Development of a General Method for Modeling Asphaltene Stability[†]

Francisco M. Vargas,[‡] Doris L. Gonzalez,[§] Jefferson L. Creek,[||] Jianxin Wang,[||]
Jill Buckley,[⊥] George J. Hirasaki,[‡] and Walter G. Chapman*[,‡]

Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77251, Data Quality Group, Schlumberger, Houston, Texas 77056, Chevron Energy Technology Company, Houston, Texas 77002, and New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801

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Asphaltenes constitute a potential problem in deep-water production because of their tendency to precipitate and deposit. A universal model to predict the stability of these species, under different conditions, is desirable to identify potential asphaltene problems. In our study, we present important advances in developing a general method to model asphaltene stability in oil. The perturbed chain-statistical associating fluid theory equation of state (PC-SAFT EoS), which has been previously validated, has been used to generate simulation data for a model oil containing different asphaltene precipitants. When dimensionless parameters are defined, the equilibrium curves of different multicomponent mixtures collapse onto one single curve. Universal plots for the bubble point and the onset of asphaltene precipitation have been obtained, which are in excellent agreement with results obtained from simulations. Extension of this model to mixtures containing dissolved gases, such as methane, CO_2, and ethane, is also included. In the present work, we show a derivation of a new mixing rule for solubility parameters of mixtures containing liquids and dissolved gases. The agreement with simulation results and refractive index measurements is good. Results obtained in this work are very promising in providing new tools to model asphaltene stability under reservoir conditions.

Introduction

Asphaltenes, a polydisperse mixture of the heaviest and most polarizable fraction of the oil, are defined according to their solubility properties. Asphaltenes are well-known for their potential tendency to precipitate and deposit during oil production, because of changes in pressure, temperature, and composition. Unfortunately, the knowledge that we have about asphaltenes is limited, and the mechanisms of aggregation and deposition are not completely understood. Additionally, the relationships that are available between ambient condition data and reservoir precipitation onsets are specific for each crude oil and are strongly dependent upon the procedure used to perform such measurements.

A universal model to predict the stability of these species has been previously followed by de Boer.[1] This first attempt to develop a universal plot for asphaltene stability was based on the Flory−Huggins theory (FHT) with the assumption of a crude oil saturated with asphaltenes at reservoir conditions. The de Boer method has been widely used in the oil industry to forecast asphaltene problems. However, this model produces false positives.[2] Alternatively to the FHT, the perturbed chain-statistical associating fluid theory equation of state (PC-SAFT EoS) has been successfully applied in modeling asphaltene stability.

In our study, we present important advances in developing a general method to model asphaltene stability in oil, using the PC-SAFT EoS in a simulation tool. When defining dimensionless parameters are defined, the equilibrium curves of different multicomponent mixtures collapse onto one single curve. Universal plots for the bubble point and the onset of asphaltene precipitation have been obtained, which are in excellent agreement with results obtained from simulations.

Extension of this model to mixtures containing dissolved gases, such as methane, CO_2, and ethane, is also included. This part of the study led to questions regarding the validity of the current mixing rule for solubility parameters of mixtures containing dissolved gases. It is well-known that the geometric mean for intermolecular forces of different species, assumed in application of the regular solution theory (RST) and, consequently, by the FHT, becomes increasingly poor as the difference in size between molecules increases. However, current methods ignore this limitation and, in practice, use correction factors to match the gas solubility data.

An important limitation in this area of study is the lack of data. In this work, the PC-SAFT EoS is introduced as an alternative method to generate pseudo-data, because of the accuracy that this equation of state has proven in modeling petroleum systems and the prohibitive costs of obtaining an extensive set of experimental data. In further sections, novel tools are proposed that allow for the calculation of relevant

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* To whom correspondence should be addressed: Department of Chemical and Biomolecular Engineering, Rice University, MS 362, 6100 Main St., Houston, TX 77005. Telephone: +1-(713)-348-4900. Fax: +1-(713)-348-5478. E-mail: wgchap@rice.edu.

[‡] Rice University.

[§] Schlumberger.

[||] Chevron Energy Technology Company.

[⊥] New Mexico Institute of Mining and Technology.

(1) de Boer, R. B.; Leerlooyer, K.; Eigner, M. R. P.; van Bergen, A. R. D. *SPE Prod. Facil.* **1995**.

(2) Wang, J.; Creek, J.; Buckley, J. S. SPE 103137, 2006.

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properties for the analysis, such as the solubility parameter and the cohesive energy, as well as their pressure and composition dependence. Thus, the methodology for obtaining general equations for modeling bubble points and onsets of asphaltene precipitation is introduced. A practical application of this method is also presented.

Results obtained in this work are very promising in providing new tools to model asphaltene stability under reservoir conditions.

PC-SAFT Equation of State

The statistical associating fluid theory (SAFT) is a molecular-based equation of state that has demonstrated its ability to accurately describe and predict the effects of large molecular size differences and association on phase behavior of complex mixtures.[3] The equation of state models molecules as flexible chains of spherical segments similar to a pearl necklace. Chapman et al.[4,5] derived the SAFT equation of state (EoS) by applying and extending Wertheim's first-order perturbation theory[6,7] to chain molecules. Gross and Sadowski[8] developed the perturbed chain modification of SAFT (PC-SAFT), by extending the perturbation theory of Barker and Henderson[9] to a hard chain reference. PC-SAFT employs a hard sphere reference fluid described by the Mansoori–Carnahan–Starling–Leland[10] EoS. This version of SAFT accurately predicts the phase behavior of high-molecular-weight fluids similar to the large asphaltene molecules.

In PC-SAFT, three parameters are required for each non-associating component. These parameters correspond to the diameter of each segment in a molecule (σ), the number of segments per molecule (m), and the segment–segment interaction energy (ε/k). The pure component parameters are determined to match the saturated liquid density and vapor pressure data of the pure components for several homologous series.[3,8] One advantage of the SAFT-based equations of state is the ability to easily correlate the molecular-weight dependence of the pure component parameters. Well-behaved correlations exist for *n*-alkanes and polynuclear aromatics between m, σ, ε/k, and the component molecular weight in PC-SAFT.[11] In this way, the parameters for the pseudo-components in the oil can be determined on the basis of their average molar mass and using correlations for aromatic and aliphatic components. The parameters for asphaltenes are tuned to titration data at ambient conditions and/or to asphaltene precipitation onset data at reservoir conditions depending upon availability.

The PC-SAFT association term is not used in this work because of the assumption that asphaltenes are pre-aggregated. Further asphaltene aggregation is neglected, and only van der Waals interactions and molecular size are considered to dominate the phase behavior in crude oil. The evidence obtained at this point[11−13] validates this assumption, leading to a simplified model with the minimum number of parameters.

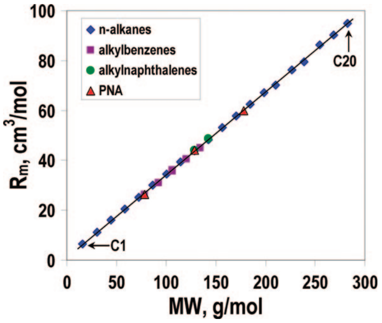
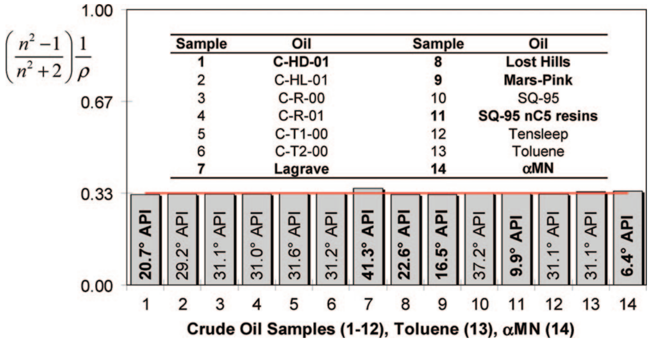


Figure 1. Molar refraction as a function of the molecular weight for different pure hydrocarbons.



Sample	Oil	Sample	Oil
1	**C-HD-01**	8	**Lost Hills**
2	C-HL-01	9	**Mars-Pink**
3	C-R-00	10	SQ-95
4	C-R-01	11	**SQ-95 nC5 resins**
5	C-T1-00	12	Tensleep
6	C-T2-00	13	Toluene
7	**Lagrave**	14	**αMN**

Figure 2. Validation of the one-third rule for 12 crude oil samples, pure toluene, and α-methyl naphaltene. Experimental data were from ref 15.

General Relationships for Crude Oil Systems

One-Third Rule. The molar refraction, R_m, of a pure component can be correlated to its refractive index, n, molecular weight, MW, and mass density, ρ, using the Lorentz–Lorenz model, according to eq 1

$$R_m = \left(\frac{n^2-1}{n^2+2}\right)\frac{\mathrm{MW}}{\rho} = F_{\mathrm{RI}}\frac{\mathrm{MW}}{\rho} \tag{1}$$

When the molar refractions of different aliphatic, aromatic, and polyaromatic hydrocarbons are plotted with respect their molecular weights, a common linear trend with a slope equal to about $^1/_3$ is obtained, as shown in Figure 1.

This result implies that the function of the refractive index, F_{RI}, divided by the mass density, ρ, is a constant equal to $^1/_3$ for all of the different tested substances.

The rediscovery of this relationship, proposed originally by Bykov[14] in 1984, opens the possibility of a practical application to real crude oil systems. In fact, the agreement of this model with the data reported by Wang and Buckley[15] for 12 different crude oils is remarkable, as observed in Figure 2. The wide range of American Petroleum Institute (API) gravities, ranging from 9.9 to 41.3, assures the broad application of the one-third rule. Furthermore, in Figure 3, a test for more than 200 crude oils is also presented. The agreement with the one-third rule is very good for most of the systems.

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(3) Ting, P. D.; Hirasaki, G. J.; Chapman, W. G. *Pet. Sci. Technol.* **2003**, *21*, 647–661.

(4) Chapman, W. G.; Jackson, G.; Gubbins, K. E. *Mol. Phys.* **1988**, *65*, 1057–1079.

(5) Chapman, W. G.; Jackson, G.; Gubbins, K. E. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709–1721.

(6) Wertheim, M. S. *J. Stat. Phys.* **1986**, *42*, 459–476.

(7) Wertheim, M. S. *J. Stat. Phys.* **1986**, *42*, 477–492.

(8) Gross, J.; Sadowski, G. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260.

(9) Barker, J. A.; Henderson, D. J. *J. Chem. Phys.* **1967**, *47*, 4714–4721.

(10) Mansoori, G. A.; Carnahan, N. F.; Starling, K. E.; Leland, T. W. *J. Chem. Phys.* **1971**, *54*, 1523.

(11) Gonzalez, D. L.; Hirasaki, G. J.; Creek, J.; Chapman, W. G. *Energy Fuels.* **2007**, *21*, 1231–1242.

(12) Gonzalez, D. L.; Ting, P. D.; Hirasaki, G. J.; Chapman, W. G. *Energy Fuels.* **2005**, *19*, 1230–1234.

(13) Gonzalez, D. L.; Vargas, F. M.; Hirasaki, G. J.; Chapman, W. G. *Energy Fuels.* **2008**, *22*, 757–762.

(14) Bykov, M. I. *Chem. Technol. Fuels Oils* **1984**, *20*, 310.

(15) Wang, J.; Buckley, J. S. *Energy Fuels* **2003**, *17*, 1445–1451.

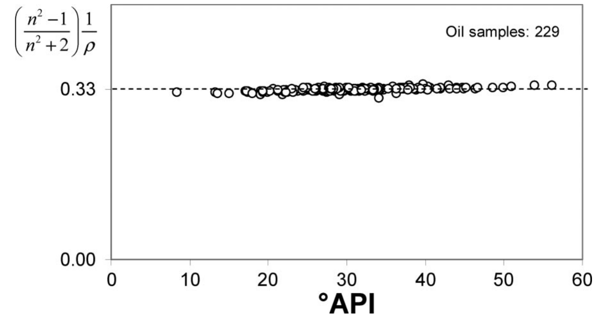

Figure 3. Validation of the one-third rule for 229 crude oils. Circles represent experimental data at ambient conditions from ref 25.

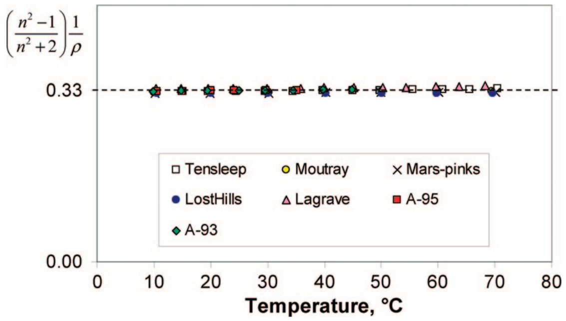

Figure 4. Validation of the one-third rule in a wide range of temperatures for different crude oils. Experimental data was taken from Wang.[16]

In eq 1, the molar refraction, R_m, represents the volume occupied by molecules per unit mole, whereas MW/ρ represents the total or apparent molar volume, including the free space between molecules. The refractive index function, F_{RI}, is, therefore, the fraction of the total volume occupied by molecules.

Because R_m is nearly independent of the temperature and pressure, the one-third rule can also be applied over a wide range of temperatures and pressures. Figure 4 shows the remarkable agreement of the one-third rule compared to experimental data of seven crude oils[16] in a temperature range of about 60 °C (108 °F).

A linear correlation between the solubility parameter, δ, and F_{RI} at 20°C was proposed by Wang and Buckley[17]

$$\delta = 52.042F_{RI} + 2.904 \tag{2}$$

where δ is in units of MPa$^{0.5}$.

The one-third rule can now be applied to estimate the solubility parameters of liquid hydrocarbons as a function of their mass densities at ambient temperature

$$\delta = 17.347\rho + 2.904 \tag{3}$$

where δ is in units of MPa$^{0.5}$ and ρ is units of g/cm^3.

The one-third rule is a good alternative for the estimation of the mass density or the refractive index when one of these properties is known and no other laboratory data are available. However, it is important to mention that not all of the oil components satisfy this relationship. Light substances, such as methane, ethane, and propane, do not obey the one-third rule.

Cohesive Energy and Solubility Parameter as a Function of the Pressure. The cohesive energy, e, is defined as the negative value of the residual internal energy, $-u^{res}$, and can be calculated as the product of the molar volume, v, and the solubility parameter squared, δ^2.

$$e = -u^{res} = -(u^L(P, T) - u^{ig}(T)) \tag{4a}$$

$$e = v\delta^2 \tag{4b}$$

According to eq 4a, the cohesive energy can be readily calculated using an equation of state, such as PC-SAFT, by obtaining the internal energies of the liquid at the pressure and temperature of interest and the internal energy of a gas at the same temperature but for $P \rightarrow 0$, i.e., internal energy of an ideal gas.

Along a co-existence curve at constant temperature, e.g., bubble point or cloud point, both pressure and composition of the mixture are changing. To calculate the cohesive energy or the solubility parameter of the mixture along this curve, both effects need to be taken into account.

The pressure dependence of the cohesive energy and the solubility parameter can be derived from thermodynamic relationships.

The pressure dependence of the cohesive energy, e, of a pure component is given by eq 5

$$\left(\frac{\partial e}{\partial P}\right)_T = -\left(\frac{\partial u^{res}}{\partial P}\right)_P = T\left(\frac{\partial v}{\partial T}\right)_P + P\left(\frac{\partial v}{\partial P}\right)_T \tag{5}$$

The thermal expansion, α_P, and the isothermal compressibility, κ_T, are defined according to eqs 6 and 7, respectively.

$$\alpha_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \tag{6}$$

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{7}$$

For small finite differences in pressure and temperature, α_P and κ_T can be assumed to be constant; i.e., we can obtain average values $\bar{\alpha}_P$ and $\bar{\kappa}_T$ in that interval, and eq 5 can be integrated to obtain eq 8

$$e(P, T) = e_0(P_0, T) + \left(\frac{1 - T\bar{\alpha}_P}{\bar{\kappa}_T}\right)(v - v_0) + Pv - P_0v_0 \tag{8}$$

where v and v_0 are evaluated at actual pressure, P, and at reference pressure, P_0, respectively.

Similarly, for the solubility parameter, eq 9 can be derived

$$\delta^2(P, T) = P + \frac{v_0}{v}[\delta_0{}^2(P_0, T) - P_0] + \left(\frac{1 - T\bar{\alpha}_P}{\bar{\kappa}_T}\right)\left(1 - \frac{v_0}{v}\right) \tag{9}$$

In eq 9, it can be clearly seen that, at constant temperature, the solubility parameter only depends upon pressure and volumetric quantities, i.e., volume, isothermal compressibility, and thermal expansion.

Using eq 9, the solubility parameter of a component can be calculated at a given P, starting from a known solubility parameter value at a reference pressure, P_0. If this pressure range is wide, it can be split into several small intervals, and then use successive calculations. It is necessary to know the volumetric behavior of the system, as a function of the pressure. At every interval, the corresponding values of $\bar{\alpha}_P$ and $\bar{\kappa}_T$ are calculated.

This procedure was implemented for the calculation of the solubility parameter of benzene and hexane as a function of the pressure. Volume data were obtained from the National Institute of Standards and Technology (NIST) database.[18] Figure 5 shows the excellent agreement between successive calculations using eq 9 and molecular simulation data reported by Rai et al.[19]

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(16) Wang, J. New Mexico Institute of Mining and Technology, Socorro, NM, 2000.

(17) Wang, J. X.; Buckley, J. S. *Energy Fuels* **2001**, *15*, 1004–1012.

(18) Linstrom, P. J.; Mallard, W. G. National Institute of Standards and Technology (NIST) Chemistry WebBook, NIST Standard Reference Database, 2005.

(19) Rai, N.; Siepmann, J. I.; Schultz, N. E.; Ross, R. B. *J. Phys. Chem. C* **2007**, *111*, 15634–15641.

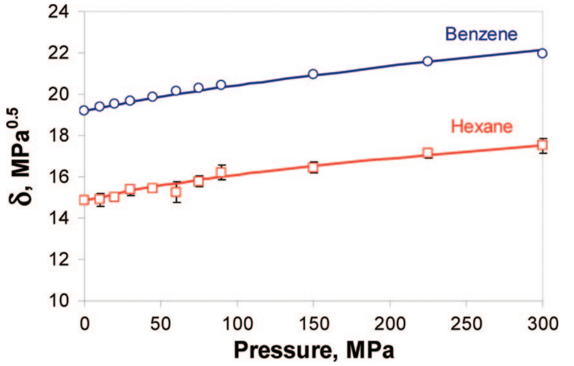

Figure 5. Comparison between proposed model (continuous lines) and data[19] (open markers) for the solubility parameters of benzene and hexane, as a function of the pressure.

New Mixing Rule for Solubility Parameters. The current expression used to calculate the solubility parameter of a mixture, δ_{mix}, from the solubility parameter of the pure constituents is given by eq 10

$$\delta_{\text{mix}} = \sum_i \phi_i \delta_i \tag{10}$$

where ϕ is the volume fraction and δ is the solubility parameter of the pure component i.

This equation is an extension of the Scatchard−Hildebrand regular solution theory to mixtures containing polymers and solvents. The interaction energy of two different molecules is estimated assuming a geometric mean for the cohesive energy.[20] However, even at that time, it was well-known that this was an approximate result. The interaction energy density is, in general, less than or equal to the geometric mean, a result demonstrated by London.[21]

This mixing rule offers a simple and accurate enough method for estimating the solubility parameters of mixtures containing liquids. However, as originally recognized by Hildebrand et al.,[22] the presence of dissolved gases requires a special treatment. At that time, the effective volume and solubility parameter for hypothetical liquid-like dissolved gases were fit, assuming that the same mixing rule held. Even though this is a procedure that even in current references is followed,[23] it has been known that the geometric mean for intermolecular forces becomes increasingly poor as the difference in size between different molecules increases.[24]

A different approach can be followed starting from the definition of the cohesive energy and the molar volume of the mixture in terms of the partial molar properties of the constituents, according to eqs 11 and 12

$$e_{\text{mix}} = \sum_i x_i \tilde{e}_i \tag{11}$$

$$v_{\text{mix}} = \sum_i x_i \tilde{v}_i \tag{12}$$

where x_i is the mole fraction of component i and $\tilde{e}_i$ and $\tilde{v}_i$ are the partial molar cohesive energy and the partial molar volume of component i, respectively.

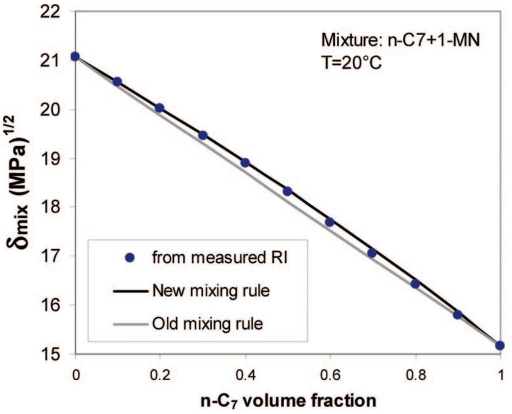

Figure 6. Comparison between the old mixing rule and the new mixing rule proposed in this work, with experimental data.[25]

When the definition of the solubility parameter is combined with eqs 11 and 12, a quadratic mixing rule for the solubility parameter can be readily obtained

$$\delta_{\text{mix}}^2 = \sum_i \hat{\phi}_i \hat{\delta}_i^2 \tag{13}$$

where $\hat{\phi}_i = x_i \tilde{v}_i / v_{\text{mix}}$ and $\hat{\delta}_i^2 = \tilde{e}_i / \tilde{v}_i$.

Equation 13 represents an exact relationship to calculate the solubility parameter of the mixture. However, it is difficult to calculate the partial molar properties of the components, and certain assumptions need to be made. Effective molar volumes and cohesive energies can be proposed for this effect.

The mixing rule proposed in this work has been validated for the system *n*-heptane/α-methyl naphtalene and is reported in Figure 6. Experimental data have been reported by Wang.[25] From the figure, it is clear that the new mixing rule provides a better estimate for the solubility parameter of the mixture in a wide range of concentrations of *n*-heptane.

Several simulations were performed using the PC-SAFT EoS, and the results led to two important conclusions: (1) The two mixing rules give similar results for mixtures formed by similar liquids. (2) The new mixing rule is in excellent agreement with the simulation results, even for mixtures containing dissolved gases. In this case, the difference with the old mixing rule was observed to be a maximum.

The effectiveness of the new mixing rule depends upon the accuracy of the values of partial molar properties of the different components. In some cases, effective values can be used; however, it may be necessary to obtain correlations for these partial molar properties as a function of the composition. An approach to correlate the cohesive energy at the bubble point or asphaltene precipitation onset is proposed in the next section.

Universal Curves for Bubble Point and Asphaltene Precipitation Onset

The correlations presented in the previous sections are useful in estimating the solubility parameters of a mixture as a function of the pressure and composition. These tools can be applied to the analysis of petroleum systems to obtain a general method for modeling the phase behavior. Relationships between the solubility parameters, cohesive energy, pressure, and composition along the bubble point and onset of asphaltene precipitation curves can be readily obtained.

Although an extensive experimental database for the phase behavior of multiple crude oil systems is desirable to validate

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(20) Scott, R. L.; Magat, M. *J. Chem. Phys.* **1945**, *13*, 172.

(21) London, F. *Z. Phys. Chem.* **1930**, *B11*, 222–251.

(22) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold Company: New York, 1970.

(23) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1991.

(24) Prausnitz, J. M.; Shair, F. H. *AIChE J.* **1961**, *7*, 682–687.

(25) Wang, J. X. Personal communication.

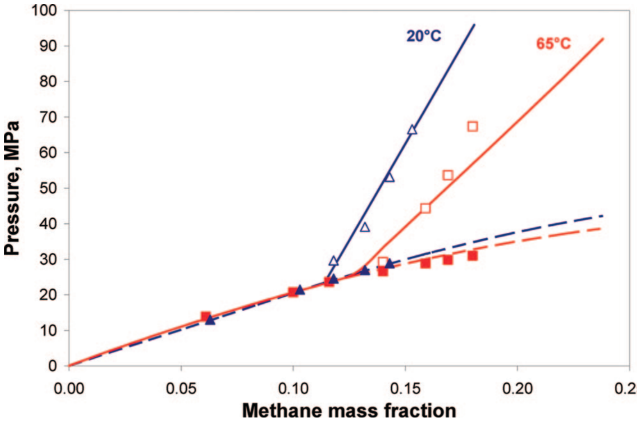

Figure 7. Asphaltene instability onsets (open symbols) and bubble points (filled symbols) for a model oil at two different temperatures. Lines represent the simulation results using PC-SAFT. This figure was adapted from Ting.[3]

the proposed models, the time and cost are prohibitive. Alternatively, computer simulations using reliable equations of state, such as PC-SAFT, can be successfully applied to represent the systems of interest. The PC-SAFT EoS has been effectively used for modeling the bubble point and onset of asphaltene precipitation in multiple cases, considering, for example, the effect of oil-based mud,[11] gas injection,[12] commingling of oils,[26] and CO_2-induced asphaltene precipitation.[13]

In this initial stage, a model dead oil composed of 1 g of *n*-C_7 precipitated asphaltene in 100 mL of toluene is used. Several asphaltene precipitants can be proposed to study their effect on the onset of asphaltene precipitation and, ultimately, to elucidate a universal method for modeling the asphaltene instability.

This model oil mixed with methane was previously studied and characterized by Ting.[3] Figure 7 presented the comparison between experimental data and simulation results using the PC-SAFT EoS. PC-SAFT parameters and binary interaction parameters have been previously reported.[3,8,12] The agreement is very good, even assuming that asphaltenes are a monodisperse fraction. The good quantitative agreement between simulations and experimental data gives confidence in the effectiveness of the PC-SAFT EoS in the prediction of the phase behavior of crude oil systems, when no other experimental data are available.

As observed from conventional pressure−composition ($P-x$) diagrams for asphaltene stability, there is a different set of curves with no apparent relationship between them, for different asphaltene precipitants.

A different approach is now proposed in which, instead of a $P-x$ diagram, a cohesive energy−composition ($e-x$) diagram is used. Because of the lack of reported data in the literature and the prohibitive cost of performing extensive experimental measurements, the cohesive energy of a mixture of the model dead oil containing different asphaltene precipitants is calculated using the PC-SAFT EoS. It has been found that the cohesive energy behaves linearly as a function of the asphaltene precipitant content, along a co-existence curve, e.g., bubble point or precipitation onset. Figure 8a reports the simulation results for the bubble points of different mixtures as a function of the precipitant mole fraction. The corresponding trend lines are also included to emphasize the linearity obtained. Because the cohesive energies are normalized with respect the cohesive energy of dead oil, a common intercept equal to unity is obtained. Furthermore, the slope of each straight line is related to the cohesive energy of the corresponding precipitant, as shown in Figure 8a. With these two parameters, i.e., intercept and slope, a universal curve for the bubble point can be constructed. Figure 8b presents the simulation results for the asphaltene precipitation onset. The bubble point curves are shown in a light color as a reference. The corresponding trend lines are also shown. These straight lines converge to a single intercept that corresponds to the energy of incipient asphaltene precipitation for the model dead oil. This energy is a hypothetical value that cannot be measured or calculated directly, but it can be estimated by extrapolation. In this particular case, for the model oil and the temperature studied, the value is 0.86. This value is of great importance because it defines the stability of the oil. The oil is less stable as this intercept increases; i.e., less amount of precipitant or pressure depletion is required to induce asphaltene precipitation.

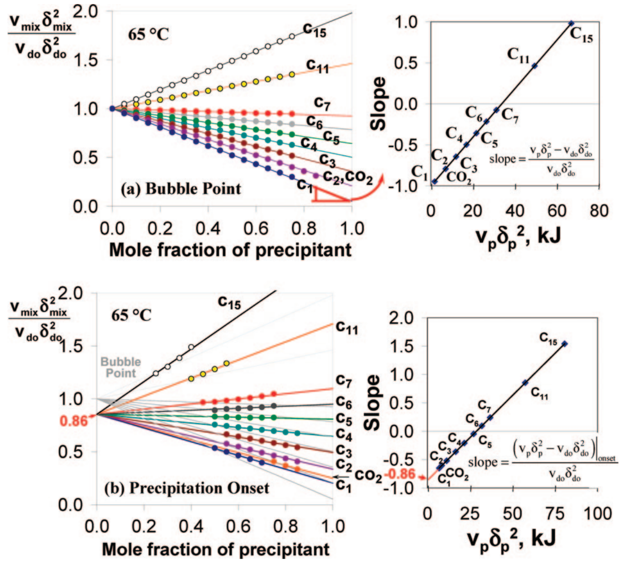

Figure 8. Simulation results using the PC-SAFT EoS for (a) bubble points and (b) onsets of asphaltene precipitation, for a mixture containing a model dead oil and multiple asphaltene precipitants. The slopes of the different straight lines are related to the effective cohesive energy of the precipitant used, evaluated at the corresponding conditions.

This analysis leads to general equations for the bubble point and onset of asphaltene precipitation, eqs 14 and 15, respectively

$$\frac{v_{\mathrm{mix}}\delta_{\mathrm{mix}}{}^2}{v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2} = \frac{1}{v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2}[(v_{\mathrm{p}}\delta_{\mathrm{p}}{}^2 - v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2)x_p + v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2] \qquad (14)$$

$$\frac{v_{\mathrm{mix}}\delta_{\mathrm{mix}}{}^2}{v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2} = \frac{1}{v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2}[(v_{\mathrm{p}}\delta_{\mathrm{p}}{}^2 - v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2)_{\mathrm{onset}}x_{\mathrm{p}} + (v_{\mathrm{do}}\delta_{\mathrm{do}}{}^2)_{\mathrm{onset}}] \qquad (15)$$

where the subscript onset refers to the effective cohesive energy of the dead oil and the pure precipitants along the precipitation onset curve. Because this condition is associated with very extreme pressures, these parameters may need to be extrapolated in practice.

Equations 14 and 15 can be rearranged to obtain the form

$$\delta_{\mathrm{mix}}{}^2 = \frac{v_{\mathrm{p}}x_{\mathrm{p}}}{v_{\mathrm{mix}}}\delta_{\mathrm{p}}{}^2 + \frac{v_{\mathrm{do}}(1-x_{\mathrm{p}})}{v_{\mathrm{mix}}}\delta_{\mathrm{do}}{}^2 = \phi_{\mathrm{p}}\delta_{\mathrm{p}}{}^2 + \phi_{\mathrm{do}}\delta_{\mathrm{do}}{}^2 \qquad (16)$$

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(26) Gonzalez, D. L. Rice University, Houston, TX, 2008.

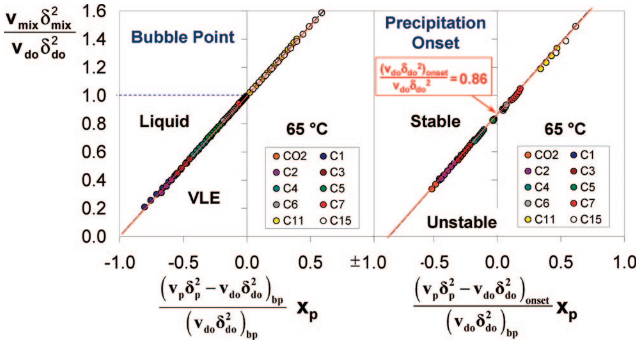

Figure 9. Masters curves for the bubble point and the onset of asphaltene precipitation of a mixture containing a model dead oil and different asphaltene precipitants. The curve is the prediction of eqs 14 and 15, respectively, and the circles correspond to simulation results using the PC-SAFT EoS. Subscripts bp and onset correspond to the conditions of bubble point and onset of asphaltene precipitation at which the cohesive energies are evaluated.

Equation 16 corresponds to a mixing rule of a pseudo-binary mixture that is consistent with the new mixing rule proposed in this work, i.e., eq 13, if we recall that the volumes and cohesive energies in eqs 14 and 15 are effective or apparent values.

In Figure 9, the master curves for the bubble point and the onset of asphaltene precipitation, represented by eqs 14 and 15, are compared to the simulation results using the PC-SAFT EoS. The different phases and stability and instability regions are detailed.

From these results, we learned that the simple models described by eqs 14 and 15 and, consequently, the new mixing rule for the solubility parameters are consistent and in excellent agreement with the results predicted by the PC-SAFT EoS. Therefore, the proposed models are very promising in providing new alternatives for characterizing the asphaltene stability of a crude oil and modeling the phase behavior. An extension for its practical application and the proposed procedure for experimental analysis are now addressed.

Application of the General Method for Modeling Asphaltene Stability

The insights that have been found from the proposed models and the thermodynamic analysis using the PC-SAFT EoS lead to the definition of a new approach for characterizing the crude oil and describing its phase behavior, with a few data points.

The cohesive energy of a system, e_{mix}, can be assumed to be a linear function of the precipitant mole fraction along the co-existence curve, i.e., bubble point or asphaltene precipitation curves.

The cohesive energy is the negative of the residual internal energy of the mixture, $-u^{res}_{mix}$, and can be estimated from the solubility parameter, δ_{mix}, and the molar volume, v_{mix}.

$$e_{mix} = -u^{res}_{mix} = v_{mix}\delta_{mix}{}^2 \qquad (17)$$

The solubility parameter can be estimated from refractive index measurements using eq 2

$$\delta = 52.042F_{RI} + 2.904 \qquad (2)$$

where δ is in units of MPa$^{0.5}$.

If no refractive index measurements are available, a good estimation for the solubility parameter can be obtained from mass density, by implementing the one-third rule and applying eq 3

$$\delta = 17.347\rho + 2.904 \qquad (3)$$

where δ is in units of MPa$^{0.5}$ and ρ is in units of g/cm^3.

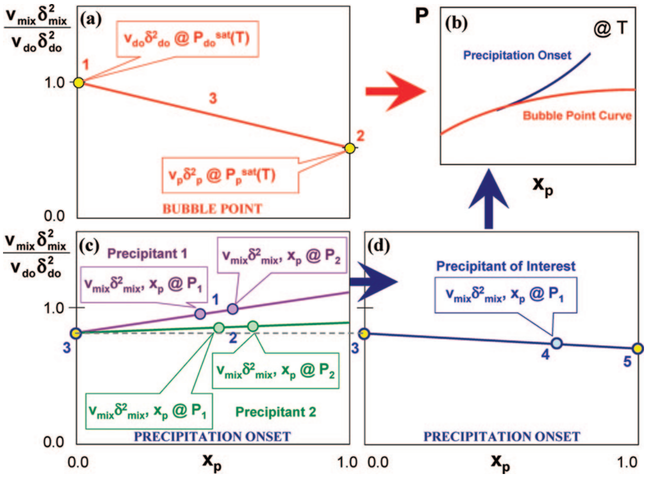

Figure 10. Application of the general method for modeling asphaltene stability. (a) The bubble point can be determined by the cohesive energy density of dead oil and pure precipitant, at the corresponding conditions. (b) Using the relationships for the cohesive energy as a function of the pressure, eq 8, it is possible to determine the $P-x$ curve. (c) Cohesive energy of incipient precipitation (point 3) can be obtained by extrapolating the precipitation onset curves using different precipitants. (d) With the common intercept and at least one precipitation onset, with the precipitant of interest, it is possible to define the cohesive energy along the onset of asphaltene precipitation. Similarly, a $P-x$ curve can be obtained.

A sketch of the application of the general model for modeling asphaltene stability at a constant temperature T is presented in Figure 10. For the bubble point curve, several data points along the co-existence curve are required, according to Figure 10a. One point can be the cohesive energy of the dead oil at its saturation pressure. This value is used to normalize all of the cohesive energies. If the asphaltene precipitant is liquid at low or moderate pressures and the experimental measurement is feasible, this is taken as the second data point. Otherwise, any measurement along the bubble point curve is useful. Obviously, the more data points obtained, the better. However, for description purposes, we will keep the figures as simple as possible with the fewest number of data points. The straight line drawn represents the bubble point curve for that particular system.

The pressure−composition diagram, Figure 10b, can be recovered by solving eq 8 for P

$$P = P_0\frac{v_0}{v} + \frac{e(P,T) - e_0(P_0,T)}{v} + \left(\frac{1 - T\bar{\alpha}_P}{\bar{\kappa}_T}\right)\left(\frac{v_0}{v} - 1\right) \qquad (18)$$

The asphaltene precipitation onset requires one additional step, as described in Figure 10c. Because the cohesive energy of incipient precipitation cannot be measured directly, this value can be determined by measuring at least three data points along the precipitation onset curve with one single asphaltene precipitant. Alternatively, measurements with two asphaltene precipitants can also be used.

Then, the precipitation onset curve can be drawn by measuring a few data points with the asphaltene precipitant of interest, according to Figure 10d. Finally, if desired, the pressure−composition curve can be recovered by applying eq 18 with the variables evaluated at the corresponding conditions.

The stability test of a sample of crude oil under given conditions can be readily performed by locating the cohesive

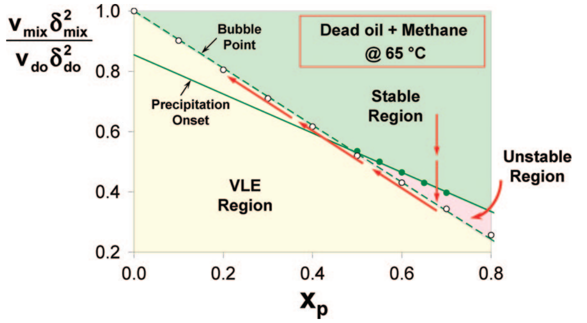

Figure 11. Stability diagram for a model dead oil and methane at 65 °C. The circles correspond to simulation data, and the lines correspond to the expressions for bubble point and precipitation onset proposed in this work.

energy density in the corresponding phase diagram. For instance, for the model oil described in the previous section, the phase diagram obtained from simulation results is shown in Figure 11. The circles correspond to simulation data, whereas the lines represent the correlations proposed. As we can expect, there is a region of asphaltene stability at high pressure that also corresponds to a high cohesive energy. If we deplete pressure, the cohesive energy of the mixture decreases and, at some point, the asphaltene precipitation onset is reached. Upon further depletion, the system arrives at its bubble point. At this condition, the methane escapes from the liquid phase, the oil becomes more stable, and the cohesive energy of the remaining liquid phase starts to increase again.

The analysis is similar to the corresponding pressure–composition diagram. However, because of the linear trend between the cohesive energy and the mole fraction of asphaltene precipitant, using this new approach, the experimental data can be easily extrapolated to forecast the behavior at other compositions. Furthermore, the cohesive energy of incipient precipitation is a characteristic value of a dead oil, at a given temperature, which can be used as a common point for estimating the precipitation onset curve, regardless of the asphaltene precipitant involved.

The method presented in this work is promising in offering better prediction capabilities.

Conclusions

Important progress has been made in developing a general method for modeling asphaltene stability under a wide range of conditions. New equations are presented that contribute to the calculation of important variables, such as the solubility parameter and the cohesive energy of a mixture and its components.

A new correlation, named the one-third rule, can relate the refractive index and the mass density of a crude oil, over a wide range of temperatures and pressures. An extension for the estimation of the solubility parameter as a function of the mass density was also presented.

The effect of pressure over the solubility parameter and the cohesive energy was derived from thermodynamic relationships. The equation obtained is in excellent agreement with data reported in the literature. This equation is capable of relating the cohesive energy of a mixture with pressure along a co-existence curve, i.e., bubble point or precipitation onset.

A new mixing rule for solubility parameters was derived and proposed as an alternative to handle systems containing dissolved gases. Although, the current and new mixing rules predict the same behavior for systems containing normal liquids, it is well-known that the current mixing rule becomes increasingly poor as the difference in size between molecules increases. This is the case where the mixing rule proposed in this work should be especially valuable.

To find a general method for modeling the phase behavior of crude oils containing asphaltenes, mixtures containing a common dead oil and different asphaltene precipitants were studied. Because of the prohibitive costs and technical difficulties of performing extensive experiments, a simulation approach using the PC-SAFT EoS was adopted. This equation of state has demonstrated its ability to successfully modeling the phase behavior of petroleum systems. From simulation results, it was found that the cohesive energy of a mixture, normalized with respect the cohesive energy of dead oil, follows a linear trend with respect to the mole fraction of asphaltene precipitant, along a co-existence curve. Furthermore, the slopes of such lines are related to the cohesive energies of the dead oil and the corresponding precipitant. The precipitation onset curves of the different mixtures converge to a single point when no asphaltene precipitant is present. This hypothetical value is characteristic of a dead oil at a given temperature and can be used to estimate the onset of the asphaltene precipitation curve when any asphaltene precipitant is added.

From this analysis, master equations for the bubble point and the onset of asphaltene precipitation were obtained, which are in excellent agreement with the simulation results. Moreover, these relationships can be readily derived from the new mixing rule proposed in this work.

A procedure for applying these findings in modeling any particular system was also discussed. By exploiting the linear behavior of the cohesive energy/composition relationship, a few data points are required to obtain the curves for bubble point and onset of asphaltene precipitation.

In this way, the framework for future experimental analysis is established.

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Nomenclature

e = cohesive energy, J/mol
$\tilde{e}_i$ = partial molar cohesive energy of component i, J/mol
$F_{RI} = (n^2 - 1)/(n^2 + 2)$ = function of refractive index, dimensionless
MW = molecular weight, g/mol
n = refractive index, dimensionless
P = pressure, MPa
R_m = molar refraction, cm^3/mol
T = temperature, K
u^{res} = residual internal energy, J/mol
v = molar volume, cm^3/mol
$\tilde{v}_i$ = partial molar volume of component i, cm^3/mol

Greek Letters

α_P = thermal expansion, K^{-1}
$\bar{\alpha}_P$ = average thermal expansion, K^{-1}
$\delta = \sqrt{(e/v)}$ = solubility parameter, MPa$^{0.5}$
$\hat{\delta}_i = \sqrt{(\tilde{e}_i/\tilde{v}_i)}$ = effective solubility parameter of component i, MPa$^{0.5}$

κ_T = isothermal compressibility, Pa^{-1}
$\bar{\kappa}_T$ = average isothermal compressibility, Pa^{-1}
$\phi_i = x_i v_i / v_{mix}$ = volume fraction of component *i*
$\hat{\phi}_i = x_i \tilde{v}_i / v_{mix}$ = effective volume fraction of component *i*
ρ = mass density, g/cm^3

Subscripts
0 = reference condition
do = property of the dead oil
i = property of the component *i*
mix = property of the mixture
p = property of the precipitant
P = at constant pressure
T = at constant temperature

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