



# Generalization of SAFT + Cubic equation of state for predicting and correlating thermodynamic properties of heavy organic substances

Ilya Polishuk\*

Department of Chemical Engineering and Biotechnology, Ariel University Center of Samaria, 40700 Ariel, Israel

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## ABSTRACT

The current study proposes a scheme for generalizing parameters of SAFT + Cubic EoS (GSAFT + Cubic) for predicting and correlating thermodynamic properties of heavy (18 and more carbon atoms) organic substances and of ionic liquids. The accuracy of the proposed approach might usually be compared with the multi-parameter empirical Tait equation. However, unlike the latter one, it has a predictive character. In the cases of the substances included in the databanks such as DIPPR, GSAFT + Cubic requires input of a single experimental density datum point. In the cases of complex fluids, such as the heavy oils, the ionic liquids or the ester lubricants, the proposed approach requires input of two experimental points of density and estimation of the ideal gas heat capacity for predicting various auxiliary properties in wide *PVT* range. A major advantage of GSAFT + Cubic over the empirical correlations is its applicability for estimating phase equilibria and other thermodynamic properties of mixtures while using the one-fluid approach. In particular, it has been demonstrated that GSAFT + Cubic yields accurate predictions of the available VLE and LLE data of mixtures of the heavy *n*-alkanes and the ionic liquids.

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## 1. Introduction

The basic principle of engineering equations of state (EoS) models is utilization of the available data for estimating the unavailable ones. Consequently, significance of these models as predictive tools is defined not only by their accuracy, but also by the ratio between the input and the output information. For example, the Cubic EoS models typically require as an input just the experimental values of the pure compound critical temperatures, pressures and acentric factors. Although Cubic equations might sometimes be particularly imprecise, this small piece of the easily accessible input information versus the significant amount of the output data justifies their success in engineering practice.

The theoretically based models such as various versions of the Statistical Association Fluid Theory (SAFT) have doubtless advantages over the mostly empirical in nature Cubic equations [1,2]. Nevertheless, their values as predictive tools are affected by the need to evaluate their parameters on the basis of the relatively large amount of experimental information, such as vapor pressure curves and volumetric data. The latter practice not only requires application of sophisticated fitting procedures, but also restricts implementation of these models to the previously investigated

compounds. The predictive character of SAFT models can be enhanced by generalizing their parameters. Already the initial publications of the most popular versions of SAFT [3–5] have included simple parameter correlations evaluated for few groups of compounds as functions of molecular weight. Later on, several sophisticated group-contribution approaches for evaluating the SAFT parameters have been developed and they have been recently reviewed by Ref. [6].

Unlike most SAFT models and similarly to the majority of Cubic equations, three of the five parameters of the recently proposed SAFT + Cubic [7–12] are evaluated at the experimental pure compound critical points. However the remaining two parameters of this model are still fitted to the experimental vapor pressure and density data. Therefore in order to attach SAFT + Cubic by predictive character, the effective generalization schemes should be developed.

The current study aims at making initial steps in this direction while considering the heavy organic substances. Since most of these substances decompose already at the sub-critical temperatures, their critical constants usually have imaginary values. Thus, the actual data that might characterize such compounds are their molecular weights. However since the molecular weights do not reflect structural and chemical properties, they cannot serve as the only input information for approaches valid for various groups of compounds. At the same time, the successful and universal predictive schemes should relay on the easily accessible

\* Tel.: +972 3 9066346; fax: +972 3 9066323.

E-mail address: [polishuk@ariel.ac.il](mailto:polishuk@ariel.ac.il)

**List of symbols**

$a, c$	parameters of SAFT + Cubic EOS
$C_p, C_v$	isobaric and isochoric heat capacities
$d$	effective Lennard–Jones segment diameter (Å)
$g_{ii}(d_{ii})^{hs}$	Mansoori et al.'s correction function for mixtures of hard spheres
$m$	effective number of segments
$M_w$	molecular weight
$N_{av}$	Avogadro's number
$P$	pressure
$R$	universal gas constant
$T$	temperature
$v$	molar volume
$W$	speed of sound
$x$	molar fraction in the liquid phase
$y$	molar fraction in the vapor phase

**Greek letters**

$\varepsilon/k$	segment energy parameter divided by Boltzmann's constant
$\zeta_k$	Mansoori et al.'s correction functions for mixtures of hard spheres
$\eta$	reduced density
$\kappa_T, \kappa_s$	isothermal and isentropic compressibility factors
$\rho$	density
$\sigma$	Lennard–Jones temperature-independent segment diameter (Å)

**Subscripts**

$c$	critical state
$r$	reduced property

**Abbreviations**

EOS	equation of state
SAFT	Statistical Association Fluid Theory

input information. As known, the density data are available for numerous heavy compounds or, at least, they might be extrapolated from the similar substances. Consequently, the input of experimental or pseudo-experimental liquid phase density data at any known arbitrary conditions does not present a major difficulty or substantially affect the predictive character of the model. Thus it has been selected to include in the input information for the current predictive scheme the three following data:

- The molecular weight.
- The estimated imaginary critical temperature which can be obtained from the databases such as DIPPR.
- One experimental or estimated liquid phase density datum point.

In the cases of complex fluids the critical temperature might be replaced by a second experimental density datum point. The details of the proposed approach are given below.

**2. Theory**

For the non-associating compounds the SAFT+Cubic EoS is given as follows:

$$A^{res} = A^{hs} + A^{disp} + A^{chain} - \frac{a}{v+c} \quad (1)$$

where  $A$  is the Helmholtz free energy,  $v$  is the molar volume,  $a$  and  $c$  are the parameters of the cohesive correction term. The hard-sphere contribution is given as:

$$A^{HS} = RT \frac{m}{\zeta_0} \left( \frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left( \frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln[1-\zeta_3] \right) \sqrt{\frac{d^3(\zeta_3-1)}{\zeta_3\sigma^3-d^3}} \quad (2)$$

where

$$\zeta_k = \frac{\pi N_{av}}{6v} \sum_i x_i m_{ii} d_{ii}^k \quad (3)$$

$N_{av}$  is the Avogadro's number,  $m$  is the effective number of segments,  $d$  is the effective Lennard–Jones segment diameter,  $\sigma$  is Lennard–Jones temperature-independent segment diameter and:

$$d_{ii} = \sigma_{ii} \left( \frac{1 + 0.2977(k/\varepsilon)_{ii}T}{1 + 0.33163(k/\varepsilon)_{ii}T + 0.0010477(k/\varepsilon)_{ii}^2T^2} \right) \quad (4)$$

$\varepsilon$  is the inter-segment interaction's dispersion energy and  $k$  is Boltzmann's constant.

For pure compounds:

$$A^{HS} = mRT \frac{4\eta - 3\eta^2}{(1-\eta)^{3/2}(1-\eta(\sigma/d)^3)^{1/2}} \quad (5)$$

where  $\eta = \zeta_3$ .

The chain contribution is:

$$A^{chain} = RT \sum_{i,j} x_i x_j (1 - m_{ij}) \ln [g_{ij}(d_{ij})^{hs}] \quad (6)$$

where the segment radial distribution function given as:

$$g_{ij}(d_{ij})^{hs} = \frac{1}{1-\zeta_3} + \frac{3d_{ii}d_{jj}\zeta_2}{(d_{ii}+d_{jj})(1-\zeta_3)^2} + 2 \left( \frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}} \right)^2 \frac{\zeta_2^2}{(1-\zeta_3)^3} \quad (7)$$

For pure compounds:

$$A^{chain} = RT(1-m) \ln \frac{1-\eta/2}{(1-\eta)^3} \quad (8)$$

And the dispersion contribution is:

$$A^{disp} = mR \left( \frac{\varepsilon}{k} \right) \left( a_{o1}^{disp} + \frac{a_{o2}^{disp}(\varepsilon/k)}{T} \right) \left( 1 + \frac{2A^{chain}}{A^{HS}} \right) \quad (9)$$

where

$$a_{o1}^{disp} = \frac{3\sqrt{2}}{\pi} [-8.5959\zeta_3 - 6.1344\zeta_3^2 - 3.87882\zeta_3^3 + 25.3316\zeta_3^4] \quad (10)$$

$$a_{o2}^{disp} = \frac{3\sqrt{2}}{\pi} [-1.9075\zeta_3 + 13.4675\zeta_3^2 - 40.5171\zeta_3^3 + 39.1711\zeta_3^4] \quad (11)$$

Thus, for the non-associating compounds the SAFT+Cubic EoS has 5 parameters, namely  $m$ ,  $\sigma$ ,  $\varepsilon/k$ ,  $a$  and  $c$ . Originally [7] it has been proposed to solve  $\sigma$ ,  $\varepsilon/k$  and  $a$  at the pure compound critical point conditions, while adjusting  $m$  and  $c$  to the experimental vapor pressure and density data of particular compounds (the last parameter might be generalized with  $\sigma$ ).

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