# EQUATION OF STATE DEVELOPMENT

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The aim of this work is to develop an equation of state that is simple enough for use in the process simulation of the supercritical fractionation of oligomer mixtures, whilst maintaining a satisfactory degree of accuracy close to the mixture critical point.

Two statistical mechanics approaches, the Perturbed Hard Chain Theory and Statistical Associating Fluid Theory, were used to extend the original Patel Teja EOS to mixtures with a high degree of asymmetry between the components.

It is shown that the chained Patel Teja equations are successful in modelling pure n-alkane saturated data using only 2 chaining parameters, and compare favourably with the more complex statistical mechanical equations when representing supercritical solvent – n-alkane phase equilibrium data.

## INTRODUCTION

Supercritical fractionation as a means of producing narrow molecular weight fractions from heat labile oligomer mixtures is currently under investigation [1].  For this purpose an accurate mathematical description of the process system is required to enable process modelling, design and optimisation.

The equations of state (EOS) currently available to model these extraction processes are either too computationally intensive, and thus unsuitable for use in routine process modelling, or lack the required accuracy in the desired operating range (at high pressures near the mixture critical point), requiring a large dataset of experimental work to fit the equations and introducing a high degree of uncertainty in the calculations.

The two types of EOS, which lend themselves to multi-component phase equilibrium modelling, are the traditional empirical Van der Waals type equations and the equations derived from statistical mechanical theories.  The Van der Waals type equations are normally cubic in volume and have a simple mathematical form, facilitating the rapid calculations of phase equilibria and other thermodynamic properties.  Although these equations are empirical in nature, they are quite accurate in representing systems with small spherical molecules with no complex intermolecular forces, such as association or dipole forces.  The theoretically based statistical mechanical EOS on the other hand have been specifically developed to incorporate non-idealities such as association and structural complexity of the fluid system, but are mathematically intensive.

In this work we investigate the effect of extending the application of a Van der Waals type EOS to chained molecules by using the PHCT and SAFT approaches.  The performance of an EOS is evaluated by comparing the phase equilibrium predictions with equilibrium data for high asymmetrical alkane-alkane systems.

## SELECTION OF VAN DER WAALS TYPE EOS

As the starting point for the EOS development the selected Van der Waals (VDW) type EOS, needs to be able to represent the low molecular weight pure components accurately in the PVT region of interest.

As reported previously [2], it was found that the all Van der Waals type EOS experience some difficulty in representing the PVT behaviour of a supercritical pure component such as ethane. It was found to be necessary to relax the restriction that the EOS has to pass through the pure component critical point, in order to successfully model supercritical ethane.

The fitting of the EOS parameters could be interpreted as effectively moving the component critical point to a pseudo value in the PVT space. A two parameter EOS such as the Peng-Robinson equation with fixed critical compressibility would therefore not be as effective in modelling the supercritical data as a three parameter EOS with a completely mobile pseudo critical point. The Patel-Teja, PT, EOS [3] was selected as a suitable 3 parameter EOS.

A different functional form was used for the EOS temperature dependence than in the original PT EOS, in order to ensure the correct behaviour of the attractive term at temperature extremes.

$$P = \frac{RT}{v-b} - \frac{a.f\left(\widetilde{T}\right)}{v(v+b)+c(v-b)} \tag{1}$$

$$f(\widetilde{T}) = \exp(C1(1-\widetilde{T}^{C2})) \tag{2}$$

In these equations $\widetilde{T}$ is a reduced temperature, and the remaining parameters retain their original definitions.

## CHAINING THE VAN DER WAALS TYPE EOS

The next step in the EOS development is to extend the equation to chained molecules. Two approaches were followed and are discussed separately:

*PERTURBED HARD CHAIN APPROACH*

Beret and Prausnitz [4] and Donohue and Prausnitz [5] used the generalised Van der Waals partition function and the assumptions of Prigogine [6] to develop the PHCT. Sako et al [7] utilised the same approach to develop a chained equation based on the 2-parameter SRK EOS.

For spherical molecules only the translational motions are influenced by the system density, and need to be represented in an equation of state. However, with chained molecules the rotational and vibrational movements are also density dependent and need to be taken into account when describing the system. Prigogine [6] made the assumption that the density dependent rotational and vibrational contributions to the configurational integral could be assumed to be equivalent to the translational contributions.

Using a similar approach with the PT EOS as base equation, a chained EOS was developed [2]. (The *ch* term is the chaining term or shape parameter and the rest of the parameters have the same meaning as in the original PT EOS.)

$$P = \frac{RT(v+(ch-1)b)}{v(v-b)} - \frac{a(T)}{v(v+b)+c(v-b)} \tag{3}$$

Each pure component is seen as comprising of a chain of *r* equal segments. The equation parameters can be determined from the base segment parameters (indicated by an apostrophe ′):

$$a(T) = r^2 \cdot a' = r^2 \cdot (a'_0 \cdot f'(\tilde{T}))$$

$$b = r \cdot b' \quad c = r \cdot c' \tag{4}$$

$$\tilde{T} = ch \cdot kT/e \quad e = r \cdot e'$$

*k* is the botzman constant and *e'* a measure of the system potential energy, the temperature dependence of the *a* parameter, $f'(\tilde{T})$, is similar to equation 2.

Using ethane as building block for a chained alkane, the segment parameters *a', b', c'* and *e'* as well as the $f'(\tilde{T})$ parameters *C1* and *C2* were determined by fitting the EOS to ethane PVT data in the range 60-100 bar and 315-355 K and saturated VLE data from 276 K, whilst setting the chaining parameters *ch* and *r* equal to 1. The chaining parameters for higher molecular weight alkanes were then determined by fitting the EOS to vapour pressure and liquid density data using the ethane segment parameters. It was found that the chaining parameters are linear functions of the n-alkane carbon numbers [2].

*STATISTICAL ASSOCIATING FLUID THEORY*

The SAFT approach, developed by Chapman [8,9], is based on the perturbation theory, and gives Helmholtz energy expressions for the association and chain formation effects based on a series of papers by Wertheim [10-13] on resummed cluster expansion.

According to the SAFT approach the residual Helmholtz energy of a system may be expressed as follows: (The residual energy is here defined as the difference between the Helmholtz energy of the real system and that of an ideal gas at the same T and V.)

$$\frac{A^r(T,V)}{RT} = \frac{A^{Seg}(T,V)}{RT} + \frac{A^{Chain}(T,V)}{RT} + \frac{A^{Assoc}(T,V)}{RT} \tag{5}$$

For a non-associating system the *Assoc* term is zero. The *Seg* term represents the intermolecular attractive and repulsive forces between the segments. In this work the residual Helmholtz energies as derived from the base PT EOS were used. The *Chain* term represents the Helmholtz energy contribution due to the formation of chains by the molecular segments. As a first approximation it was assumed that the segments bonded together to form chains of tangent hard spheres. The *Chain* term could than be expressed as follows:

$$\frac{A^{Chain}(T,V)}{RT} = (1-m)\ln g^{HS}(\boldsymbol{s}) \tag{6}$$

Here *m* is the number of bonded segments in the chain, and $g^{HS}$ is the radial distribution function for hard spheres at the hard sphere diameter σ. The Carnahan Starling hard sphere radial distribution function was used. The reduced density is defined as $\eta = b/(4v)$ .

$$g^{HS}(\boldsymbol{s}) = g^{CS}(\boldsymbol{s}) = \frac{2-\boldsymbol{h}}{2(1-\boldsymbol{h})^3} \tag{7}$$

The complete residual Helmholtz energy expression for this PT_SAFT formulation can then be written as follows:

$$\frac{A^r(T,V)}{RT} = m\ln\left(\frac{1}{1-4h}\right) + \frac{a(T)}{4\sqrt{h^2+6hg+g^2}}\ln\left(\frac{0.5+(h+g)-\sqrt{h^2+6hg+g^2}}{0.5+(h+g)+\sqrt{h^2+6hg+g^2}}\right)$$

$$+ (1-m)\ln\left(\frac{2-h}{2(1-h)^3}\right) \tag{8}$$

With $a(T) = a(T)/(vRT)$ and $g = c/(4v)$. The equation parameters, *a*, *b* and *c*, can be determined from the base segment (indicated by an apostrophe $'$):

$$a(T) = m^2 \cdot a' = m^2 \cdot (a_0' \cdot f'(\tilde{T}))$$
$$b = m \cdot b' \quad c = m \cdot c' \tag{9}$$
$$\tilde{T} = \cdot kT/e$$

Temperature dependence, *f'(T),* is similar to equation 2.

Setting the chaining parameter *m* equal to 1, equation 8 reduces to the residual Helmholtz energy of the PT EOS. The segment parameters *a', b', c'* and temperature functionality parameters *C1* and *C2* were fitted to the same ethane data as used in perturbed hard chain section above. For high molecular weight alkanes the chaining parameter *m* and the energy parameter *e* were fitted to vapour pressure en liquid density data, using the ethane segment and temperature functionality parameters. The chaining parameter *m* was found to increase linearly with n-alkane carbon number, whilst the *e/k* parameter appears to asymptotically tend towards a constant value for high molecular weight alkanes.

## PURE COMPONENT PVT REPRESENTATION

The ability of the two chained Patel-Teja equations to represent n-alkane data is compared with the original PT [3], the SAFT EOS as derived by Huang and Radosz [14], and the simplified PHCT (SPHCT) as derived by Kim et al. [15]. EOS parameters used in these equations were used as published in the original papers, with the exception of the SPHCT where the pure component parameters published in [16] were used.
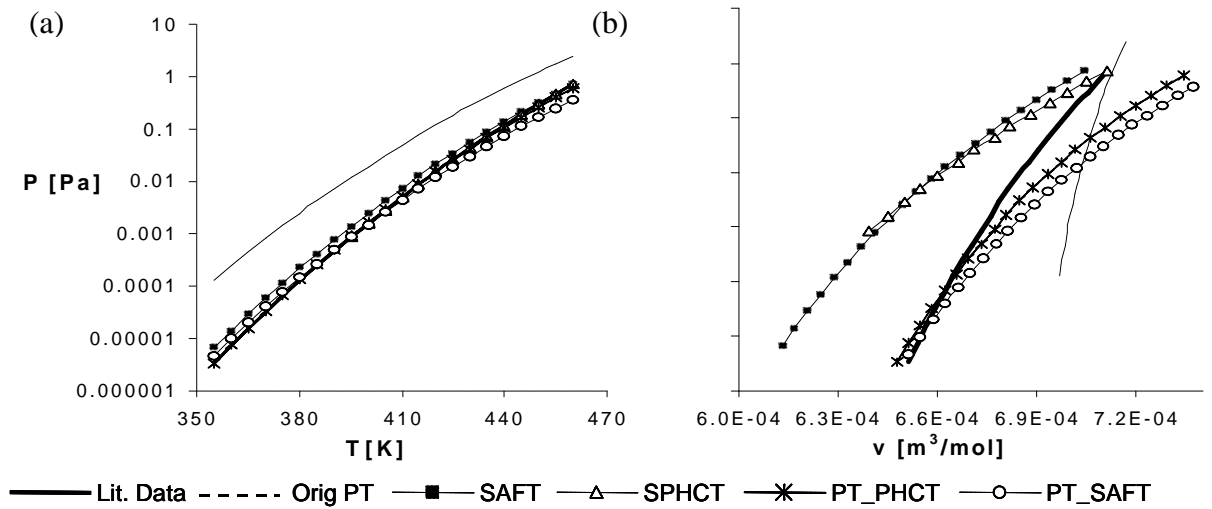


**Figure 1   n-C$_{36}$ saturated data. (a) P-T curve (b) Liquid P-V curve, on the same logarithmic pressure scale**

From figure 1(a) it is clear that the original PT is unable to represent the long-chain alkane vapour pressure data. Although the inaccuracy in the representation of the vapour pressure curve is fairly small, it appears as if the SAFT and PT_SAFT EOS are slightly less accurate than the equations based on the PHCT. This trend was also observed with the other n-alkane data sets investigated (n-$C_{16}$ to n-$C_{32}$). As can be seen from figure 1(b), it is clear that the saturated liquid volume curve still is not correctly represented although the chained PT EOS now have a more correct slope, when compared to the original form.

## BINARY MIXTURE P-x-y REPRESENTATION

In this section only the predictive abilities of the equations were investigated, i.e. no binary interaction parameters were fitted to experimental data.

A clear advantage of the chained PT equations is their simple mathematical form. For any spherical molecule in the mixture, the equations would reduce to the original PT form. The PT_PHCT equation is quartic in volume, and can therefore still be solved analytically. Unfortunately the use of the Carnahan-Starling radial distribution function raises the order of the PT_SAFT equation even higher. However, when applying the equation to mixtures, it is still much simpler that the original SAFT approach [14] where a complex expression for mixtures of hard spheres is used [9], and the perturbation term is a complex polynomial.

After fitting the PT_PHCT and PT_SAFT parameters to pure ethane and n-$C_{36}$ PVT data, the equations were then used to represent the ethane – n-$C_{36}$ high-pressure binary equilibria. It can be seen that these chained Van der Waals type EOS' performance compare favourably to the more mathematically intensive statistical mechanical equations.
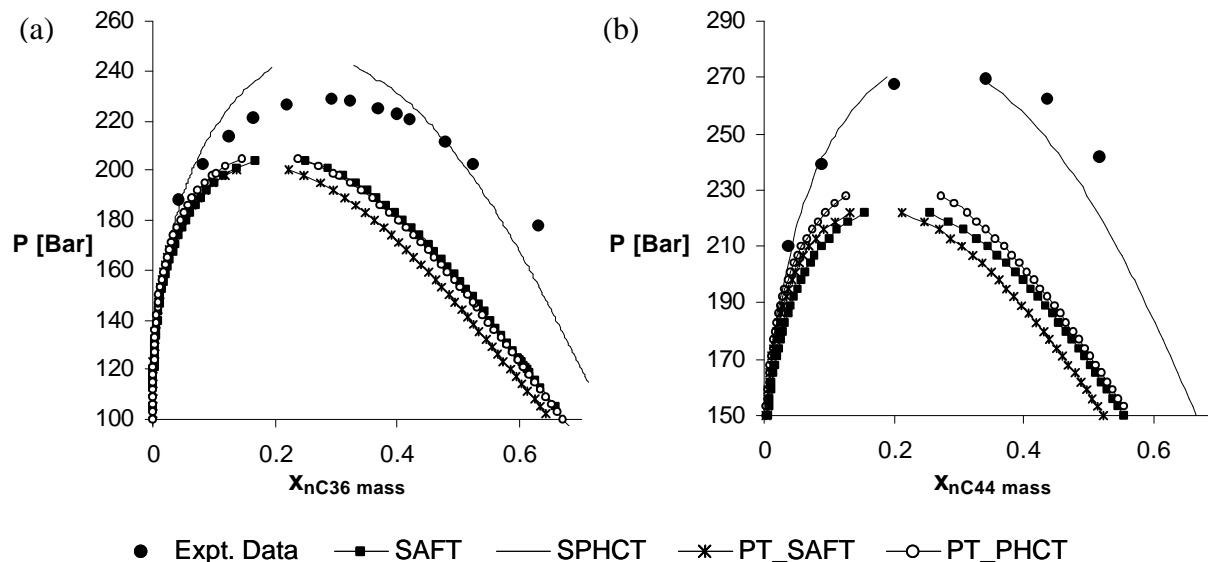


**Figure 2   (a) Ethane –n-$C_{36}$  and  (b) Ethane – n-$C_{44}$  experimental data and the EOS representation.**

The chaining parameters ($r$ and $ch$ for PT_PHCT  and  $m$ for PT_SAFT) displays a linear correlation with the n-alkane carbon number. It was possible to determine the parameters for n-$C_{44}$ from the parameters fitted to n-alkenes from n-$C_{16}$ to n-$C_{36}$. The strength of the correlation is shown in figure 2(b) where the PT_SAFT and PT_PHCT EOS are used with these extrapolated parameters, and still perform similarly to the SAFT with component

specific published parameters. Binary interaction parameters can be introduced to get the EOS to give a very good fit of the experimental data [2].

## CONCLUSIONS

It was shown that it is possible to extend the Patel-Teja equation of state, applicable to small spherical molecules, to chain molecules. These chained equations are able to accurately represent high molecular weight n-alkane vapour pressures, and are successful in modelling supercritical ethane – n-alkane binary mixtures.

The equations require only two component specific parameters, which show a strong linear dependence on chain length, and are mathematically much simpler than the statistical mechanics equations of state, resulting in much faster and more stable process simulations.

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