

# Crossover soft-SAFT modelling of the $\text{CO}_2 + \text{NO}_2 / \text{N}_2\text{O}_4$ mixture

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## ABSTRACT

Accurate thermo-physical properties are mandatory for all industrial applications. However, experimental data are often scarce and models are needed for the estimation of properties. Such is the case in supercritical processes like the selective oxidation of vegetal macromolecules in mixture  $\text{NO}_2 / \text{N}_2\text{O}_4$  – supercritical  $\text{CO}_2$  aiming at producing body-degradable polymers readily usable for inside body surgery. The so-called crossover soft-SAFT equation of state is used to model the pure compounds and the mixture. The quadrupolar effect is explicitly considered when modeling carbon dioxide, obtaining excellent agreement for the whole phase equilibrium diagram.  $\text{NO}_2$  is modeled as a self associating molecule with a single association site. Finally,  $\text{CO}_2$  and  $\text{NO}_2$  pure compound parameters are used to predict the vapor – liquid coexistence of the  $\text{CO}_2 + \text{NO}_2 / \text{N}_2\text{O}_4$  mixture at different temperatures. Experimental pressure –  $\text{CO}_2$  mass fraction isotherms recently measured are used for comparison. Good agreement is obtained with the use of a unique binary parameter, independent of thermodynamic conditions, although more experimental data would be useful to conclude about the accuracy of the calculation.

**Keywords:** soft-SAFT, crossover, reacting systems,  $\text{CO}_2$ ,  $\text{NO}_2 / \text{N}_2\text{O}_4$

## INTRODUCTION

The capability of some supercritical fluids to replace toxic industrial solvents, the ability of tuning solvent characteristics for highly specific separation or reactions and the possibility to make new materials at mild conditions, are the main considerations which lead to the current industrial and scientific interest in supercritical fluids. Supercritical and fractionation of petroleum are both good examples [1]. Even though experimental data is always preferred, this information is often scarce and it does not cover all mixtures and operating conditions, thus inducing a persistent effort to derive accurate thermodynamic models. When classical Equations of State (EoS) describe quite well the thermodynamic properties of fluids far from the critical point, they drastically fail near the critical region where a specific treatment is required.

The statistical associating fluid theory [2-5] is a very successful approach to describe the phase behavior and the thermodynamic properties of complex fluids. Based on Wertheim's first order perturbation theory [6-8], the theory has been used to predict the phase

behavior of several pure components and mixtures in a broad range of thermodynamics conditions [4] and it is becoming a standard equation for engineering purposes.

The objective of this paper is to check the accuracy of the soft-SAFT EoS for describing the vapour-liquid equilibrium diagrams and association of the  $\text{CO}_2 + \text{NO}_2 / \text{N}_2\text{O}_4$  mixture. The prediction of the vapour – liquid equilibrium of this mixture is of utmost importance to correctly assess the  $\text{NO}_2$  monomer amount that is the oxidizing agent of vegetal macromolecules in the  $\text{CO}_2 + \text{NO}_2 / \text{N}_2\text{O}_4$  reacting medium. Such a mixture is the reacting media in a novel process where body-degradable polymers readily usable for inside body surgery treatment are produced through the oxidation of polysaccharides and cellulose macromolecules by  $\text{NO}_2/\text{N}_2\text{O}_4$  in a reactor where  $\text{CO}_2$  is present in excess under supercritical conditions [9].

The oxides of nitrogen are worth interest, notably for their occurrence in biological and environmental chemistry. Nitrogen dioxide ( $\text{NO}_2$ ) is notoriously known to self associate in the liquid phase to produce dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) according to Equation 1. In the liquid phase,  $\text{N}_2\text{O}_4$  can also isomerizes [12]. In this work  $\text{NO}_2$  is modeled as a self associating molecule with a single association site to account for the strong associating character of the  $\text{NO}_2$  molecule. The dissociation reaction to be considered is:



The approach used in this work concerns the use a molecular based equation of state, namely the soft-SAFT EoS, developed by Blas and Vega [10-11] taking into account the treatment near the critical region using the crossover version of soft-SAFT [12-13] to investigate the phase behavior of pure  $\text{CO}_2$ ,  $\text{NO}_2$  and their mixtures in the whole temperature range they are concerned with.

## THE CROSSOVER SOFT-SAFT EOS

The soft-SAFT EoS is a variant of the original SAFT equation proposed by Chapman and co-workers [2-3] and Huang and Radosz [4]. SAFT-type equations of state are written in terms of the residual Helmholtz energy:

$$a^{res}(T, P, N) = a(T, P, N) - a^{id}(T, P, N) \quad (2)$$

Where  $a(T, V, N)$  and  $a^{ideal}(T, V, N)$  are the total Helmholtz energy per mole and the ideal gas Helmholtz energy per mole at the same temperature and density, respectively. The residual Helmholtz energy is the sum of the microscopic contributions to the total free energy of the fluid, where each term in the equation represents different microscopic contributions to the total free energy of the fluid:

$$a^{res} = a^{LJ} + a^{chaune} + a^{assoc} + a^{quad} \quad (3)$$

The main difference between the soft-SAFT [10-11] equation and the original equation [2-3] is the use of the Lennard–Jones (LJ) intermolecular potential for the reference fluid (with dispersive and repulsive forces into the same term), instead of the perturbation scheme based on a hard-sphere reference fluid plus dispersive contributions to it that was originally proposed. This difference also appears in the chain and association term, since both terms use

the radial distribution function of the reference fluid. The accurate LJ EoS of Johnson et al. [14] is used for the reference term.

The chain term in the equation comes from Wertheim's theory, and it is formally identical in the different versions of SAFT. In our case, it is expressed as:

$$a^{chain} = k_B T \sum_i x_i (1 - m_i) \ln g_{LJ} \quad (4)$$

Where  $\rho$  is the molecular density of the fluid,  $T$  is the temperature and  $k_B$  is the Boltzmann constant. In the soft-SAFT case, it is applied to tangent LJ spheres of chain length  $m$  that are computed following the pair correlation function  $g_{LJ}$ , evaluated at the bond length  $\sigma$ .

The association term comes from the first-order Wertheim's TPT for associating fluids. The Helmholtz free energy change due to association is calculated from the following equation:

$$a^{assoc} = k_B T \sum_i x_i \sum_{\alpha} \left( \ln X_i^{\alpha} - \frac{X_i^{\alpha}}{2} \right) + \frac{M_i}{2} \quad (5)$$

Where  $M_i$  is the number of associating sites of component  $i$  and  $X_i^{\alpha}$  the mole fraction of component  $i$  not bonded at site  $\alpha$  which accounts for the contributions of all associating sites in each species:

$$X_i^{\alpha} = \frac{1}{1 + N_{avog} \rho \sum_j x_j \sum_{\beta} X_j^{\beta} \Delta^{\alpha\beta_j}} \quad (6)$$

The extension of the equation to polar systems is done by adding a new contribution that consists in a perturbed polar term proposed by Gubbins and Twu [15].

$$a^{qq} = a_2^{qq} \left[ \frac{1}{1 - \left( \frac{a_3^{qq}}{a_2^{qq}} \right)} \right] \quad (7)$$

Expressions for  $a_2^{qq}$  and  $a_3^{qq}$ , the second and third-order perturbation terms, were derived for an arbitrary intermolecular reference potential and can be found in the original papers [16-17]. These expressions include the quadrupolar moment of the molecule ( $Q$  for the quadrupole case, which we consider in this work [18]), whose value is taken from experimental measurements.

Llovel et al [12-13] have recently proposed an extension of the equation by the addition of a crossover treatment to take into account the contribution of the long-wavelength density fluctuations in the near critical region, which we have called crossover soft-SAFT EoS. Based on White's work [18], from the Wilson's renormalization group theory [19], this term is implemented by using recursive relations where the density fluctuations are successively

incorporated. The Helmholtz energy density of a system at density  $\rho$  can be described in recursive manner as:

$$a^{total} = \sum_{n=1}^{\infty} a_n(\rho) = \sum_{n=1}^{\infty} [a_{n-1}(\rho) + da_n(\rho)] \quad (8)$$

Where  $a_n$  is the Helmholtz energy density and  $da_n$  the term where long wavelength fluctuations are accounted for in the following way:

$$da_n(\rho) = -K_n \frac{\Omega^s(\rho)}{\Omega^l(\rho)} \quad (9)$$

Where  $\Omega^s$  and  $\Omega^l$  represent the density fluctuations for the short-range and the long-range attraction respectively, and  $K_n$  is a coefficient that depends on the temperature and the cut off length:

$$K_n = \frac{k_B T}{2^{3n} \cdot L^3} \quad (10)$$

$$\Omega_n^\beta(\rho) = \int_0^\rho \exp\left(\frac{-G_n^\beta(\rho, x)}{K_n}\right) dx \quad (11)$$

$$G_n^\beta(\rho, x) = \frac{\bar{a}_n^\beta(\rho + x) + \bar{a}_n^\beta(\rho - x) - 2\bar{a}_n^\beta(\rho)}{2} \quad (12)$$

The superindex  $\beta$  refers to both long ( $l$ ) and short ( $s$ ) range attraction, respectively, and  $G^\beta$  is a function that depends on the evaluation of the function  $\bar{a}$ , calculated as:

$$\bar{a}_n^l(\rho) = a_{n-1}(\rho) + \alpha \cdot (m \cdot \rho)^2 \quad (13)$$

$$\bar{a}_n^s(\rho) = a_{n-1}(\rho) + \alpha \cdot (m \cdot \rho)^2 \cdot \frac{\phi \cdot w^2}{2^{2n+1} \cdot L^2} \quad (14)$$

Where  $m$  is the chain length (number of LJ segments forming the chain),  $\phi$  is an adjustable parameter,  $\alpha$  is the interaction volume with units of energy-volume, and  $w$  refers to the range of the attractive potential.

We have used this generalized equation soft-SAFT with crossover along the present work.

## RESULTS

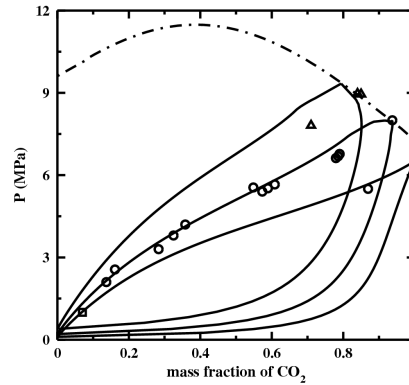
In this work the CO<sub>2</sub> molecule is modeled as a fully flexible LJ chain of length  $m$ , where the quadrupole was explicitly taken into account. The molecular parameters are:  $m$ , the chain length;  $\sigma$ , the size parameter;  $\varepsilon$ , the energy parameter, the quadrupolar moment  $Q$  and the  $x_p$  fraction of segments that contains the quadrupole ( $x_p = 1/3$ ). NO<sub>2</sub> was also modeled as a fully flexible LJ chain of length  $m$ , with  $\sigma$  and  $\varepsilon$  as the size and energy parameters, respectively; to mimic the strong associating character of this fluid, an associating site was also included in this case, with two additional parameters,  $\varepsilon^{HB}$  and  $\kappa^{HB}$ , representing the

energy and volume of association per site located in the N atom. From the observations of Huang and Radosz [4] about the relation between the association strength  $\epsilon^{HB}$  and volume  $\kappa^{HB}$  value,  $\text{NO}_2$  can be classified as a strong associating fluid, in agreement with experimental observations. In our modeling approach this translates into a large  $\epsilon^{HB}$  value and a small  $\kappa^{HB}$  value. The association volume is significantly smaller than for moderately associating fluids (alkanols) modeled with the soft-SAFT equation [13]. Contrary to the association in alkanols, or even in carboxylic acid dimers that corresponds to loose hydrogen bonds from 2.1 to 2.8 Å, chemical association in the  $\text{NO}_2$  corresponds to a shorter and stronger bond (1.78 Å according to Chesnut and Crumbliss [20]). The crossover parameters  $\phi$  and  $L$ , are enough to describe all thermodynamic properties of the pure components. The molecular parameters are summarized in table 1.

**Table 1:** crossover soft-SAFT optimized parameters for the compounds.

	$m$	$\sigma$ (Å)	$\epsilon/k_B$ (K)	$\Phi$	$L$	$Q$ (C.m <sup>2</sup> )	$\epsilon^{HB}/k_B$ (K)	$\kappa^{HB}$ (Å <sup>3</sup> )	$T_{range}$ (K)	% AAD $P_{vap}$	% AAD $\rho$
$\text{CO}_2$	1.606	3.174	158.5	5.70	1.130	$4.4 \cdot 10^{-40}$	-	-	220-290	0.61	0.94
$\text{NO}_2$	1.295	3.200	247.8	6.50	1.172	-	6681	1.0	294-420	0.35	0.22

Belkadi et al. [21] give more detailed results by presenting the curves of the vapour – liquid equilibrium of  $\text{CO}_2$  and  $\text{NO}_2/\text{N}_2\text{O}_4$  with and without crossover treatment. A good agreement was observed comparing with the experimental data. As stated, an advantage of using the crossover soft-SAFT equation versus a classical equation without a crossover treatment is that the same set of parameters can be used to describe equally well the regions of the phase diagram far from and close to the critical point.



**Figure 3** Pressure –  $\text{CO}_2$  mass fraction diagram of the  $\text{CO}_2 + (\text{NO}_2 / \text{N}_2\text{O}_4)$  mixture at three different temperatures. Symbols are experimental data [25] at ( $\square$ ) 298.15K, ( $\circ$ ) 313.15K and ( $\Delta$ ) 328.45K, while the lines are crossover soft-SAFT predictions. The top line indicates the calculated critical line.

The phase behaviour of the mixture  $\text{CO}_2 + \text{NO}_2/\text{N}_2\text{O}_4$  is shown in Figure 3. It depicts the pressure–mass fraction of  $\text{CO}_2$  projection of the phase diagram of this mixture predicted by the use of the crossover soft-SAFT equation and compared to available experimental data [22]. We note that the prediction is done with the use of a unique binary parameter  $\zeta_{ij}$  introduced by fitting the experimental data of the isotherm at 313K (which is the only one

with enough experimental information to perform satisfactory regression). The dotted-dashed line represents the predicted critical line. All calculations of the isotherms were done with the mass fraction of CO<sub>2</sub> not as usually done with the molar fraction. For such systems containing reacting system it is better to use the monomer as a reference molecule and its non bonded fraction in the mixture X, in our case provided by the crossover soft-SAFT EoS.

## CONCLUSION

We have applied the crossover soft-SAFT EoS to describe the CO<sub>2</sub> + NO<sub>2</sub> / N<sub>2</sub>O<sub>4</sub> vapor – liquid equilibrium properties at subcritical and supercritical conditions. The quadrupolar interactions were explicitly considered. NO<sub>2</sub> was treated as a self associating compound with a single association site. Compared to other self associating fluids, the large  $\epsilon^{HB}$  and small  $\kappa^{HB}$  optimized values defined NO<sub>2</sub> as a strong associating fluid, in agreement with the experimental observations. The association volume  $\kappa^{HB}$  found is significantly smaller than that used for moderately associating fluids (alkanols) modeled with the same crossover soft-SAFT equation [13]. The need of a unique binary parameter  $\zeta_{ij}$  to describe this complicated mixture at several temperatures shows the capability of the equation to model complex mixtures near to and far from the critical region.

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