



# Implementation of the critical point-based revised PC-SAFT for modelling thermodynamic properties of aromatic and haloaromatic compounds



Helena Lubarsky, Ilya Polishuk\*

Department of Chemical Engineering & Biotechnology, Ariel University, 40700 Ariel, Israel

## ARTICLE INFO

### Article history:

Received 11 September 2014  
Received in revised form 12 October 2014  
Accepted 12 October 2014  
Available online 22 October 2014

### Keywords:

Predictive modelling  
SAFT  
High pressures  
Thermodynamic properties

## ABSTRACT

The current study aims at assessing universality of the recently proposed generalized predictive critical point-based PC-SAFT EoS (CP-PC-SAFT). Phase equilibria and the single phase thermodynamic properties of aromatic compounds and their mixtures are compared with the available experimental information in a wide range reaching at times the pressures of 6000 bars and the super-critical temperatures, while covering nearly 9000 data points. It is demonstrated that in spite of their significant density variations, the compounds under consideration can be included in the applicability range of CP-PC-SAFT. In addition, this model is an effective estimator of data in mixtures. However a major drawback of CP-PC-SAFT is the underestimation of vapour pressures away from critical points. A conceptually different predictive approach, namely the Hybrid Group-Contribution PC-SAFT (H-GC-PC-SAFT, Burgess et al., 2014) is considered as well. Although this model is often less precise than CP-PC-SAFT, in several cases, such as the low temperature vapour pressures, it exhibits noticeable advantages.

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## 1. Introduction

Among various aspects defining the practical value of Equations of State (EoS) models, the universality and the predictive capacity should be recognized as the most important ones. Universality of the EoS approaches is demarcated by their accuracy in modelling various properties of diverse compounds and their mixtures in the entire thermodynamic phase space. The predictive capacity can basically be described as a ratio between the amounts of the input experimental and the output estimated data. Decreasing this ratio obviously increases the predictive value of EoS models.

The molecular-based approaches belonging to the family of Statistical Association Fluid Theory (SAFT) equations are currently considered as the particularly perspective models [1]. During the last years significant progress in upgrading their universality has been achieved [2–25]. However the predictive capacity of SAFT approaches still presents a challenging problem, since their substance-dependent parameters are typically evaluated by fitting relatively large and vague experimental databases. Apparently, this practice might result in lack of standardization and transparent

implementations of these models, which currently hinder their wide implementation in industrial simulators [26].

One of the possible solutions to this problem is a replacement of sophisticated fitting procedures by standardized numerical solution of the SAFT's substance-dependent parameters at the pure compound critical points [27–29]. In the latter reference the critical point-based approach (CP) modifying the popular Perturbed-Chain (PC)-SAFT EoS [30,31] has been proposed and implemented for predicting various thermodynamic properties of light compounds, *n*-alkanes, 1-alkenes and their mixtures.

At the same time, a conceptually different approach for addressing the universality and the predictive capacity issues of the PC-SAFT EoS has been recently developed by Burgess et al. [32–34]. While keeping the aforementioned EoS basically unchanged, it has been suggested to improve its universality by evaluating different values of the substance-dependent parameters at low and high pressures, with their further assembly by empirical pressure-dependent functionalities. This method has been termed as “Hybrid” (H). In addition, the Group-Contribution (GC) schemes based on the method of Tihic et al. [35] for both the low- and the high-pressure substance-dependent parameters of hydrocarbons have been proposed.

Due to their practical significance for process design in chemical and petrochemical industries, the properties of aromatic compounds and their mixtures have attained a comprehensive

\* Corresponding author. Tel.: +972 3 9066346; fax: +972 3 9066323.  
E-mail address: [polishuk@ariel.ac.il](mailto:polishuk@ariel.ac.il) (I. Polishuk).

**Table 1**  
Values of the universal model parameters in Eqs. (8) and (9).

$i$	$a_{0i}$	$a_{1i}$	$a_{2i}$	$b_{0i}$	$b_{1i}$	$b_{2i}$
0	0.880823927666	-0.349731891574	-0.041574194083	0.7240946941	-0.5755498075	0.0976883116
1	1.26235042398	1.06133747189	-0.828880456022	2.2382791861	0.6995095521	-0.2557574982
2	-2.88916037036	-9.92662697237	10.6610090572	-4.0025849485	3.8925673390	-9.1558561530
3	-0.791682734039	55.1147516007	-42.2676046130	-21.003576815	-17.215471648	20.642075974
4	31.4414035626	-158.619888888	93.3498157944	26.855641363	192.67226447	-38.804430052
5	-67.7739765931	237.469601780	-119.982855050	206.55133841	-161.82646165	93.626774077
6	37.6471023573	-146.917589624	69.3982688833	-355.60235612	-165.20769346	-29.666905585

experimental coverage in the remarkably wide PVT range. In addition, significant amount of data are available for the haloaromatic compounds as well. Consequently, the current implementation of CP-PC-SAFT EoS [29] for predicting these data presents a challenging universality assessing test. A comparison with the results of H-GC-PC-SAFT [34] in the cases of substances already covered by its current GC matrix is performed as well. A brief description of the CP-PC-SAFT EoS is provided below.

## 2. Theory

Most SAFT approaches express the residual Helmholtz energy for the non-polar compounds as a sum of hard-sphere, chain and dispersion contributions:

$$A^{res} = A^{HS} + A^{chain} + A^{disp} \quad (1)$$

In order to prevent certain numerical pitfalls and inconsistencies characteristic for the original PC-SAFT, such as appearance of the additional pure compound critical points, the isotherms crosses, the negative heat capacities at extreme pressures and the wrong representation of the Joule curve [36–44], several modifications have been introduced in the CP-PC-SAFT EoS [29]. The pertinent partly revised expressions for the residual Helmholtz energy contributions are:

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

where  $m$  is the number of segments,  $\sigma$  is the segment diameter (Å),  $\varepsilon/k$  segment energy parameter divided by Boltzmann's constant,  $d = \sigma\theta$ , and  $\theta$  is given as:

$$\theta = \frac{1 + 0.2977(k/\varepsilon)T}{1 + 0.33163(k/\varepsilon)T + 0.0010477(k/\varepsilon)^2T^2} \quad (3)$$

In addition:

$$\zeta_k = \frac{\pi N_{av}}{6v} \sum_i x_i m_{ii} d_{ii}^k \quad (4)$$

$$A^{chain} = RT \sum_{i,j} x_i x_j (1 - m_{ij}) \ln[g_{ij}(d_{ij})^{hs}] \quad (5)$$

where the segment radial distribution function given as:

$$g_{ij}(d_{ij})^{hs} = \frac{1}{1-\zeta_3} + \frac{3d_{ii}d_{jj}\zeta_2}{(d_{ii}+d_{jj})(1-\zeta_3)^2} + 2 \left( \frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}} \right)^2 \frac{\zeta_2^2}{(1-\zeta_3)^3} \quad (6)$$

$$A^{disp} = -RN_{av} \left( \frac{2\pi(\varepsilon/k)m^2\sigma^3}{v} I_1 + \frac{\pi(\varepsilon/k)^2m^3\sigma^3}{vT(1+m(8\zeta_3-2\zeta_3^2)/(1-\zeta_3)^4 + (1-m)(20\zeta_3-27\zeta_3^2+12\zeta_3^3-2\zeta_3^4)/((1-\zeta_3)(2-\zeta_3))^2)} I_2 \right) \quad (7)$$

In Eq. (7)  $I_1$  and  $I_2$  are the analytical functions representing the integrals of the radial distribution function in 1st and 2nd order perturbation terms:

$$I_1 = \sum_{i=0}^{i=6} \left( a_{0i} + \frac{m-1}{m} a_{1i} + \frac{m-1}{m} \frac{m-2}{m} a_{2i} \right) \zeta_3^i \quad (8)$$

$$I_2 = \sum_{i=0}^{i=6} \left( b_{0i} + \frac{m-1}{m} b_{1i} + \frac{m-1}{m} \frac{m-2}{m} b_{2i} \right) \zeta_3^i \quad (9)$$

where  $a_{0-2i}$  and  $b_{0-2i}$  are the universal model parameters whose values are listed in Table 1. The additional mixing rules are:

$$\frac{\varepsilon}{k} = \frac{\sum_i \sum_j x_i x_j m_{ii} m_{jj} \sigma_{ij}^3 (\varepsilon/k)_{ij}}{\sigma^3 (\sum_i x_i m_{ii})^2} \quad (10)$$

$$\sigma = \sqrt[3]{\frac{\sum_i \sum_j x_i x_j m_{ii} m_{jj} \sigma_{ij}^3}{(\sum_i x_i m_{ii})^2}} \quad (11)$$

$$m = \sum_i x_i m_i \quad (12)$$

where:

$$\left( \frac{\varepsilon}{k} \right)_{ij} = (1 - k_{ij}) \sqrt{\left( \frac{\varepsilon}{k} \right)_{ii} \left( \frac{\varepsilon}{k} \right)_{jj}} \quad (13)$$

$$m_{ij} = (1 - l_{12}) \frac{m_{ii} + m_{jj}}{2} \quad (14)$$

In this study  $l_{12}$  was set to zero.

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (15)$$

The values of four substance-dependent model parameters, namely  $m$ ,  $\sigma$ ,  $\varepsilon/k$  and  $\delta$  (the critical volume displacement, a ratio between the EoS's and the experimental values) are solved numerically. The pertinent system of four equations is:

$$\left( \frac{\partial P}{\partial v} \right)_{T_c} = \left( \frac{\partial P^2}{\partial^2 v} \right)_{T_c} = 0 \Big|_{v_c, EoS = \delta v_c} \quad (16,17)$$

$$P_{c,EoS} = P_c \quad (18)$$

$$\rho_{L,EoS} = \rho_{L,experimental} \Big|_{\text{at the triple point}} \quad (19)$$

Unsurprisingly, this critical-point based approach can hardly been implemented for the low volatile substances whose critical constants are imaginary [29]. The pertinent standardized methods for implementing the current revised version of PC-SAFT in such cases are currently under development. The detailed description of the procedure solving Eqs. (16)–(19) has been provided in Ref. [29]. The values of parameters obtained for the compounds considered in this study are listed in Table 2. The complete list of properties used

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