component vapor pressure. Particularly in the case of water this specific generalized alpha function improve the vapor pressure calculation abilities of the PR EoS. The means absolute deviations are smaller than those with the other specific generalized functions. Even for the totality of the selected components this function is more successful.

In vapor-liquid calculation involving supercritical components this alpha function produces reliable prediction equivalent to those produced by the Trebble-Bishnoi function. However in the case of light hydrocarbons a better bias is observed with the new alpha function. This function is successful in classical VLE calculation.

### List of symbols:

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

### Greek letters:

$\alpha_{ij}$	NRTL model parameter
$\tau_{ij}$	NRTL model binary interaction parameter [J/mol]
$\omega$	Acentric factor
$\Delta$	Deviation

### Superscript

E	Excess property
Ref	reference property
L	Liquid state
V	Vapor state
Sat	Property at saturation
$\infty$	Infinite dilution

### Subscripts

C	Critical property
cal	Calculated property
exp	Experimental property
$i,j$	Molecular species
$\infty$	Infinite pressure reference state
(1)	Water
(2)	Gas
T	Total

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Table I :Temperature dependence of alpha functions and generalization

<i>Functions</i>	<i>Generalization</i>	<i>References</i>
$\alpha = [1 + m(1 - T_R^{1/2})]^2$	For SRK Eos $m = 0.480 + 1.574 \omega - 0.175 \omega^2$	Soave [1]
	For SRK EoS $m = 0.47830 + 1.6337 \omega - 0.3170 \omega^2 + 0.760 \omega^3$ For PR EoS $m = 0.374640 + 1.542260 \omega - 0.26992 \omega^2$	Soave [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. $m = 0.480 + 1.574 \omega - 0.175 \omega^2$	Stryjek and Vera [4]
if $T < T_C$ $\alpha = [1 + c_1(1 - T_R^{1/2}) + c_2(1 - T_R^{1/2})^2 + c_3(1 - T_R^{1/2})^3]^2$ if $T > T_C$ $\alpha = [1 + c_1(1 - T_R^{1/2})]^2$		Mathias and Copeman [5]
$\exp [m \times (1 - T_r)]$	$m = 0.418 + 1.58 \omega - 0.580 \omega^2$ when $\omega < 0.4$ $m = 0.212 + 2.2 \omega - 0.831 \omega^2$ when $\omega \geq 0.4$	Daridon et al [6]
$\alpha(T) = \alpha^{(0)}(T) + \omega(\alpha^{(1)}(T) - \alpha^{(0)}(T))$ with $\alpha(T) = T_R^{N(M-1)} [\exp(-L(1 - T_R^{NM}))]$		Twu et al. [7]

Table II: Mathias-Copeman alpha parameters for the SRK EoS and PR EoS

<i>Component</i>	<i>P<sub>c</sub> (Pa)</i>	<i>T<sub>c</sub> (K)</i>	<i>ω</i>	<i>C<sub>1</sub>(SRK)</i>	<i>C<sub>2</sub>(SRK)</i>	<i>C<sub>3</sub>(SRK)</i>	<i>C<sub>1</sub>(PR)</i>	<i>C<sub>2</sub>(PR)</i>	<i>C<sub>3</sub>(PR)</i>
Hydrogen	1296960	33.19	-0.2160	0.161	-0.225	-0.232	0.0948721	-0.275148	-0.0293089
Methane	4600155	190.564	0.0110	0.549	-0.409	0.603	0.415742	-0.172651	0.348424
Oxygen	5080435.5	154.58	0.0222	0.545	-0.235	0.292	0.412931	-0.0171321	0.0917141
Nitrogen	3394387.5	126.2	0.0377	0.584	-0.396	0.736	0.448322	-0.156813	0.468652
Ethylene	5041628.025	282.35	0.0865	0.652	-0.315	0.563	0.511967	-0.0870728	0.349025
Sulfur dioxide	8936865	373.53	0.0942	0.641	-0.183	0.513	0.507354	0.0075766	0.342291
Ethane	4883865	305.32	0.0995	0.711	-0.573	0.894	0.531245	-0.0618124	0.214238
Propane	4245517.5	369.95	0.1523	0.775	-0.476	0.815	0.600066	-0.0063038	0.173899
Isobutane	3639594	408.8	0.1808	0.807	-0.432	0.910	0.652444	-0.149356	0.599234
n-Butane	3799687.5	425.15	0.2002	0.823	-0.267	0.402	0.677341	-0.0810913	0.298538
Cyclohexane	4073001.6	553.58	0.2096	0.860	-0.566	1.3751	0.68359	-0.0887233	0.549514
Benzene	4895000.6	562.05	0.2103	0.840	-0.389	0.917	0.701169	-0.25207	0.976107
Carbon dioxide	7377000	304.21	0.2236	0.867	-0.674	2.471	0.704606	-0.314862	1.89083
Isopentane	3381002.5	460.43	0.2275	0.876	-0.386	0.660	0.723543	-0.166075	0.514866
Pentane	3369056.25	469.7	0.2515	0.901	-0.305	0.542	0.762864	-0.224305	0.669507
Ammonia	11287600	405.65	0.2526	0.916	-0.369	0.417	0.748279	-0.0253527	0.0013571
Toluene	4107999.2	591.75	0.2640	0.923	-0.301	0.494	0.761717	-0.0419637	0.27072
Hexane	3014418.75	507.4	0.3013	1.005	-0.591	1.203	0.870257	-0.587964	1.50392
Acetone	4701003.8	508.2	0.3065	0.993	-0.322	0.265	0.821044	0.0063948	-0.0900398
Water	22055007.45	647.13	0.3449	1.095	-0.678	0.700	0.919263	-0.332035	0.317204
Heptane	2740000.3	540.2	0.3495	1.036	-0.258	0.488	0.877648	-0.0307285	0.301866
Octane	2490001.1	568.7	0.3996	1.150	-0.587	1.096	0.958273	-0.134073	0.48666

Table III : Comparison of pure component vapor pressure using the SRK EoS

<i>Component</i>	MC generalized alpha function		Soave alpha function	
	Biais %	AAD %	Biais %	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
Sulfur dioxide	-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 dioxide	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
<b>Overall</b>	<b>0.4</b>	<b>1.42</b>	<b>2.69</b>	<b>3.37</b>

Table IV: Alpha parameters for the new alpha function

<i>Component</i>	$C_1$	$C_2$	$C_3$	$F (\times 10^4)$
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
Sulfur dioxide	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 dioxide	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

Table V : Comparison of pure component vapor pressure using the PR EoS

<i>Component</i>	Soave generalized		M-C generalized		New alpha generalized	
	Biais %	AAD %	Biais %	AAD %	Biais %	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
Sulfur dioxide	-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 dioxide	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
<b>Water</b>	<b>3.30</b>	<b>4.28</b>	<b>5.27</b>	<b>6.00</b>	<b>4.07</b>	<b>4.95</b>
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
<b>Overall</b>	<b>-1.21</b>	<b>2.11</b>	<b>0.47</b>	<b>1.22</b>	<b>0.01</b>	<b>1.19</b>

Table VI: Comparison of pure component vapor pressure using the PR EoS

<i>Component</i>	TB generalized		M-C generalized		New alpha generalized	
	Biais %	AAD %	Biais %	AAD %	Biais %	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
Sulfur dioxide	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
<b><i>Water</i></b>	<b><i>0.75</i></b>	<b><i>1.16</i></b>	<b><i>0.28</i></b>	<b><i>0.44</i></b>	<b><i>0.02</i></b>	<b><i>0.44</i></b>
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
<b>Overall</b>	<b>-0.59</b>	<b>3.30</b>	<b>0.14</b>	<b>0.80</b>	<b>0.11</b>	<b>0.80</b>

Table VII: Source of vapor-liquid equilibrium data for water – gas mixture

<i>Component</i>	<i>Reference</i>	<i>T<sub>min</sub></i> <i>(Kelvin)</i>	<i>T<sub>max</sub></i> <i>(Kelvin)</i>	<i>P<sub>min</sub></i> <i>(MPa)</i>	<i>P<sub>max</sub></i> <i>(MPa)</i>
Methane	Chapoy et al (2003) [13]	283.08	318.12	1	34.5
	Althaus (1999) [14]	253.15	293.15	0.5	10
	Gillepsie et al (1982) [15]	323.15	588.70	1.4	13.8
	Rigby (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 (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 et al (1971) [22]	298.15	373.15	2.3	3.6
	Culberson (1951) [23]	310.93	310.93	4.2	12
	Reamer et al (1943) [24]	310.93	510.93	2.2	68.2
Propane	Klausutis (1968) [25]	310.93	310.93	0.545	1.31
	Kobayashi et al (1953) [26]	310.93	422.04	0.703	19.33
n-Butane	Brooks et al (1951) [27]	310.93	377.59	7.27	68.36
	Reamer et al (1952) [28]	310.93	510.93	0.14	68.95
Carbon dioxide	Takenouchi S et al 1964[29]	383.15	423.15	10	150
	Coan et al (1971) [22]	298.15	373.15	1.7	5.2
	Briones et al (1987) [30]	323.15	323.15	6.8	17.7
	Nakayama et al (1987) [31]	298.2	298.2	3.6	6.4
	Mueller 1983 [32]	373.15	413.15	0.3	3.2
	Wiebe et al (1941) [33]	298.15	348.15	0.1	70.9
	D'Souza et al (1988) [34]	323.15	348.15	10	15.2
	Dohrnet al (1993) [35]	323.15	323.15	10	30.1
Sidorov et al (1953) [36]	323.15	348.15	2.5	30.4	
Nitrogen	Maslennikova et al (1971) [37]	298.15	623.15	5.1	50.7
	Sidorov et al (1953) [36]	373.15	373.15	5.1	40.5
	Ugrozov et al (1996) [38]	310.15	310.15	1.4	13.8
Sulfur dioxide	Burgess et al. (1969) [39]	323.15	443.15	1.7	2.3
	Sellecket al (1952) [40]	310.93	444.26	0.7	20.7



Table VIII: Parameters for the Henry's Law constant correlation (Eq.37).

<i>Component</i>	<i>A</i>	<i>B</i> ( $\times 10^{-3}$ )	<i>C</i>	<i>D</i> ( $\times 10^3$ )	<i>T</i> <sub>min</sub> (Kelvin)	<i>T</i> <sub>max</sub> (Kelvin)
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

Table IX: Methane-Water System

<i>Reference</i>	<i>T (Kelvin)</i>	<i>kij TB</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij new alpha</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij MC</i>	<i>Fobj</i>	<i>BIAS (%)</i>
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 (1951) [15]	310.93	0.457	1.448	2.786	0.467	1.411	2.54	0.463	1.421	2.61
Rigby (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
Gillepsie et al (1982) [17]	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
	477.594	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
Yokoama 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) [19]	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) [20]	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

<i>Reference</i>	<i>T (Kelvin)</i>	<i>kij TB</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij new alpha</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij MC</i>	<i>Fobj</i>	<i>BIAS (%)</i>
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 et al (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 (1951) [23]	310.93	0.454	1.769	4.382	0.458	1.694	3.99	0.457	1.711	4.07
Reamer et al (1943) [24]	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

<i>Reference</i>	<i>T (Kelvin)</i>	<i>kij TB</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij new alpha</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij MC</i>	<i>Fobj</i>	<i>BIAS (%)</i>
Klausutis (1968) [25]	310.93	0.853	0.155	-0.173	0.897	0.168	-0.34	0.886	0.164	-0.32
Kobayashi et al (1953) [26]	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

<i>Reference</i>	<i>T (Kelvin)</i>	<i>kij TB</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij new alpha</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij</i>	<i>Fobj</i>	<i>BIAS (%)</i>
Brooks et al (1951) [27]	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) [28]	310.93	0.414	0.004	0.203	0.585	$7.3 \times 10^{-5}$	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

<i>Reference</i>	<i>T (Kelvin)</i>	<i>kij TB</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij new alpha</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij MC</i>	<i>Fobj</i>	<i>BIAS (%)</i>
Takenouchi et al 1964 [29]	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 et al (1971) [24]	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) [30]	323.15	0.182	0.030	0.05	0.188	0.030	-0.31	0.187	0.029	-0.26
Nakayama et al (1987) [31]	298.2	0.187	1.324	2.36	0.188	1.310	2.35	0.187	1.317	2.38
Mueller (1983) [32]	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 et al (1941) [33]	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) [34]	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
Dohmet al (1993) [35]	323.15	0.173	1.555	4.00	0.178	1.374	3.66	0.177	1.411	3.75
Sidorov et al (1953) [36]	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

<i>Reference</i>	<i>T (Kelvin)</i>	<i>kij TB</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij new alpha</i>	<i>Fobj</i>	<i>BIAS (%)</i>	<i>kij MC</i>	<i>Fobj</i>	<i>BIAS (%)</i>
Maslennikova et al (1971) [37]	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) [36]	373.15	0.433	0.008	-0.29	0.473	0.041	-0.78	0.028	0.481	-0.63
Ugrozov et al (1996) [38]	310.95	0.428	0.043	1.10	0.476	0.003	0.28	0.023	0.462	0.82

Table XV: Sulfur dioxide-water system

<i>Reference</i>	<i>T (Kelvin)</i>	<i>kij TB</i>	<i>Fobj (<math>\times 10^4</math>)</i>	<i>BIAS (%)</i>	<i>kij new alpha</i>	<i>Fobj (<math>\times 10^4</math>)</i>	<i>BIAS (%)</i>	<i>kij MC</i>	<i>Fobj (<math>\times 10^4</math>)</i>	<i>BIAS (%)</i>
Burgess et al. (1969) [39]	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
Sellecket al (1952) [40]	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



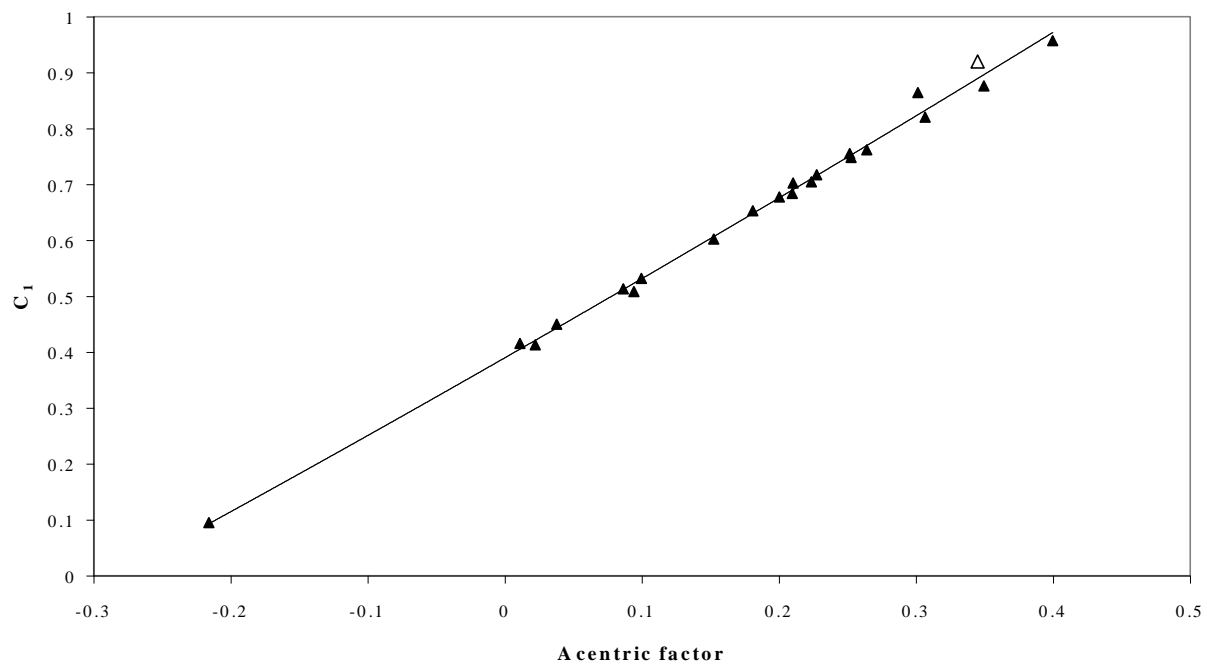


Figure 1: Mathias Copeman  $c_1$  parameter as a function of the acentric factor for the PR EoS

$\triangle$ :  $c_1$  parameter for water.

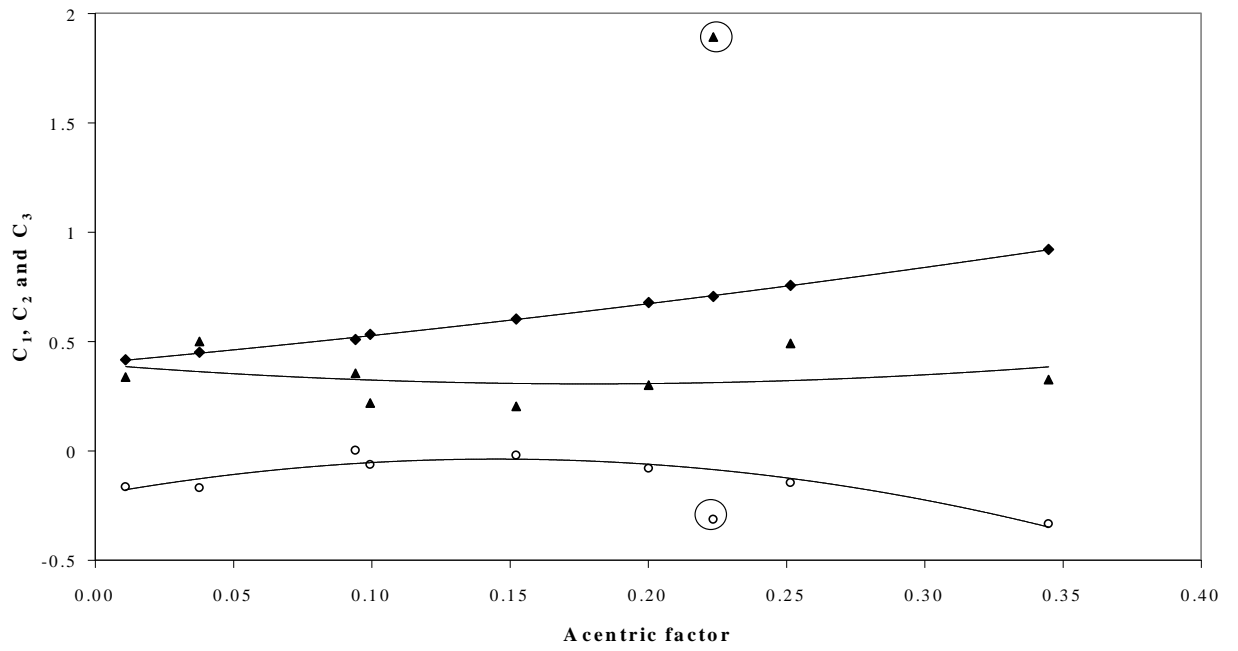


Figure 2: Mathias Copeman parameters as a function of the acentric factor for the PR EoS

for the selected components.

◆:  $c_1$  parameter

○:  $c_2$  parameter

▲:  $c_3$  parameter

Circled points are the  $c_2$  and  $c_3$  parameter for the carbon dioxide

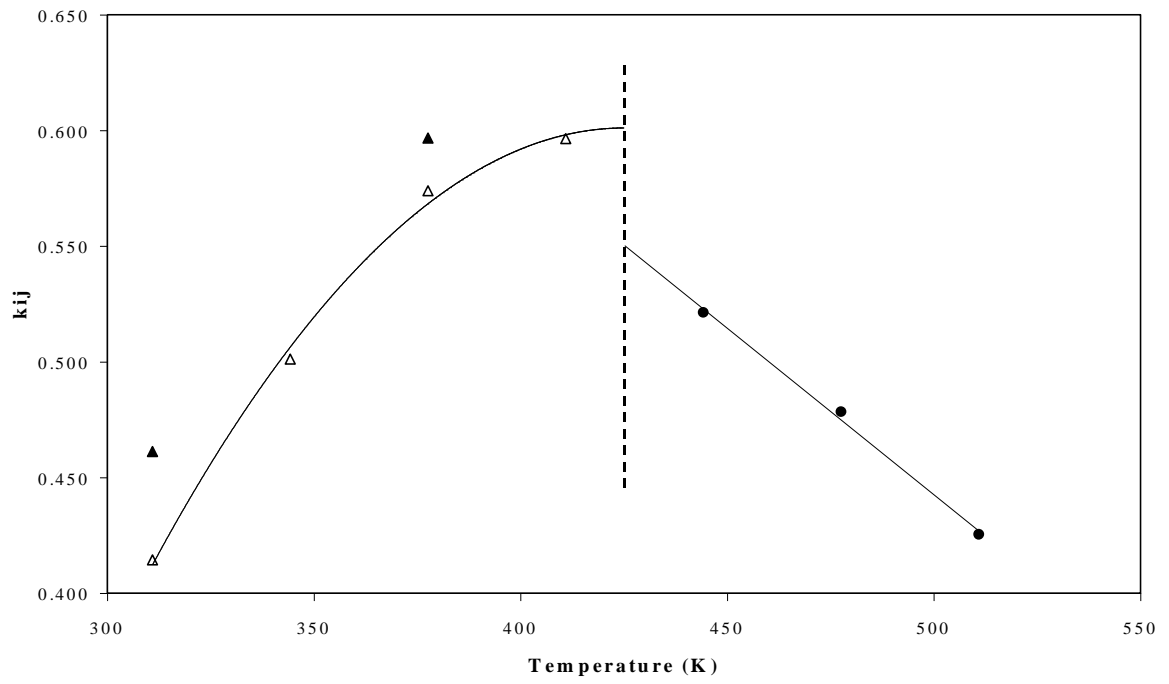


Figure 3: binary interaction parameter for the butane-water system.

●: supercritical parameters

▲, △ : subcritical parameters