

Brief Description PC-SAFT Equation of State

PC-SAFT EoS

The PC-SAFT EoS was developed by Gross and Sadowski [1]. It has its basis on SAFT EoS, which was originally developed by Chapman et al [2]. The PC-SAFT EoS uses hard-chain fluid as a reference for the perturbation theory while the SAFT EoS uses hard spherical segments. The PC-SAFT EoS can be written in terms of residual Helmholtz free energy (A^{res}) as shown in equation (1). Please consult the “List of Symbol” and “Greek Letters” sections for the meaning of each symbols used in the following equations.

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

where A^{hs} , A^{chain} , A^{disp} and A^{assoc} are the Helmholtz free energy contributions for the hard sphere repulsion, hard chain formation from the hard spherical segments, dispersion forces and association contributions between chains respectively. For more details of the PC-SAFT EoS, the reader is referred to literature [1,2]. There are five model parameters for a pure compound, (1) number of spherical segments per chain/molecule (m) (2) temperature independent diameter of spherical segment ($\sigma(\text{\AA})$) (3) potential energy (ϵ/k (K)) (4) associating energy (ϵ/R (K)) and (5) associating volume \mathcal{K} . For non-associating pure compounds, only the first three parameters are required while for associating pure compound all the five parameters are needed.

$$\frac{A^{hs}}{RT} = \frac{m}{\xi_0} \left[\frac{3\xi_1\xi_2}{(1-\xi_3)} + \frac{\xi_2^3}{\xi_3(1-\xi_3)^2} + \left(\frac{\xi_2^3}{\xi_3^2} - \xi_0 \right) \ln(1-\xi_3) \right] \quad (2)$$

$$\frac{A^{chain}}{RT} = \sum_i x_i (1 - m_i) \ln(g_{ii}^{hs}) \quad (3)$$

$$g_{ij}^{hs} = \frac{1}{(1-\xi_3)} + \left(\frac{d_i d_j}{d_i + d_j} \right) \frac{3\xi_2}{(1-\xi_3)^2} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\xi_2^2}{(1-\xi_3)^3} \quad (4)$$

$$\xi_n = \frac{\pi}{6} \hat{\rho} \sum_i x_i m_i d_i^n \quad (5)$$

$$d_i = \sigma_i \left[1 - 0.12 \exp \left(-3 \frac{\epsilon_i}{kT} \right) \right] \quad (6)$$

$$\frac{A^{disp}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT} \quad (7)$$

$$\frac{A_1}{RT} = -2\pi\hat{\rho} \left(\sum_{i=0}^6 a_i(m)\eta^i \right) \left(\sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT} \right) \sigma_{ij}^3 \right) \quad (8)$$

$$\frac{A_2}{RT} = -\frac{\pi\hat{\rho}m}{C} \left(\sum_{i=0}^6 b_i(m)\eta^i \right) \left(\sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT} \right)^2 \sigma_{ij}^3 \right) \quad (9)$$

$$C = 1 + m \frac{8\eta - 2\eta^2}{(1 - \eta)^2} + (1 - m) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1 - \eta)(2 - \eta)]^2} \quad (10)$$

$$m = \sum_i x_i m_i \quad (11)$$

Conventional combining rules are applied to calculate the parameters for a pair of two different segments.

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (12)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}) \quad (13)$$

$$a_i(m) = a_{0i} + \frac{m-1}{m} a_{1i} + \left(\frac{m-1}{m} \right) \left(\frac{m-2}{m} \right) a_{2i} \quad (14)$$

$$b_i(m) = b_{0i} + \frac{m-1}{m} b_{1i} + \left(\frac{m-1}{m} \right) \left(\frac{m-2}{m} \right) b_{2i} \quad (15)$$

The universal constants (total 42) for the a_{0i} , a_{1i} , a_{2i} , b_{0i} , b_{1i} , b_{2i} can be found from Gross and Sadowski [2].

$$\eta = \frac{\pi\hat{\rho}}{6} \sum_i x_i m_i d_i^3 \quad (16)$$

$$\rho = \frac{\hat{\rho}}{N_{AV}} \quad (17)$$

$$\frac{A^{assoc}}{RT} = \sum_i x_i \left[\sum_{A_i} \left(\ln X_{A_i} - \frac{X_{A_i}}{2} \right) + \frac{M_i}{2} \right] \quad (18)$$

$$X_{A_i} = \left[1 + \sum_j \sum_{B_j} \rho_j X_{B_j} \Delta^{A_i B_j} \right]^{-1} \quad (19)$$

$$\Delta^{A_i B_j} = g_{ij}^{hs} \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] (d_{ij}^3) (\mathcal{K}^{A_i B_j}) \quad (20)$$

$$\beta^{A_i B_j} = \mathcal{K}^{A_i B_j} \quad (21)$$

Same combining rules, as mentioned in the section of CPA EoS, are applied for cross association energy and cross-association volume.

Mole Fraction of *n*-paraffin at Asphaltene Onset

Table I shows the mole fraction of *n*-paraffin at the onset of precipitation for Crude-1 to 6. The predictions from approaches-1 to 3 show that the mole fraction of *n*-paraffin decreases with the carbon number of *n*-paraffin, except negligible increase for Crude-4. The predictions from approach-4 do not follow the same trend as the predictions from approaches-1 to 3. Therefore, while calculating the model parameters, the model should also comply with certain physical characteristics of asphaltene precipitation as discussed above. Since the approaches-1 to 3 fitted results are in agreement with the experimental data of asphaltene onset conditions for Crudes-1, 5 and 6, it can be concluded that the trend of approaches-1 to 3 results is physically correct.

Table I

Mole fraction of different *n*-paraffin at the onset of asphaltene precipitation using CPA and PC-SAFT approach.

<i>n</i> -paraffin	Mole Fraction of <i>n</i> -paraffin at Asphaltene Onset										
	Crude-1		Crude-2	Crude-3		Crude-4		Crude-5		Crude-6	
	Approach-1	Approach-4	Approach-1	Approach-2	Approach-4	Approach-2	Approach-4	Approach-3	Approach-4	Approach-3	Approach-4
<i>n</i> C5	0.716	0.633	0.575	0.830	0.809	0.870	0.798	0.892	0.887	0.917	0.890
<i>n</i> C6	-	-	0.544 ^a	0.827 ^a	0.835	0.874 ^a	0.810	0.889	0.900	0.916	0.901
<i>n</i> C7	0.681	0.697	0.516	0.818	0.863	0.874	0.824	0.881	0.913	0.909	0.913
<i>n</i> C8	-	-	0.491 ^a	0.730 ^b	0.846	0.796 ^b	0.801	0.877	0.899	0.904	0.899
<i>n</i> C9	-	-	0.467	0.724 ^b	0.869	0.779 ^b	0.815	0.866	0.911	0.896	0.910
<i>n</i> C10	0.616	0.643	0.445 ^a	0.706 ^b	0.914	0.773 ^b	0.830	0.855	0.933	0.887	0.930
<i>n</i> C11	-	-	0.406 ^a	0.690 ^b	0.793	0.759 ^b	0.747	0.838	0.857	0.874	0.856
<i>n</i> C12	0.550	0.593	0.387	0.672 ^b	0.774	0.745 ^b	0.721	0.826	0.843	0.865	0.847
<i>n</i> C13	-	-	0.371 ^b	0.657 ^b	0.701	0.741 ^b	0.666	0.812	0.794	0.854	0.798
<i>n</i> C14	-	-	0.358 ^b	0.642 ^b	0.701	0.718 ^b	0.655	0.785	0.790	0.831	0.796
<i>n</i> C15	-	-	0.322 ^b	0.628 ^b	0.639	0.716 ^b	0.605	0.774	0.742	0.822	0.749
<i>n</i> C16	0.445	0.436	0.291 ^b	0.615 ^b	0.640	0.694 ^b	0.610	0.752	0.738	0.800	0.747

^a Cross-association energy value between *n*C*N* -asphaltene is interpolated.

^b Cross-association energy value between *n*C*N* -asphaltene is assumed same as that of between maltene/(A+R)-asphaltene as a conservative measure to show the mole fraction trend with carbon number of *n*-paraffin.

References

- 1 Gross, J., & Sadowski, G. (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & engineering chemistry research*, 40(4), 1244-1260.
- 2 Chapman, W. G., Gubbins, K. E., Jackson, G., & Radosz, M. (1990). New reference equation of state for associating liquids. *Industrial & Engineering Chemistry Research*, 29(8), 1709-1721.