Prediction of Asphaltene Instability under Gas Injection with the PC-SAFT Equation of State[†]

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Proper prediction of the potential for asphaltene precipitation in deepwater reservoirs represents a challenge for the flow assurance area due to both high intervention costs in case of asphaltene problems and extreme conditions of pressure, temperature, and composition. The probability of asphaltene precipitation increases when light-oil gases are considered for miscible gas injection processes. In this work, the applicability of simple and recombined live oil models using the PC-SAFT equation of state to predict the onset of asphaltene precipitation is demonstrated by studying pressure depletion and gas injection (carbon dioxide (CO_2), nitrogen (N_2), methane, and ethane) in oil reservoirs. The recombined model input includes the SARA characterization, the oil compositional analysis, and the gas−oil ratio. The pure component PC-SAFT parameters are fitted to the saturated liquid density and vapor pressure data, and the oil/gas pseudocomponent parameters are estimated from molecular-weight-based correlations. The EOS asphaltene parameters are fitted to precipitation data from oil titration with *n*-alkanes at ambient conditions. When asphaltene experimental data are not available, the asphaltene parameters are tuned to data at reservoir conditions, and then the model is run in a predictive mode. The PC-SAFT model was found to be in qualitative agreement with experimental data for the precipitant/crude oil systems in this study. In the prediction of the asphaltene onset using the model live oil, the results indicate that the ethane and CO_2 mass fraction concentrations required to produce asphaltene precipitation is greater than for methane at the same pressure. Simulation results using the recombined model show that N_2 addition produces a high asphaltene precipitation effect even at low concentrations. The simulated phase envelope for liquid−liquid asphaltene phase separation shows asphaltene stability bounded by an upper critical solution temperature and a lower critical solution temperature. The approach demonstrates that only molecular size and van der Waals interactions can explain laboratory and field observations of asphaltene phase behavior.

Introduction

Composition of in-situ hydrocarbons is affected by gas injection. Field data confirm that changes in composition due to miscible gas during flooding processes can cause a considerable amount of deposits composed mostly by asphaltenes.[1,2] The application of enriched or dry natural gas (mostly methane and ethane), carbon dioxide (CO_2), or nitrogen (N_2) flooding schemes to enhance oil recovery can induce precipitation and deposition of asphaltenes. The consequences generally include changes in reservoir wettability, formation damage, and wellbore and downhole facilities plugging, affecting the project economics due to production delays and costly clean up procedures. The amount of gas that can be dissolved into the oil before having asphaltene precipitation is an important parameter to consider in the design of the optimal gas injection scheme.

Asphaltene deposition problems are also encountered during normal production due to pressure depletion and temperature changes. Depending on the drive mechanism of an oil reservoir, pressure might decrease considerably as hydrocarbons are produced and asphaltene precipitation can be induced. An oil production system can also experience significant temperature change from the reservoir to the separator. Lower temperatures within the well and flow lines increase the probability of asphaltene precipitation. This effect is even more important in deepwater production where seafloor temperatures are near 4 °C (40 °F). The prediction of the pressure−temperature onset window is fundamental in the design of well completion and/or surfaces facilities.

In this work, the PC-SAFT equation of state will be used to model asphaltene phase behavior as liquid−liquid equilibria in model live oils (mixtures of asphaltene, toluene, and precipitant gases) and in recombined live oils under reservoir conditions. This solubility model uses a minimum number of physically relevant parameters possible to predict the onset of precipitation by including only essential interactions.[3] In this approach, London dispersion interactions (contribution to the van

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der Waals forces) and molecular size dominate the precipitation and aggregation of asphaltenes. The occurrence of these forces is due to induced polarizability which determines the ability of hydrocarbons to serve as a precipitant or as a solvent for asphaltenes; the more polarizable components (the resins and aromatics) solubilize the asphaltenes, and the less polarizable components (saturates) destabilize the asphaltenes. This approach assumes that asphaltenes have already pre-associated to form aggregates in crude oil systems and there is no need to consider additional association. The asphaltene molecular weight in this model represents the molecular weight of the aggregate. This approach is justified since oil systems (and the model systems investigated in this work) are neither infinitely dilute in asphaltenes nor very good solvents for asphaltenes. Because of this assumption, the association term in the PC-SAFT equation of state is not used in this asphaltene modeling work. In some other situations, the role of polar or hydrogen-bonding interactions is important, for example, asphaltenes may aggregate on the water−oil interface and stabilize water emulsions.[4] However, the basic hypothesis of this work is that asphaltene phase behavior in the reservoir is shaped by nonpolar interactions in the oil.

Theory

The statistical association fluid theory (SAFT) is a molecular-based equation of state that had demonstrated its ability to accurately describe and predict the effects of large molecular size differences.[5] Chapman et al.[6,7] derived the SAFT equation of estate by applying and extending Wertheim's first-order perturbation theory[8,9] to chain molecules. Gross and Sadowski[10] developed the perturbed chain modification (PC-SAFT) to SAFT by extending the perturbation theory of Barker and Henderson[11] to a hard-chain reference. PC-SAFT employs a hard sphere reference fluid described by the Mansoori−Carnahan−Starling−Leland[12] equation of state. This version of SAFT properly predicts the phase behavior of high-molecular-weight fluids similar to the large asphaltene molecules.

In PC-SAFT, three parameters are required for each nonassociating component (all the species considered in this work are nonassociating compounds). These parameters correspond to the diameter of each segment of a molecule (σ), the number of segments per molecule (m), and the segment−segment interaction energy (ϵ/k). Gross and Sadowski[10] and Ting et al.[3] fitted pure component parameters to the saturated liquid density

and vapor pressure data of the pure components for several homologous series. One advantage of the SAFT-based equations of state is its ability to predict chain-length dependence of the pure component parameters. Well-behaved correlations exist for *n*-alkanes and poly-nuclear aromatics between m, σ, ϵ/k, and the component molar constant in PC-SAFT. In this way, the parameters for the pseudocomponents in the oil can be determined on the basis of their average molar mass between the aromatic and *n*-alkane correlations depending on their degree of aromaticity. In the case of asphaltenes, this feature was used to define the upper and lower bounds of the asphaltene SAFT parameters. The parameters for asphaltene were originally estimated by Ting et al.[3] from titration data based on the correlation between the solubility parameter and the experimental precipitated refractive index (P_{RI}) that exist for materials with only London dispersion interactions (Buckley et al.[13]). In those cases where asphaltene experimental data was not available, the asphaltene parameters were tuned to data at reservoir conditions.

PC-SAFT describes the residual Helmholtz free energy (A^{res}) of a mixture of nonassociating fluid as

$$\frac{A^{res}}{RT} = \frac{A^{seg}}{RT} + \frac{A^{chain}}{RT} = m\left(\frac{A_0^{hs}}{RT} + \frac{A_0^{disp}}{RT}\right) + \frac{A^{chain}}{RT} \quad (1)$$

where A^{seg}, A^{chain}, A_0^{hs}, and A_0^{disp} are the segment, chain, hard-sphere, and dispersion contributions to the mixture Helmholtz free energy, respectively. In eq 1, R is the gas constant and T is temperature. The average segment number of the mixture, m, is an average of the pure species' segment number, m_i, weighted by the species' compositions:

$$m = \sum_i x_i m_i \quad (2)$$

where x_i is the mole fraction of species i.

The Mansoori−Carnahan−Starling−Leland[12] equation of state provides the free-energy contribution of the hard-sphere mixtures:

$$\frac{A_0^{hs}}{RT} = \frac{6}{\pi\rho}\left[\frac{\zeta_2^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2\zeta_3^2}{\zeta_3(1-\zeta_3)^2} - \left(\zeta_0 - \frac{\zeta_2^3}{\zeta_3^2}\right)\ln(1-\zeta_3)\right] \quad (3)$$

where

$$\zeta_k = \left(\frac{\pi}{6}\rho\right)\sum x_i m_i d_{ii}^k \quad (4)$$

and

$$d_{ii} = \sigma_i\left\{1 - 0.12\exp\left[\frac{-3\epsilon_{ii}}{kT}\right]\right\} \quad (5)$$

where ρ is the mixture number density and d_{ii} the temperature-dependent segment diameter of species i.

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The contribution to A^{res} due to chain formation from Wertheim theory[6,7] is given by

$$\frac{A^{chain}}{RT} = \sum x_i(i - m_i) \ln g_{hs}(d_{ii}) \qquad (6)$$

where $g_{hs}(d_{ii})$ is the hard-sphere pair correlation function at contact given by[12]

$$g_{hs}(d_{ii}) = \left[\frac{1}{1 - \zeta_3} + \frac{3d_{ii}}{2}\frac{\zeta_2}{(1 - \zeta_3)^2} + 2\left(\frac{d_{ii}}{2}\right)^2\frac{\zeta_2{}^2}{(1 - \zeta_3)^3}\right] \qquad (7)$$

PC-SAFT incorporates the effects of chain length on the segment dispersion energy. The perturbed chain dispersion contribution is given by[10]

$$\frac{A_0^{disp}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT} \qquad (8)$$

where

$$\frac{A_1}{RT} = -2\pi\rho I_1(\eta,m)\sum_i\sum_j x_i x_j m_i m_j\left(\frac{\epsilon_{ij}}{kT}\right)\sigma_{ij}{}^3 \qquad (9)$$

$$\frac{A_2}{RT} = -\pi\rho m I_2(\eta,m)\frac{1}{W}\sum_i\sum_j x_i x_j m_i m_j\left(\frac{\epsilon_{ij}}{kT}\right)\sigma_{ij}{}^3 \qquad (10)$$

$$W = 1 + m\frac{8\eta - 2\eta^2}{(1 - \eta)^4} + \\ (1 - m)\frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1 - \eta)(2 - \eta)]^2} \qquad (11)$$

$$\epsilon_{ij} = (1 - k_{ij})\sqrt{\epsilon_{ii}\epsilon_{jj}} \qquad (12)$$

$$\sigma_{ij} = 0.5(\sigma_i + \sigma_j) \qquad (13)$$

where η is the package fraction (same as ζ_3), k_{ij} is the binary interaction parameter between species i and j and σ_i is the temperature-independent segment diameter. I_1 and I_2 are functions of the system packing fraction and average segment number, m, and can be found in the work by Gross and Sadowski.[10] The PC-SAFT association term is not used in this work because of the assumption that molecular size and van der Waals interactions dominate asphaltene phase behavior in crude oil.

Modeling Procedure

Two different oil models were considered in this study: a model live oil (mixture asphaltene, toluene, and precipitant gas) and a recombined oil (reservoir oil and its separator gas)

In the *model live oil* investigations, onset, and bubble point pressures are predicted by PC-SAFT when ethane or CO_2 is added to 1 g of n-C7 precipitated asphaltene dissolved in 100 mL of toluene. The simulated results are compared to a methane−toluene−asphaltene system previously evaluated by Ting et al.[3] The PC-SAFT parameters for the pure species are from Gross and Sadowski,[10] and the n-C$_7$ monodisperse asphaltene parameters are the same as those fitted to meet the measured composition and mixture refractive index data at the onset of asphaltene instability with n-alkane titration[3] (Table 1). This asphaltene has a PC-SAFT calculated solubility param-

Table 1. SAFT Parameters for the Components of the Model Live Oil

component	MW	SAFT parameters		
		σ (Å)	m	ϵ/k
methane	16.04	3.7039	1.0000	150.03
ethane	30.07	3.5206	1.6069	191.42
CO_2	44.01	2.7852	2.0729	169.21
toluene	92.14	3.7169	2.8149	285.69
asphaltene	4000.00[a]	4.0500	80.0000	350.80

[a] Molecular weight of pre-aggregated asphaltene.

Table 2. Binary Interaction Parameters (k_{ij}) for the Model Live Oil

components	k_{ij}	experimental data reference
methane−toluene	0.029	VLE at 422.3−461.89 K by Lin et al.[14]
ethane−toluene	0.015	VLE at 313.1−473.0 K by Richon et al.[15]
CO_2−toluene	0.105	VLE at 353.0−413.0 K by Morris et al.[16]

parameter of 21.85 MPa$^{0.5}$ and a molar volume of 3334 cm³/mol. Given that the density of asphaltenes is between 1.12 and 1.20 g/cm³ at ambient conditions, the PC-SAFT-calculated model oil asphaltene would then have an implied molecular weight between 3767 and 4000.

The temperature-independent binary interaction parameters (k_{ij}) used in these calculations were determined from vapor−liquid equilibria (VLE) at corresponding temperature ranges (Table 2). To reduce the number of fitted parameters in the model live oil, all binary interaction parameters between asphaltenes and other species were set to zero. The bubble point curves and the asphaltene stability limits are predicted for different compositions of methane, ethane, and CO_2 as precipitant gases.

The *recombined oil* is the closest representation of the reservoir oil. This model considers fluid analysis data from a (PVT) laboratory report which includes the saturated−aromatic−resins−asphaltene (SARA) weight content, the gas−oil ratio (GOR), and the gas chromatography composition analysis (GC) for the gas and liquid phases of the sample.

To evaluate the effect on asphaltene instability onset due to N_2 injection, modeling work using the PC-SAFT equation of state will be compared with results from several light-transmittance experiments conducted by contacting various molar concentrations (5, 10, and 20%) of N_2 gas with the reservoir fluid 'A' from Jamaluddin et al.[17] In this work is used a seven-pseudocomponent recombined oil system: four subfractions (methane, N_2, CO_2, and light n-alkanes) are used to describe the separator gas and three subfractions (saturates, aromatics + resins, and asphaltenes) are used to describe the stock tank oil. The amount and average molecular weight of each subfraction is calculated on the basis of composition data from GC, SARA, and GOR data. A summary of the reservoir 'A' fluid properties is provided in Tables 3 and 4.

The PC-SAFT parameters for each pseudocomponent (except for the asphaltenes) are determined from correlations with the average molecular weight. For instance, m for saturates subfraction (Table 5) was obtained from a correlation of m with molecular weights of n-alkanes up to eicosane, and m for the aromatics and resins subfraction was obtained from a function of m with molecular weights of polynuclear aromatics and benzene derivatives. The asphaltene PC-SAFT parameters in the recombined oil were tuned to meet the onset of asphaltene precipitation of 3800 psia that characterize the original oil. This asphaltene has a PC-SAFT-calculated solubility param-

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Table 3. Reservoir Fluid Characterization: Formation Reservoir 'A'[17]

measured depth	14 134 ft
reservoir temperature	296 °F
reservoir pressure	3256 psia
bubble point pressure @ 255 °F	3045 psia
gas-oil ratio	900 scf/stb
oil API gravity	32°
wax content	1.2% w/w
cloud point	72 °F

| SARA Contents (ASTM D4124−97)	
saturates	57.4 wt%
aromatics	30.8 wt%
resins	10.4 wt%
asphaltenes (*n*-pentane insoluble)	1.4 wt%

Table 4. Reservoir Fluid 'A' Composition[17]

components	flashed liquid (mol%)	flashed gas (mol%)	monophasic fluid (mol%)
nitrogen	0.00	0.77	0.49
carbon dioxide	0.00	17.67	11.37
hydrogen sulfide	0.00	5.00	3.22
methane	0.00	42.49	27.36
ethane	0.14	14.54	9.41
propane	0.66	10.05	6.70
1-butane	0.23	1.13	0.81
n-butane	1.48	4.11	3.17
1-pentane	1.17	1.26	1.22
n-pentane	2.71	1.57	1.98
pseudo C_6H_{14}	5.32	0.92	2.49
pseudo C_7H_{16}	7.38	0.37	2.87
pseudo C_8H_{18}	8.62	0.10	3.14
pseudo C_9H_{20}	7.67	0.02	2.74
pseudo $C_{10}H_{22}$	6.49	0.01	2.32
pseudo $C_{11}H_{24}$	5.31	0.01	1.90
$C_{12}+$	52.82	0.01	18.82
MW	229.21	31.69	102.04
mole ratio	0.3562	0.6438	
molar mass, $C_{12}+$	337.98	167.11	337.94
density (g/cm³), $C_{12}+$	0.906	−	0.906

Table 5. SAFT Parameters for the Pseudocomponents of the Recombined Oil

component	MW_n	(mole fraction)$_n$	SAFT parameters σ (Å)	m	ϵ/k (K)
CO_2/H_2S	41.80	0.14583	2.7852	2.0729	169.21
N_2	28.01	0.00495	3.3130	1.2053	90.96
methane	16.04	0.27334	3.7039	1.0000	150.03
light gases	44.60	0.21917	3.6130	2.0546	204.96
saturates	207.63	0.23853	3.932	5.967	254.05
aromatics + resins	270.50	0.11750	3.816	6.473	342.08
asphaltene	1700.00[a]	0.000676	4.300	29.500	420.00

[a] Molecular weight of pre-aggregated asphaltene.

eter of 23.05 MPa$^{0.5}$ and a molar volume of 1409 cm³/mol. Table 5 lists the PC-SAFT parameters of the pseudocomponents for this particular recombined oil. The binary interaction parameters (k_{ij}) between pseudocomponents are determined by fitting VLE experimental data from the literature of each combination of the subfractions represented by a pure component. For instance, the interaction parameter between light alkanes and saturates subfractions was estimated from the interaction parameter between propane and decane adjusted to experi-
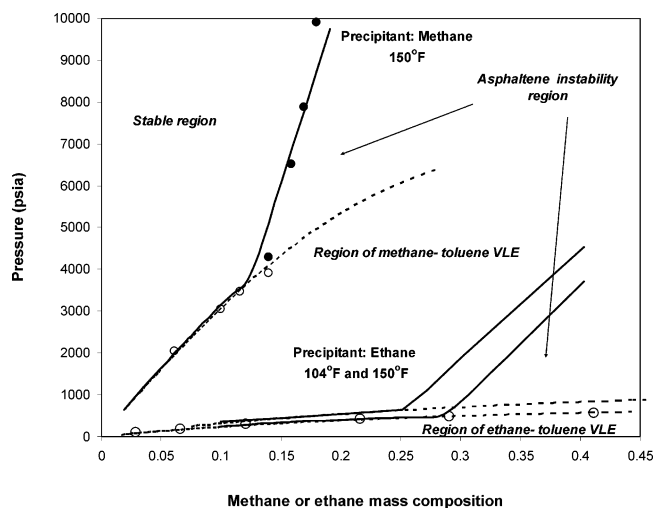
Figure 1. Ethane versus methane. Predicted onset and bubble point curves (solid and dashed lines) for a model oil versus experimental onsets[3] (filled circles) and bubble point pressures[3,15] (open circles).
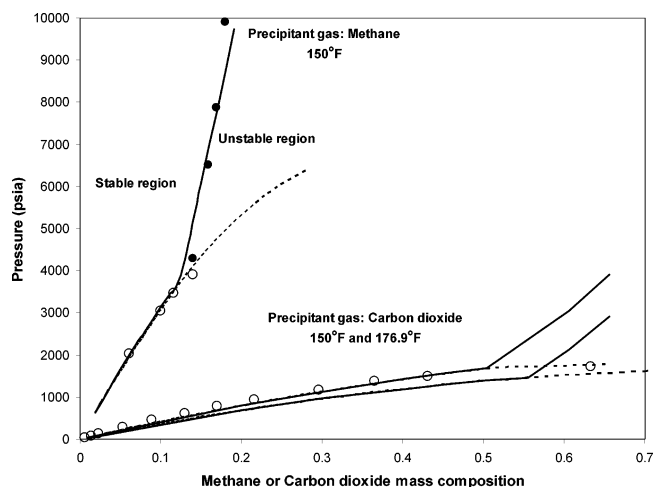
Figure 2. CO_2 injection versus methane addition. Experimental bubble point[3,16] (open circles), experimental asphaltene stability onset[3] (filled circles), and SAFT predictions (lines).

mental data. The binary interaction parameters for asphaltenes are set equal to those for aromatics (see Table 6).

Additionally, reservoir fluid 'A' is used to predict the complete phase envelope to evaluate the asphaltene precipitation characteristics during crude oil cooling or heating in the production process.

Results and Discussions

The predicted asphaltene onset precipitation and bubble point pressure when ethane and CO_2 are added to a *model oil* system are presented in Figures 1 and 2, respectively. These curves are compared with predicted results for methane as precipitant, which was shown

Table 6. Binary Interaction Parameters (k_{ij}) in the Recombined Oil

|	N_2	methane	light alkanes	saturates	aromatics + resins	asphaltenes
CO_2/H_2S	0.000	0.050	0.010	0.130	0.09	0.09
N_2		0.030	0.060	0.120	0.110	0.110
methane			0.000	0.030	0.029	0.029
light alkanes				0.010	0.010	0.010
saturates					0.007	0.007
aromatics + resins						0.000
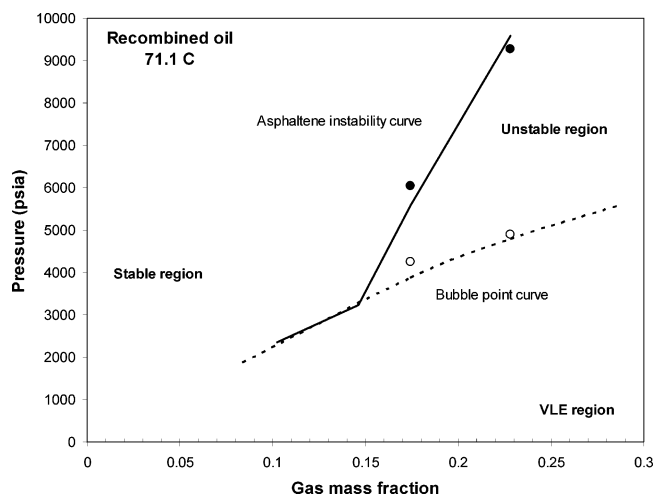
Figure 3. Reservoir fluid phase behavior as a function of methane addition. Comparison of SAFT-predicted bubble point and onset pressures (dashed and solid lines) to experimental data.[3]
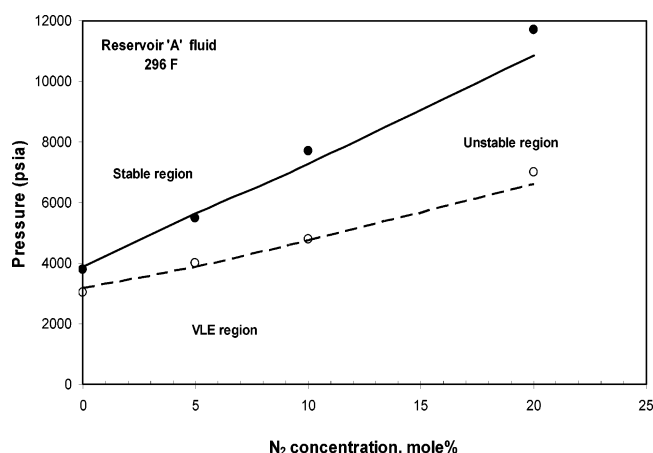
Figure 4. Addition of nitrogen to a live reservoir fluid. Comparison of PC-SAFT-predicted bubble point and onset pressures of asphaltene instability (dashed and solid lines) to experimental data[17] (circles).

to be in good agreement with experimental data.[3] Simulation results using the model live oil indicate that precipitation of asphaltene due to ethane addition occurs at lower pressures than for methane and at higher concentrations (about 25 mass% at 150 °F in comparison to about 15 mass% for methane at the same temperature). When the added gas is CO_2, asphaltene precipitation onset is expected to occur at about 50 mass% at 177 °F. These results suggest that methane is a stronger precipitant than ethane and CO_2.

The asphaltene stability curve in a *recombined oil* as a function of pressure at different methane concentrations was determined in a previous work.[3] The simulated results for the recombined model reproduce the experimental data obtained in a PVT cell by Ting et al.[3] at D.B. Robinson (Figure 3). N_2 addition simulated results using the recombined model are compared to experimental depressurization data at reservoir temperature of 296 °F from Jamaluddin et al.[17] in Figure 4. The addition of 5, 10, and 20 mol% of N_2 strongly increases the asphaltene instability onset. The oil is originally unstable probably due to its initial high content of CO_2 (11.37 mol%). The difference between the asphaltene onset pressure and the bubble point pressure
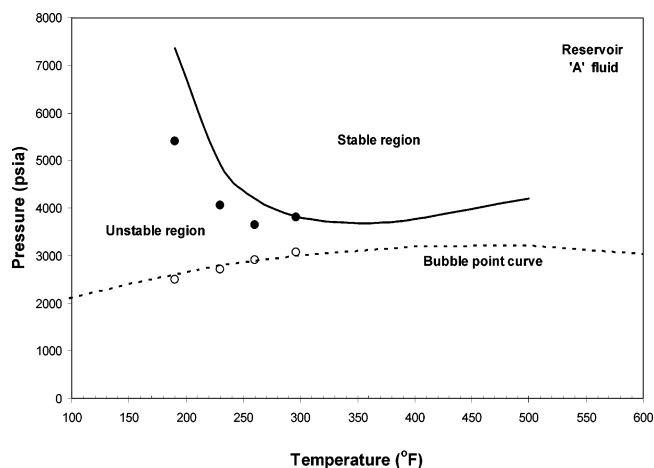
Figure 5. Reservoir fluid phase envelope. Comparison of PC-SAFT-predicted bubble point (dashed line) and asphaltene instability pressures (solid line) to experimental data[17] (circles).

$(P_{onset} - P_{bbp})$ increases with the amount of injected N_2. The SAFT predictions closely follow the experimental findings.

Figure 5 summarizes the prediction of the complete phase envelope for reservoir fluid 'A' before N_2 addition. SAFT predicts the presence of upper and lower critical solution temperature (UCST and LCST) regions at low and high temperatures. At lower temperatures (220 °F), the asphaltenes become unstable due to differences in the interaction energies between asphaltene molecules and solvent (crude oil) molecules. As temperatures increase over 310 °F, the asphaltene solution demixes as a result of the large thermal expansivity of the solvent compared to that of the asphaltene.

Conclusions

(i) The SAFT EOS predicts adequately the onset of asphaltene precipitation when a light gas such as methane, ethane, CO_2, or N_2 is added to an oil mixture. Simulation results agree with previous experimental reported work.

(ii) Simulation using the PC-SAFT EOS shows that the effect of CO_2 and ethane on asphaltene precipitation onset is weaker (i.e., requires higher concentration) compared to the addition of methane.

(iii) The prediction for the model oil shows a concentration of about 50 mass% of CO_2 is required to reach the asphaltene instability onset.

(iv) N_2 produces a high asphaltene precipitation effect even at low concentrations.

(v) PC-SAFT predicts the presence of the upper and lower critical solution temperature (UCST and LCST) regions in the asphaltene phase envelope.

(vi) The SAFT model calculations provide valuable insight into the behavior of these complex systems.