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PC-SAFT Equation of State Applied to Petroleum Reservoir Fluids

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Abstract

The PC-SAFT equation has been proposed as a potential next generation equation of state in the oil industry. It has already obtained widespread use for simulations on polymer systems, which shows that it has a capability of handling phase equilibria for systems with heavy hydrocarbons. A C_{7+} characterization procedure for use with the PC-SAFT equation has been developed and used to test how PC-SAFT performs on various types of petroleum reservoir fluids ranging from natural gas mixtures to heavy oils with asphaltenes. Promising results are seen for asphaltene onset pressures and for oil mixtures in general. With the currently published pure component parameters PC-SAFT is inferior to cubic equations of state for simulations on gas and gas condensate mixtures.

Introduction

For more than 50 years cubic equations of state have been a standard for thermodynamic calculations in the oil industry. The cubic equations of state date back to the van der Waals equation¹ from 1873. Several modifications were proposed in the twentieth century. The first cubic equation to obtain widespread use in the oil industry was the Redlich-Kwong equation² from 1949. Today the most commonly applied cubic equations are the Soave (SRK) modification³ of the Redlich-Kwong equation proposed in 1972 and the Peng-Robinson (PR) equation⁴ from 1976. Cubic equations are applicable for both phase equilibrium and density calculations, but generally provide too low liquid densities in their original form. This deficiency was for many practical purposes overcome when Peneloux et al.⁵ in 1982 proposed a volume corrected cubic equation of state providing more accurate liquid densities without influencing phase equilibrium simulation results.

When evaluating the need and potential candidates for a next generation equation of state for use in the oil industry it is obvious to start looking for deficiencies of a volume corrected cubic equation of state. At any particular P and T it is possible

to match the absolute volume by applying a convenient volume correction. To get the correct thermal expansion the volume correction can possibly be made a function of temperature⁶. The volume correction does however not influence the pressure derivative of the volume, which derivative for a liquid is often expressed as compressibility, c_o ,

$$c_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (1)$$

Most cubic equations can be represented through the generalized form

$$P = \frac{RT}{V - \delta_1} - \frac{a(T)}{(V - \delta_2)(V + \delta_3)} \quad (2)$$

where P is pressure, R Gas Constant, V molar volume, T absolute temperature, and δ_1 , δ_2 and δ_3 equation of state parameters. For P approaching infinity the molar volume will approach δ_1 (b-parameter for SRK and PR) and the compressibility factor will reduce to

$$Z = \frac{P\delta_1}{RT} \quad (3)$$

which for a constant T expresses a linear increase in compressibility factor with increasing P and a pressure derivative of $\frac{\delta_1}{RT}$. Oil compressibilities at high pressure can be difficult

to match with a cubic equation of state, which shows that Equation (3) may be inappropriate for representing how the compressibility factor varies with pressure at high P.

A correct representation of the volumetric behavior at high pressure is a precondition for accurate predictions of asphaltene onset pressures at reservoir conditions. Asphaltene precipitation takes place because it is thermodynamically favorable for the reservoir fluid to split out an asphaltene phase. If the oil field is produced by natural depletion, the reservoir pressure will decrease with time and asphaltene precipitation may be seen after some time of production. When the Gibbs Free Energy (G) of the split system is lower than of single-phase oil, it is thermodynamically favorable to split out an asphaltene phase. The change in Gibbs Free Energy with changes in P and T can be expressed as

$$dG = V dP - S dT \quad (4)$$

where V is molar volume and S is entropy. The last term in Equation (4) will be zero for T constant and the equation says

that the reservoir fluid will prefer the state of the lower total molar volume. Above the bubble point pressure the reservoir oil can either remain single-phase oil or split out an asphaltene phase. It will remain single-phase as long as the molar volume of single-phase reservoir oil is lower than the molar volume of a split system consisting of an oil phase and an asphaltene phase. Below the upper asphaltene onset pressure the total volume of the oil and asphaltene phase is lower than the volume would have been of single-phase oil. This volumetric behavior is schematically illustrated in Figure 1. The above considerations emphasize that a successful asphaltene model must provide accurate molar volumes at high pressure for both oil and asphaltene phases.

PC-SAFT Equation

The PC-SAFT equation^{7,8} was developed for polymer systems. PC-SAFT stands for Perturbed Chain Statistical Associating Fluid Theory and expresses the compressibility factor as a deviation from the ideal gas compressibility factor of 1.0

$$Z = 1 + Z^{hc} + Z^{disp} \quad (5)$$

Z^{hc} is the hard-chain contribution to the compressibility factor and accounts for repulsive molecular interactions. Z^{disp} is an attractive (dispersive) term. The PC-SAFT approach is schematically illustrated in Figure 2. PC-SAFT sees a pure fluid as consisting of hard-spheres or segments. These hard-spheres are then combined to hard-chain molecules and the hard-chain molecules interact.

Each molecule is represented through 3 parameters

- Number of segments: m
- Segment diameter: σ
- Segment energy: ε

In addition an interaction parameter (k_{ij}) is assigned to each binary pair. The number of segments is 1 for methane. For heavier hydrocarbons it is a little lower than the number of hydrocarbon segments.

Figure 3 shows a schematic view of a PC-SAFT mixture containing two molecules with m_1 and m_2 number of segments, diameters of σ_1 and σ_2 , and an inter-segment radial distance of $r_{1,2}$. ε is the segment energy, which can be understood as the maximum attraction between two molecules. A total of 42 prefixed constants enter into the expression for the Z factor.

PC-SAFT also exists in a modification with an association term⁹, but that term is not considered here.

PC-SAFT parameters have been estimated for several pure components¹⁰ including N_2 , CO_2 and lighter hydrocarbons. PC-SAFT parameters for 3 C_7 components may be seen from Table 1.

Table 2 shows the molar composition of a natural gas mixture. The contents of paraffinic (P), naphthenic (N) and aromatic (A) compounds in each of the fractions C_7 - C_9 are shown in Table 3. Four measured dewpoints are shown in Table 4. Phase envelope calculations were carried for this gas mixture using the Peng-Robinson (PR) equation and using the PC-SAFT equation. It is shown in Table 3 what components are

used to represent the P, N and A fractions in C_7 , C_8 and C_9 when calculating the phase envelope. The PC-SAFT parameters are taken from Gross and Sadowski¹⁰ and the PR-parameters from Reid et al.¹¹ Non-zero binary interaction parameters were used for pairs of N_2 -hydrocarbon (PR- $k_{ij} = 0.08$ and PC-SAFT $k_{ij}=0.08$) and CO_2 -hydrocarbon (PR $k_{ij}=0.10$ and PC-SAFT $k_{ij}=0.14$). Figure 4 shows the calculated phase envelopes plotted together with the measured dewpoints. The PR equation provides a very good match of the dewpoint data whereas the dewpoint temperatures calculated with PC-SAFT are about 10 K higher than those measured.

The PC-SAFT equation is not like a cubic equation of state bound to match the critical point of a pure component. The PC-SAFT parameters used for the components of the gas mixture in Table 2 have been estimated from vapor pressure and liquid density data¹⁰ and will generally provide too high a critical temperature and pressure for a pure component. The dewpoint of a natural gas mixture is dependent not only of the vapor pressures of the heavier hydrocarbons but also on the fugacities of light components, especially of methane. The dewpoints in Table 4 are at conditions where the lightest components in pure form would be in a gaseous state. That the critical point is not matched could suggest erroneous fugacities in the supercritical state. Simulations on mixtures¹² have however shown that the PR equation and the PC-SAFT equation will give approximately the same mixture critical points even though the pure component critical points are not matched for PC-SAFT.

C_{7+} Characterization for PC-SAFT

To use of the PC-SAFT equation for mixtures containing heavy undefined hydrocarbon fractions ending with a plus fraction a procedure is needed for

- Splitting up the plus fraction in carbon number fractions.
- Assigning PC-SAFT parameters to each C_{7+} carbon number fraction including the carbon number fractions contained in the plus fraction.
- Lumping the C_{7+} carbon number fractions into a convenient number of pseudo-components.

In this work the procedure of Pedersen et al.¹³ is used to split up the plus fraction. It is based on the assumption of a linear relation between carbon number and logarithm of mole fraction from C_7 and on. C_{80} is the heaviest hydrocarbon fraction considered. The carbon number fractions are lumped into pseudo-components of approximately equal weight amount. In this work 12-14 C_{7+} pseudo-components are used.

The content of paraffinic (P), naphthenic (N) and aromatic (A) compounds in each of the fractions C_7 - C_{40} is estimated using the procedure of Ness and Westens¹⁴. The distribution of P, N and A components in the fractions C_{40} to C_{80} is assumed to be the same as in the C_{40} fraction.

The subscript PN is used for the paraffinic plus naphthenic part of a C_{7+} fraction and A for the aromatic part. For carbon number fraction i the parameters m and ε are found from

$$m_{PN,i} = a_1 + a_2 \times M_i \quad (6)$$

$$m_{A,i} = b_1 + b_2 \times M_i \quad (7)$$

$$\frac{\varepsilon_{PN,i} \times m_{PN,i}}{k} = c_1 + c_2 \times M_i \quad (8)$$

$$\frac{\varepsilon_{A,i} \times m_{A,i}}{k} = d_1 + d_2 \times M_i \quad (9)$$

where k is Boltzmann's constant, M molecular weight and

$$a_1 = m_{PN,7} - a_2 \times M_{PN,7} \quad (10)$$

$$b_1 = m_{benzene} - b_2 \times M_{benzene} \quad (11)$$

$$c_1 = \frac{\varepsilon_{PN,7} \times m_{PN,7}}{k} - c_2 \times M_{PN,7} \quad (12)$$

$$d_1 = \frac{\varepsilon_{benzene} \times m_{benzene}}{k} - d_2 \times M_{benzene} \quad (13)$$

with

$$m_{PN,7} = \frac{m_{n-heptane} \times x_{P,i} + m_{cyclohexane} \times x_{N,i}}{x_{P,i} + x_{N,i}} \quad (14)$$

$$M_{PN,7} = \frac{M_{n-heptane} \times x_{P,i} + M_{cyclohexane} \times x_{N,i}}{x_{P,i} + x_{N,i}} \quad (15)$$

x_{Pi} and x_{Ni} are the fractions of respectively paraffinic and naphthenic compounds in the i 'th fraction. The PC-SAFT parameters for n-heptane, cyclohexane and benzene entering into the above equations may be seen from Table 1. Equations (10), (12), (14) and (15) ensure that Equations (6) and (8) for the PN part of a carbon number fraction will give m and ε parameters consistent with the parameters for n-heptane and cyclohexane. Similarly Equations (11) and (13) ensure that Equations (7) and (9) for the A part of a carbon number fraction give m and ε parameters consistent with the benzene parameters.

The following mixing rules were used to find m and ε of carbon number fraction i as a whole

$$m_i = x_{PN,i} \times m_{PN,i} + x_{A,i} \times m_{A,i} \quad (16)$$

$$\varepsilon_i = x_{PN,i}^2 \varepsilon_{PN,i} + x_{PN,i}^2 \varepsilon_{PN,i} + x_{PN,i} x_{A,i} \sqrt{\varepsilon_{PN,i} \varepsilon_{A,i}} \quad (17)$$

The same mixing rule extended to an arbitrary number of components are used to find m and ε of a pseudo-component consisting of multiple carbon number fractions.

The segment diameter σ_i is determined to match the liquid density of the carbon number fraction at atmospheric pressure and 288.15 K.

When considering asphaltene precipitation, the C_{50+} aromatic fraction is considered to be asphaltenes and each pseudo-component heavier than C_{49} is split into an asphaltene and a non-asphaltene component. The asphaltene properties are found from Equations (7) and (8) and the non-asphaltene

properties from Equations (6) and (8). The densities (ρ_P , ρ_N and ρ_A) of the P, N and A fractions contained in each of the fraction C_{50+} are assumed to be related through

$$\rho_A = 1.136 \rho_N = 1.25 \rho_P \quad (18)$$

σ of the asphaltene part is for each C_{50+} fraction determined to match ρ_A and σ of the non-asphaltene part to match the average density of the P and N part. Non-zero binary interaction parameters were used for interactions between

- Hydrocarbon and inorganics (N_2 , H_2S and CO_2). Different interaction parameters were used for asphaltenes and for other hydrocarbons.
- C_1 - C_6 hydrocarbons and aromatic C_{7+} components. Different binary interaction parameters are used for asphaltenes and for other aromatics.

The non-zero binary interaction parameters are listed in Table 5.

The constants entering into Equations (6) - (9) are estimated to

- Provide the best possible match of the saturation points of 10 different reservoir fluids covering both gas condensates and oil mixtures¹⁵. The average absolute deviation between simulated and measured saturation points was 7.3%.
- Provide the best possible match of the experimental asphaltene onset pressures^{18,19} in Table 6 for the 3 oil compositions in Table 7.

The constants in Equations (6) - (9) were determined to the values seen in Table 8.

Simulation of PVT-data with PC-SAFT

All the simulations presented are performed without tuning to actual data points (except for the tuning implicitly done through the estimation of coefficients in Equations (6)-(9)).

Figure 5 shows a measured liquid dropout curve for a gas condensate mixture¹⁵ and a simulated liquid dropout curve for the same mixture using PC-SAFT. Figure 6 shows the measured and simulated Z factors above the dewpoint. The liquid volume simulated with PC-SAFT is too low and some deviation is also seen between the experimental and simulated Z factors. It is known from a previous work¹⁵ that the volume corrected SRK and PR will give a better match than that seen with the PC-SAFT equation.

Table 9 shows a reservoir oil mixture¹⁵ characterized for the PC-SAFT equation. A differential liberation experiment for this mixture is simulated and the simulation results compared with experimental results in Figures 7-10. Figure 11 shows experimental and simulated compressibilities above the bubble point for the reservoir temperature of 97.5 °C. Simulation results are also shown in Figure 11 for the volume corrected SRK and PR equations of state. Some deviation is seen between simulated and measured gas phase Z factors. Otherwise the PC-SAFT simulation results agree well with the measured data. The PC-SAFT results for liquid compressibili-

ties are far better than with the SRK equation and the PC-SAFT deviation is only half of that seen with the PR equation.

Asphaltene Simulations with PC-SAFT

The PC-SAFT equation has shown promising results for simulating asphaltene onset pressures^{16,17}. Table 7 shows 3 fluid compositions for which experimental asphaltene onset pressure data^{18,19} is shown in Table 6. Table 10 shows one of the fluid compositions characterized for the PC-SAFT equation. The C₅₀₊ fraction has been split into asphaltene and non-asphaltene pseudo-components. Figures 11-13 show simulated asphaltene onset pressures (upper and lower) and simulated bubble points pressures together with experimental asphaltene onset pressure data points.

Considering that the uncertainty on experimental asphaltene onset pressure data is of the order of ± 50 bar, the simulation results are quite satisfactory. It has often been an item of discussion whether asphaltene onset pressures for a reservoir fluid would increase or decrease with increasing temperature. Both data and simulations results suggest that the onset pressures decrease with increasing temperature for lower temperatures, pass through a minimum and increase for higher temperatures. The intermolecular distances in the oil acting as solvent for the asphaltene molecules increase with temperature and make a split system thermodynamically favorable up to a higher pressure.

Conclusions

The PC-SAFT equation has a potential for use on oil mixtures especially in cases when it is important with an accurate representation of volumetric liquid phase changes with pressure. In reservoir simulation it is for example important to be able to simulate how much the reservoir pressure will decrease as a result natural depletion and how the reservoir pressure will be influenced by gas injection. At high pressure cubic equations of state will predict the Z factor to increase linearly with pressure. PC-SAFT has a more refined pressure dependence.

The PC-SAFT equation is generally inferior to the volume corrected SRK and PR equations for gas and gas condensate mixtures. This may have to do with the way the PC-SAFT parameters were estimated for lighter hydrocarbons. Emphasis was on vapor pressures and liquid densities whereas high-pressure gas densities did not enter. This deficiency may possibly be cured by estimating PC-SAFT parameters also giving importance to high-pressure gas (super-critical) densities.

PC-SAFT shows promising results for simulation of the conditions at which asphaltene precipitation takes place. This is most likely thanks to accurate predictions of the compressibility of oil and asphaltene phases at high pressure.

Notation

A	Aromatic
a	Constant in expression for m
Bo	Oil formation volume factor
b	Equation of state parameter or constant in expression for m
c	Constant in expression for ϵ
c ₀	Compressibility

d	Constant in expression for ϵ
G	Gibbs free energy
i	Component index
k	Boltzmann's constant
k _{ij}	Binary interaction parameter between component i and j.
m	Number of segments
N	Naphthenic
P	Pressure or Paraffinic
R	Gas constant
R _s	Solution gas/oil ratio
S	Entropy
T	Absolute temperature
V	Molar volume
x	Mole fraction
Z	Compressibility factor

Greek

δ	Equation of state parameter
ϵ	Segment energy
σ	Segment diameter

Sub and superscripts

disp	Dispersive
hc	Hard chain
i	Component index
7	C ₇ fraction

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Compound	Component class	m	σ (Å)	ε/k (K)	M
N-heptane	Paraffin	3.4831	3.8049	238.40	100.203
Cyclohexane	Naphthene	2.5303	3.8499	278.11	84.147
Benzene	Aromatic	2.4653	3.6478	287.35	78.114

Table 1 PC-SAFT parameters and molecular weights of some C₇ hydrocarbons.

Component	Mole%	M	Density (g/cm ³) at 1.01 bar and 15 °C
N ₂	0.65099		
CO ₂	11.58449		
C ₁	85.07107		
C ₂	1.83436		
C ₃	0.47640		
iC ₄	0.10659		
nC ₄	0.10315		
iC ₅	0.04051		
nC ₅	0.02542		
C ₆	0.02681		
C ₇	0.06180	82.3	0.820
C ₈	0.01571	101.2	0.807
C ₉	0.00272	113.0	0.806

Table 2 Gas mixture for which four dewpoints are given in Table 4.

	P %	N%	A%
C ₇	12 (n-heptane)	24 (cyclohexane)	64 (benzene)
C ₈	10 (n-octane)	38 (m-c-hexane)	52 (toluene)
C ₉	28 (n-nonane)	11 (ethyl-c-hexane)	61 (ethyl-benzene)

Table 3 PNA distributions of C₇-C₉ fractions of gas in Table 2. The components shown in parentheses are those used to represent the P, N and A components in the phase envelope calculations.

T (°C)	P (bar)
-8.5	40.6
-9.9	54.9
-20.0	64.4
-30.0	72.2

Table 4 Measured dewpoints for gas composition in Table 2.

	N ₂	CO ₂	H ₂ S	C ₁ -C ₆
C ₁ -C ₈₀ PN compounds	0.08	0.14	0.06	
Aromatics excl. asphaltenes	0.08	0.14	0.06	0.03
Asphaltenes	0.11	0.17	0.06	0.03

Table 5 Non-zero binary interaction parameters used with the PC-SAFT equation of state.

Reference	Temperature (°C)	Asphaltene Onset Pressure (bar)
Jamaluddin et al. (2000) Oil A ¹³	99	472.6
Jamaluddin et al. (2000) Oil A ¹³	104	454.2
Jamaluddin et al. (2000) Oil A ¹³	110	442.6
Jamaluddin et al. (2000) Oil A ¹³	116	429.2
Jamaluddin et al. (2000) Oil B ¹³	88	365.4
Jamaluddin et al. (2002) ¹⁴	83.2	372.3
Jamaluddin et al. (2002) ¹⁴	104.2	279.2
Jamaluddin et al. (2002) ¹⁴	120.0	251.7
Jamaluddin et al. (2002) ¹⁴	141.1	262.0

Table 6 Upper asphaltene onset pressures for compositions in Table 7.

Component	Jamaluddin et al. (2000) ¹³ Oil A	Jamaluddin et al. (2000) ¹³ Oil B	Jamaluddin et al. (2002) ¹⁴
N ₂	0.48	0.80	0.49
CO ₂	0.92	0.05	11.37
H ₂ S	0.00	0.00	3.22
C ₁	43.43	51.02	27.36
C ₂	11.02	8.09	9.41
C ₃	6.55	6.02	6.70
iC ₄	0.79	1.14	0.81
nC ₄	3.79	2.83	3.17
iC ₅	1.28	1.58	1.22
nC ₅	2.25	1.63	1.98
C ₆	2.70	2.67	2.49
C ₇₊	26.88	24.17	31.79
C ₇₊ M	228.1	368.9	248.3
C ₇₊ density (g/cm ³)	0.865	0.875	0.877

Table 7 Oil compositions for which upper asphaltene onset pressures are shown in Table 6.

Constant	Sub-index 1	Sub-index 2
a _i		2.9636×10 ⁻²
b _i	1.1415	1.3490×10 ⁻²
c _i		6.6287
d _i	70.486	8.1665

Table 8 Constants in correlations for PC-SAFT parameters (Equations (6) –(9)). The constants a₁ and c₁ do not have fixed values but depend on PN ratio as can be seen from Equations (10) and (12).

Component	Mole%	m	σ (Å)	ε/k (K)
N ₂	0.390	1.2053	3.313	90.96
CO ₂	0.300	2.0729	2.785	169.21
C ₁	40.200	1.0000	3.704	150.03
C ₂	7.610	1.6068	3.521	191.42
C ₃	7.950	2.0018	3.618	208.11
iC ₄	1.190	2.2616	3.757	216.53
nC ₄	4.080	2.3421	3.702	222.38
iC ₅	1.390	2.5620	3.830	230.75
nC ₅	2.150	2.6895	3.773	231.20
C ₆	2.790	3.0576	3.798	236.77
C ₇	4.280	3.0836	3.823	258.70
C ₈	4.310	3.3842	3.823	258.80
C ₉	3.080	3.7906	3.827	259.48
C ₁₀ -C ₁₁	4.380	4.3286	3.834	259.88
C ₁₂ -C ₁₄	4.500	5.2275	3.852	264.14
C ₁₅ -C ₁₆	2.250	6.2230	3.869	268.17
C ₁₇ -C ₁₉	2.510	7.1219	3.872	266.79
C ₂₀ -C ₂₄	2.030	8.5328	3.883	272.80
C ₂₅ -C ₃₀	1.644	10.4578	3.891	277.94
C ₃₁ -C ₃₇	1.206	12.6889	3.903	284.68
C ₃₈ -C ₄₉	1.066	15.7643	3.910	291.66
C ₅₀ -C ₈₀	0.695	21.8323	3.890	294.86

Table 9 Reservoir oil characterized for the PC-SAFT equation. The composition is from Pedersen and Christensen (Table 3.7)¹⁵.

Component	Mole%	m	σ (Å)	ε/k (K)
N ₂	0.490	1.205	3.313	90.96
CO ₂	11.369	2.073	2.785	169.21
H ₂ S	3.220	1.601	3.035	235.81
C ₁	27.357	1.000	3.704	150.03
C ₂	9.409	1.607	3.521	191.42
C ₃	6.699	2.002	3.618	208.11
iC ₄	0.810	2.262	3.757	216.53
nC ₄	3.170	2.342	3.702	222.38
iC ₅	1.220	2.562	3.830	230.75
nC ₅	1.980	2.690	3.773	231.20
C ₆	2.490	3.058	3.798	236.77
C ₇	2.870	3.123	3.804	257.02
C ₈	3.140	3.402	3.802	259.24
C ₉	2.740	3.797	3.805	258.43
C ₁₀ -C ₁₂	5.589	4.492	3.810	255.89
C ₁₃ -C ₁₆	4.555	5.899	3.826	257.80
C ₁₇ -C ₁₉	2.622	7.285	3.841	262.65
C ₂₀ -C ₂₃	2.693	8.483	3.845	266.60
C ₁₀ -C ₁₂	2.406	10.031	3.853	272.35
C ₂₉ -C ₃₃	1.653	11.763	3.864	279.34
C ₃₄ -C ₄₀	1.483	13.700	3.879	287.80
C ₄₁ -C ₅₀	1.112	16.634	3.879	289.99
C ₄₁ -C ₅₀ -A	0.021	9.835	4.621	525.41
C ₅₁ -C ₈₀	0.669	25.259	3.666	226.86
C ₅₁ -C ₈₀ -A	0.236	12.746	4.725	543.09

Table 10 Oil composition in last column of Table 7¹⁴ characterized for the PC-SAFT equation and with the C₅₀₊ fraction split into asphaltene (A) and non-asphaltene components.

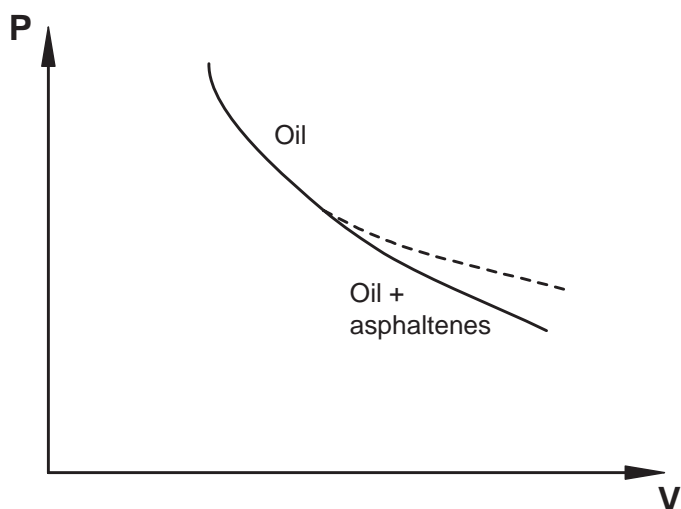


Figure 1 Pressure-volume curve for reservoir oil mixture at a constant temperature. The dashed line starts at the upper asphaltene onset pressure. For lower pressures a two-phase system consisting of oil and asphaltene will have a lower volume than that of single-phase oil, for which reason the two-phase system thermodynamically is more stable.

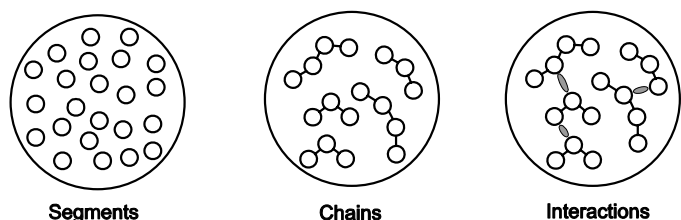


Figure 2 Graphical representation of PC-SAFT concept. A fluid consists of molecular segments. These segments are connected in chains, which chains interact.

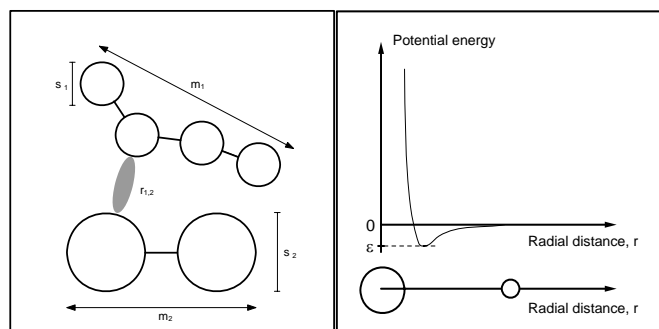


Figure 3 Schematic view of a PC-SAFT mixture consisting of two components of different chain length and different segment diameter.

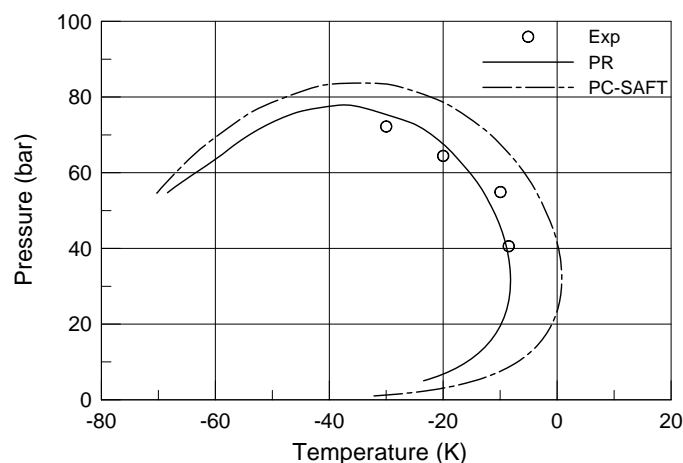


Figure 4 Phase envelope of gas mixture in Table 2 calculated using the Peng-Robinson (PR) equation and using the PC-SAFT equation. Also shown are 4 experimental dewpoints from Table 4.

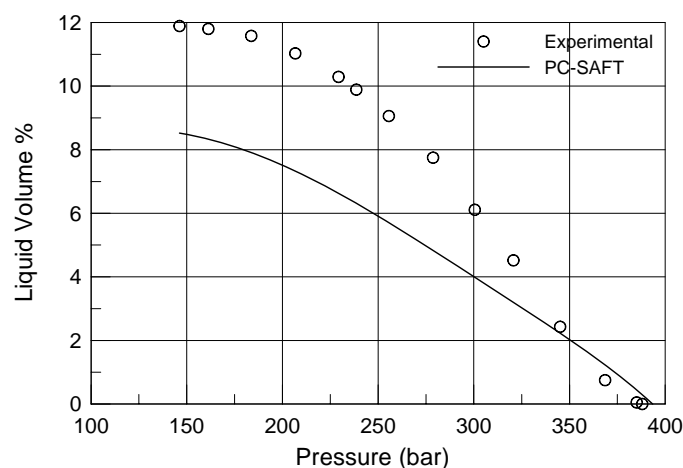


Figure 5 Liquid dropout curve (CME) simulated using the PC-SAFT equation for gas condensate mixture at 155 °C. Also shown are experimental data points. The composition and the data are from Pedersen and Christensen (Tables 3.3 and 3.4)¹⁵.

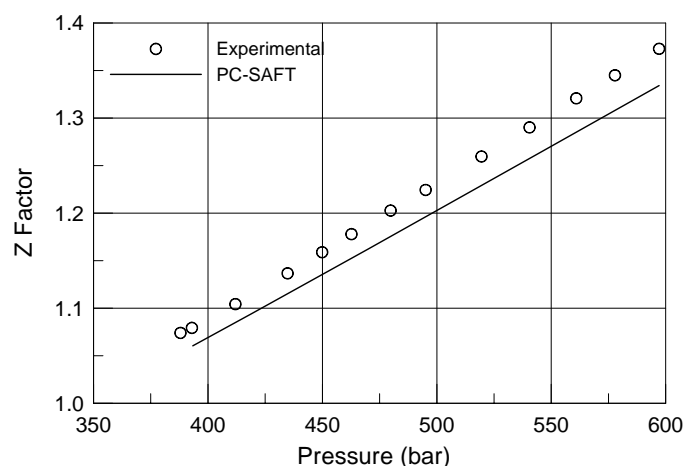


Figure 6 Z factors (CME) simulated using the PC-SAFT equation for gas condensate mixture at 155 °C. Also shown are experimental data points. The composition and the data are from Pedersen and Christensen (Tables 3.3 and 3.4)¹⁵.

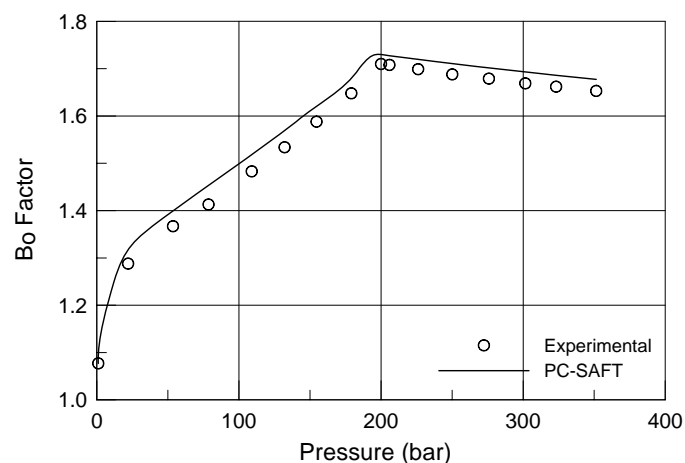


Figure 7 Differential liberation oil formation volume factors (B_o) for reservoir oil mixture in Table 9 at 97.5 °C simulated using the PC-SAFT equation. Also shown are experimental data points. The composition and the data are from Pedersen and Christensen (Tables 3.7 and 3.12)¹⁵.

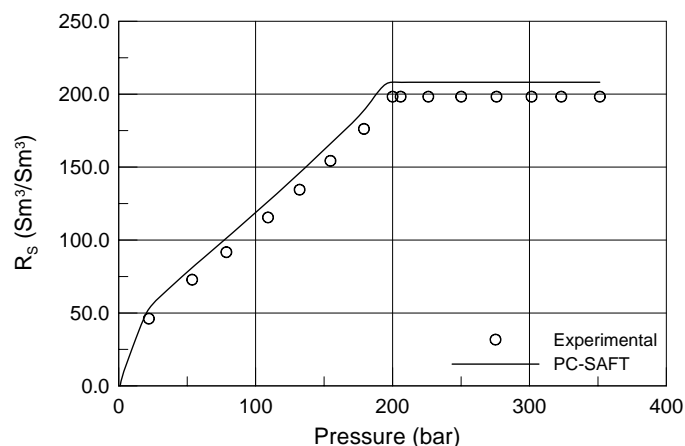


Figure 8 Differential liberation solution gas/oil ratio (R_s) for reservoir oil mixture in Table 9 at 97.5 °C simulated using the PC-SAFT equation. Also shown are experimental data points. The composition and the data are from Pedersen and Christensen (Tables 3.7 and 3.12)¹⁵.

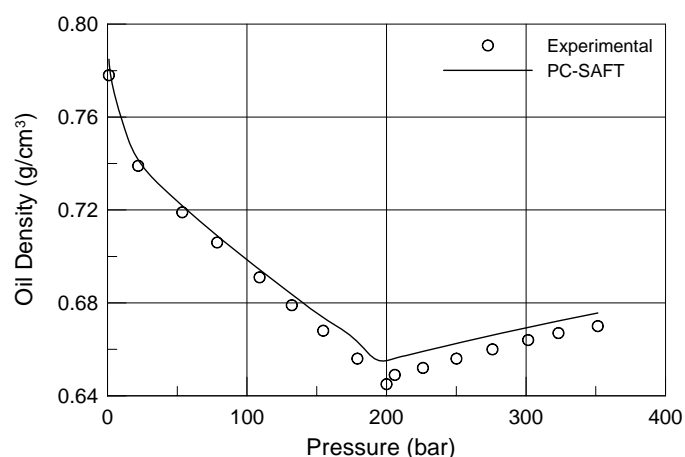


Figure 9 Differential liberation oil densities simulated using the PC-SAFT equation for reservoir oil mixture in Table 9 at 97.5 °C. Also shown are experimental data points. The composition and the data are from Pedersen and Christensen (Tables 3.7 and 3.12)¹⁵.

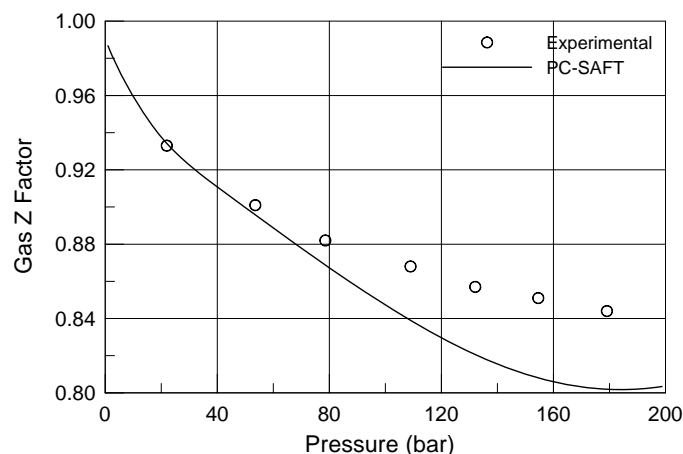


Figure 10 Gas phase Z-factors (differential liberation) for reservoir oil mixture in Table 9 at 97.5 °C simulated using the PC-SAFT equation. Also shown are experimental data points. The composition and the data are from Pedersen and Christensen (Tables 3.7 and 3.12)¹⁵.

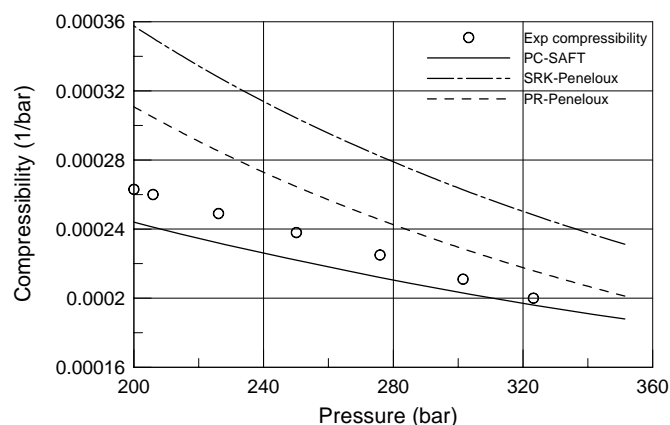


Figure 11 Oil compressibilities for reservoir oil mixture in Table 9 at 97.5 °C simulated using the PC-SAFT equation and using the (Peneloux) volume corrected SRK and PR equations. Also shown are experimental data points. The composition and the data are from Pedersen and Christensen (Tables 3.6 and 3.7)¹⁵.

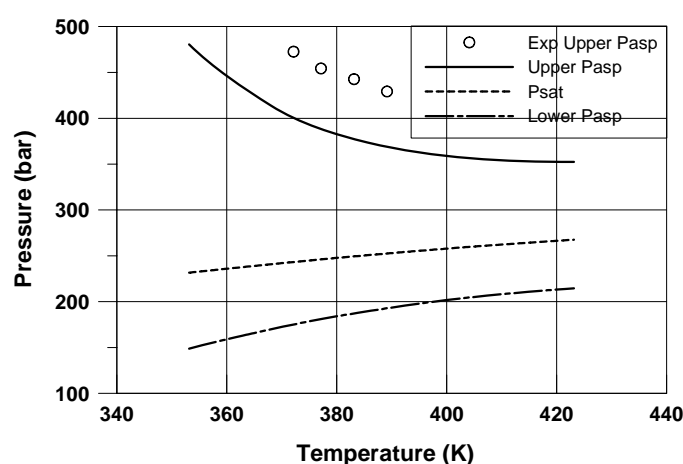


Figure 12 Upper asphaltene onset pressures, bubble points and lower asphaltene onset pressures simulated for Jamaluddin et al. (2000) Oil A¹⁸ using the PC-SAFT equation. Experimental upper asphaltene onset pressures are shown for 4 different temperatures. The oil composition is shown in Table 7.

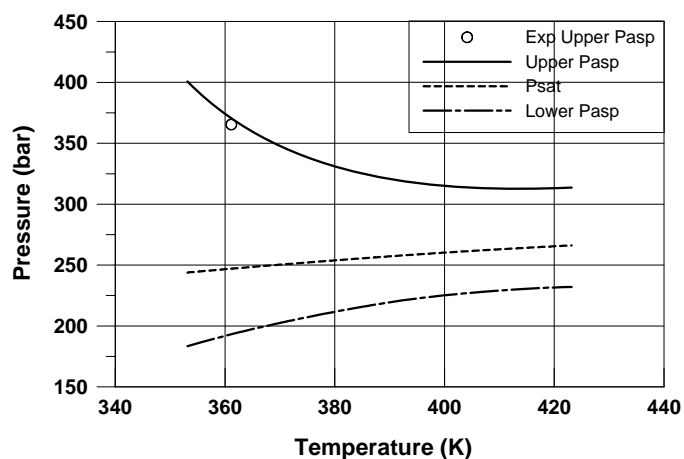


Figure 13 Upper asphaltene onset pressures, bubble points and lower asphaltene onset pressures simulated using the PC-SAFT equation for Jamaluddin et al. (2000) Oil B⁶. An experimental upper asphaltene onset pressure is also shown. The oil composition is shown in Table 7.

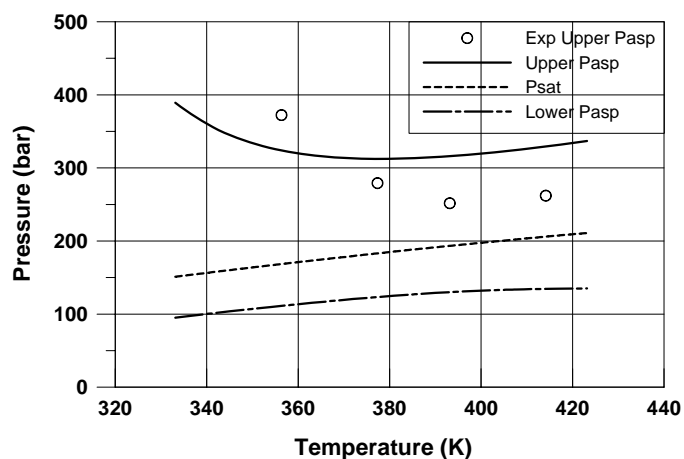


Figure 14 Upper asphaltene onset pressures, bubble points and lower asphaltene onset pressures simulated using the PC-SAFT equation for Jamaluddin et al. (2002)¹. Experimental upper asphaltene onset pressures are shown for 4 temperatures. The fluid composition characterized for PC-SAFT is shown in Table 10.