

Applying the PR-EOS to Predict the Onset of Asphaltene Precipitation from n-Alkane Diluted Bitumens

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ABSTRACT: *Asphaltenes are the n-pentane or n-heptane insoluble fractions of crude oil that remain in solution under reservoir temperature and pressure conditions. They are destabilized and start to precipitate when the pressure, temperature and/or composition changes occur during primary production. The precipitated asphaltene particles will then grow in size and may start to deposit onto the production string and/or flowlines, causing operational problems. In this paper, a combination of the modified Peng-Robinson (PR) EOS and regular solution theory is used to estimate the onset of asphaltene precipitation of some oils. The PR EOS was modified using contribution methods for the asphaltenes which are assumed to be polymeric-like compounds consisting of aggregates of monodisperse asphaltene monomers. The modified EOS with the Peneloux correction was used to estimate the molar volumes and solubility parameter of the four solubility classes (Saturates, Aromatics, Resins, Asphaltenes) of bitumens. The predicted parameter of EOS was used to determine the onset of asphaltene precipitation from bitumen upon the addition of heptane and predictions were compared with measured onsets. Liquid-Liquid equilibrium was assumed between an oil phase and an asphaltene-rich phase. The asphaltene were divided into several pseudo components based on the Schultz-Zimm distribution function. Application of this model will help operators to better forecast the onset of asphaltene precipitation as it relates to flow rate history of the well and the pace of plugging induced by asphaltenes, and thus better plan remedial measures. The agreement between the predicted and measured onsets is very good.*

KEY WORDS: *Asphaltene, Onset, Precipitation, PR equation of state, Regular solution theory.*

INTRODUCTION

It is well known that asphaltene precipitation could cause troubles in the petroleum production, transportation and processing. Asphaltenes are generally defined as the material precipitated from the crude and heavy oils upon

addition of low molecular weight n-alkanes. The onset point and the amount of asphaltene precipitation depend on the composition of the crude oil, type of precipitant and the temperature and pressure of the system. Previous

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investigators showed that changes in temperature, pressure, oil composition and electrical fields could cause asphaltene precipitation in wells, pipelines, and production equipment. In regard to the temperature effect, inconsistent observations have been reported. Some results show that a higher temperature will generate more asphaltene precipitation, while some other results indicate an opposite temperature effect.

Andersen [1] has discussed this controversy in the temperature effect. In addition, the presence of asphaltenes also aggravates fouling of catalysts, coking, and promotion of emulsions during the crude oil processing. For predicting the onset point and the amount of asphaltene precipitation, a practical and reliable mathematical model is required. The existing models basically fall into two classes:

- (I) models that involve asphaltene properties, and
- (II) models based on the scaling equation approach.

Typical class I models include thermodynamic models and thermodynamic micellization models. Such models generally require knowledge of asphaltene properties, e.g. the density, molecular weight and solubility parameter. However, due to the complex composition and chemical association behavior, it is difficult to measure the molecular weight of asphaltenes accurately. To overcome this difficulty, in all models of this type it is assumed that the asphaltene components could be lumped into a single pseudo-component. This over-simplified assumption may cause serious deviations as indicated by the PVT and vapor-liquid equilibrium calculation results of reservoir fluid mixtures. Recent investigations showed that the prevalent thermodynamic models are incapable of predicting asphaltene precipitation without extensive data fitting. On the other hand, *Rassamdana et al.*, [2] recently proposed a scaling equation approach to describe asphaltene precipitation behavior: the time-dependence and temperature-dependence of asphaltene precipitation, the molecular weight distribution of asphaltenes, and asphaltene precipitation under high pressure conditions. This approach is simple in mathematical formulation and does not involve the properties of complex asphaltenes. Recently, we have studied systematically the capability of the scaling equation approach for predicting the onset point and the amount of asphaltene precipitation under normal pressure (degassed reservoir oil systems) and high pressure (gas-

injected oil systems) conditions. Our results as well as those results reported by *Rassamdana et al.*, [2] showed that, by fitting to a limited set of experimental data, the scaling approach is capable of providing good predictions for asphaltene precipitation behavior at fixed temperature. In this work a combination of the modified PR EOS and regular solution theory is used to estimate the onset of asphaltene precipitation.

The use of cubic equations of state (CEOS) such as the SRK and PR equations is popular in the calculation of phase equilibrium values like temperature-pressure-composition relationships, as they are simple and convenient to use (*Andersen and Speight*, 1999) [1]. These models are very successful for vapor-liquid as well as liquid-liquid equilibrium calculation (*Pedersen et al.*, 1991).

In 1986, *Gupta* [3] used a combination of the SRK and PR equations to calculate asphaltene solubility. The SRK EOS is used in combination with a structural correlation (*Alexander et al.*, 1985) [4] for estimation of the critical properties and a centric factor of asphaltenes. These properties are then inputs into the PR EOS and a solid-liquid-equilibrium calculation is performed for a non-associating single component with fixed molar mass.

In the light of the well-known problems in obtaining a true molar mass for asphaltenes, the input data for the molar mass are derived from a series of values ranging from 530 to 1190 g/mol.

Gupta [3] developed a correlation for obtaining the fugacity of solid asphaltenes and used his model in calculations of solubilities of asphaltenes in n-alkanes (*Speight*, 1979) [5] and flocculation thresholds (onsets) in mixtures of non-solvent and solvent. In the model of *Thomas et al.*, (1992) [6], the precipitated asphaltenes were considered as pure solid while the oil and gas phases were modeled with a CEOS. A correlation including eight parameters was introduced for calculation of the fugacity of asphaltene fraction. *Thomas'* model had a large number of parameters and had to be tuned in order to match experimental data. Consequently, this model is highly empirical and difficult to implement (*Nghiem et al.*, 1993) [7].

In 1998, *Wu et al.*, [8] developed a molecular thermodynamic framework for asphaltene-oil equilibria. In this model, both asphaltenes and resins are represented by pseudo-pure components while all other components

in the solution are represented by a continuous medium that affects interactions among asphaltene and resin particles.

In 2000, Wu *et al.*, [9] used their thermodynamic model to predict asphaltene precipitation in reservoir fluids. The calculated results were in good agreement with the experimental measurements. However, the model includes many parameters that are estimated and is not easy to be applied.

In 1999, Szewczyk and Behar [10] developed a liquid-liquid model, which described asphaltene flocculation as the formation of a new liquid phase with high asphaltenic content (the asphaltenic deposit phase) but containing all the components initially in the crude. Asphaltenes were represented as a single fraction. This thermodynamic model, which used the translated PR EOS has several fitting parameters including the molar mass and critical properties of asphaltenes, and the critical pressure of other crude oil fractions. Other physical properties were estimated using the group contribution methods of Avallée (1996) [11] and of Rogalski and Neau (1990) [12].

PREDICTION OF THE ONSET OF ASPHALTENE PRECIPITATION

In this paper, a combination of the modified PR EOS and regular solution theory is used to estimate the onset of asphaltene precipitation. The onset of precipitation is defined as the n-haptan-to-heavy oil ratio where precipitation first occurred at ambient conditions.

EXTENSION OF THE PR EOS TO ASPHALTENE AGGREGATES

The challenge in applying an EOS to asphaltene precipitation is to determine the parameters a and b of PR EOS for mixture that include asphaltenes. Recent work demonstrates that asphaltene association can be modeled in a manner analogous to linear polymerization (Agrawala 2001) [13]. Asphaltenes are known to self-associate and the aggregates can be represented as polymer-like compounds. In this case, the association mechanism does not involve chemical bonding but rather *van der Waals* forces such as Π - Π bonding or acid-base interactions. In this view the asphaltene monomer is a repeating segment and can be considered as a group in structure of the asphaltene aggregate. The critical properties of the aggregate are approximately the same as

those of the monomer because molecular bonding is unchanged. However one weakness of an EOS is that components with the same critical properties are considered to be identical even if their molar volumes differ as in the case of a repeating segment. This shortcoming can be overcome by relating the parameters using group contribution methods.

The PR EOS has the following form:

$$P = \frac{RT}{V^{\text{PR}} - b} - \frac{a}{V^{\text{PR}}(V^{\text{PR}} + b) + b(V^{\text{PR}} - b)} \quad (1)$$

Where P is the pressure, T the temperature, R the gas constant, a and b the parameters of EOS, and V is the molar volume calculated by the PR EOS.

The PR EOS with a Peneloux correction (Peneloux *et al.*, 1982) [14] gives the corrected liquid molar volume is obtained as follows:

$$V^{\text{L}} = V^{\text{PR}} - c$$

Where c is the Peneloux correction term. It can be estimated by:

$$c = \frac{0.40678RT_c}{P_c} (0.29441 - Z_{\text{RA}}) \quad (2)$$

Where Z_{RA} is the *Rocket* compressibility factor for saturated liquid molar volumes and is reported for 200 hydrocarbon. If this parameter is not available it may be estimated from:

$$Z_{\text{RA}} = 0.29056 - 0.08775\omega \quad (3)$$

Where ω is the acentric factor. In this work we used Eq.(3) for all components.

Replacing V^{PR} in Eq. (1) by that in Eq. (2) will result in the following form of the EOS:

$$P = \frac{RT}{V^{\text{L}} - (b - c)} - \frac{a}{(V^{\text{L}} + c)(V^{\text{L}} + c + b) + b(V^{\text{L}} + c - b)} \quad (4)$$

$$a = \sum \sum v_m v_n a_{mn} \quad (5)$$

$$b = \sum v_m b_m \quad (6)$$

$$c = \sum v_m c_m \quad (7)$$

Where v_m is the number of group m in a molecule, and a_{mn} , b_m , and c_m are parameters for group m .

For a chain molecule of repeating segments such as asphaltene aggregates a segment can be considered as a

group. If \bar{r} is the average number of monomers in a given aggregate then the equation of state parameters for the aggregates related to the monomer parameters using Eqs. (5),(7) will be [15]:

$$a = \bar{r}^2 a_m \quad (8)$$

$$b = \bar{r} b_m \quad (9)$$

$$c = \bar{r} c_m \quad (10)$$

Where \bar{r} is the average number of monomer in a given aggregate, a , b and c are the aggregate parameter and a_m , b_m and c_m are the monomer parameters. The modified PR EOS is obtained by replacing a , b , c in Eq. (4) with Eqs. (8) to (10) respectively:

$$P = \frac{RT}{\bar{r}[V^L - (b - c)]} - \frac{a}{(V^L + c)(V^L + c + b) + b(V^L + c - b)} \quad (11)$$

Where $v^L = V^L / \bar{r}$ is the monomer molar volume. Note that only the parameter of asphaltene monomer and the average number of monomers in the aggregate are required to solve Eq. (11) for monomer molar volume.

The value of \bar{r} can be estimated by the following relation:

$$\bar{r} = \frac{\bar{M}^{\text{agg}}}{\bar{M}^{\text{mon}}} \quad (12)$$

Where \bar{M}^{agg} and \bar{M}^{mon} are the average molar mass of the asphaltene aggregate and the monomer molar mass respectively.

FLUID CHARACTERIZATION

In order to implement the EOS, a and b are determined for each component based on the component critical properties. In this approach, the heavy oils or bitumens are divided into pseudo components based on the SARA analysis. Saturates, aromatics, and resins are treated as individual pseudo components. Asphaltenes are divided into mass fractions according to a molar mass distribution. The critical properties of the asphaltene fractions are assumed to be identical to the monomer properties since the higher molar mass asphaltene are considered to be aggregates of monomers.

The following correlations [19] were used to estimate the critical properties and a centric factors of the SARA fractions.

Table1: VPO molar masses (g/mol) of SARA fraction.

Fraction	1	2	3	4	C_f
Saturate	520	500	480	500	0.9024
Aromatics	550	500	50	520	0.8098
Resins	950	900	820	1120	0.7910
Asphaltene	2000	1400	1800	1900	0.7940

$$T_C(\text{K}) = 77.856M^{0.4708} \quad (13)$$

$$P_C(\text{bar}) = 1891.4^{-0.7975} \quad (14)$$

$$V_C(\text{cm}^3 / \text{mol}) = 2.4988M + 116.8879 \quad (15)$$

$$\omega = C_f \{0.5837 \ln M - 2.5389\} \quad (16)$$

PSEUDO COMPONENT MOLAR MASSES

In order to implement the modified PR EOS, the molar mass of the saturate, aromatic and resin fractions is required as well as the asphaltene monomer molar mass and the degree of asphaltene association, r . The measured molar masses of SARA fractions from four bitumens/heavy oils are reported in table.1.

ASPHALTENE MOLAR DISTRIBUTION

The final step in fluid characterization is to determine the asphaltene molar mass distribution, that is the distribution of " r ". Asphaltene self-association can be considered as a step polymerization in which monomers react in such a way that groups of them which are already linked together can be coupled with other groups. For step polymerization, distributions are broad and often a good representation is achieved by the *Schulz-Zimm* distribution. This distribution is a mole fraction-based distribution and is usually represented in terms of the degree of polymerization or association, r , rather than the molar mass and is given by the following equation (Strobl, 1997) [20]:

$$f(r) = \frac{1}{\Gamma(\beta)} \left(\frac{\beta}{\bar{r}} \right)^\beta r^{\beta-1} \exp\left(-\frac{\beta r}{\bar{r}} \right) \quad (17)$$

Where β is a parameter which determines the shape of distribution and \bar{r} is the average number of monomers per aggregate or degree of association which is estimated from Eq. (12), Γ is the gamma function.

In most cases $\beta \approx 2$ provides a good data fit and when $\beta = \alpha$ Eq. (17) simplified to:

$$f(r) = \frac{4r}{\bar{r}^2} \exp\left(-\frac{2r}{\bar{r}}\right) \quad r \in [0, r_{\max}] \quad (18)$$

Where r_{\max} is the upper limit of the distribution function. A value of 45 was used in this work. As mentioned above, the asphaltene distribution was discretized into a number of internals or asphaltene fractions. The average degree of association of each asphaltene fraction can be found from the following integration:

$$\bar{r}_{ai} = \frac{\int_{r_i}^{r_i+1} r f(r) dr}{\int_{r_i}^{r_i+1} f(r) dr} \quad (19)$$

$$\bar{r}_{ai} = \quad (20)$$

$$\frac{\left\{ -\left[(r-1)^2 \alpha + 2(r-1) + 2/\alpha \right] \exp[-\alpha(r-1)] \right\}_{r_i}^{r_i+1}}{\left[1 + \alpha(r_i-1) \exp[-\alpha(r_i-1)] \right] - \left[1 + \alpha(r_{i+1}-1) \exp[-\alpha(r_{i+1}-1)] \right]}$$

$$\alpha = \frac{2}{(\bar{r}-1)} \quad (21)$$

REGULAR SOLUTION THEORY

Regular solution models have been successfully applied to asphaltenes in pure solvents. In most cases, asphaltenes in solution are assumed to be in equilibrium with a nearly pure asphaltene phase. This equilibrium may be considered as liquid-liquid equilibrium (LLE) or a liquid-solid equilibrium (SLE). In this work we assume liquid-liquid equilibrium between an oil phase and an asphaltene-rich phase

The chemical potential (μ) of component i in a solution derived from *Flory-Huggins* theory is rearranged to the following form (*Yang et al., 1999*) [16].

$$\frac{\mu_i - \mu_i^0}{RT} = \left[1 - \frac{V_i^L}{V_{\text{mix}}} + \ln \left(\frac{x_i^L V_i^L}{V_{\text{mix}}} \right) + \frac{V_i^L}{RT} (\delta_i - \delta_{\text{mix}})^2 \right] \quad (22)$$

Where μ_i^0 the chemical potential at standard state, R is the universal gas constant, and T is temperature. V_i^L and V_{max} are the liquid molar volume of component i and the average molar volume of the medium, respectively. δ_i and δ_{mix} are the solubility parameters for the same respective constituents. Molar volumes and solubility

parameters are estimated from the modified PR EOS.

In order to calculate the liquid solubility parameter *Hildebrand, Prausnitz and Scott* related this parameter of non-polar solvents, δ^L , to the internal energy of vaporization, ΔU^{LV} , and the molar volume of the liquid phase, V^L , to obtain:

$$\delta^L = \left(\frac{\Delta U^{LV}}{V^L} \right)^{1/2} \quad (23)$$

To calculate the internal energy of vaporization the following equation was used (*Reid et al., 1989*) [21]:

$$\begin{aligned} \Delta U^{LV} &= \int_{V^L}^{V^V} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \\ &= \int_{V^L}^{V^V} \frac{a_m}{(V+c)(V+b+c) + b(V-b+c)} dV \end{aligned} \quad (24)$$

Note that the number of monomers, r , does not appear in Eq. and has no direct effect on the solubility parameter of an asphaltene aggregate. The value of r has an indirect effect on the solubility parameter because it influences the monomer molar volume, V^L , determined from Eq. (11). However, the effect is small and the solubility parameter of high molar mass asphaltenes will not differ much from that of monomer or low molar mass asphaltenes.

If asphaltene fraction is taken as a pure component, the onset of asphaltene precipitation should satisfy the following condition (*Yang et al., 1999*)

$$\frac{\mu_a - \mu_a^0}{RT} = 0 \quad (25)$$

where μ_a is the chemical potential of the asphaltene fraction. From Eq. (22) we have:

$$F = \left[1 - \frac{V_a^L}{V_{\text{mix}}} + \ln \left(\frac{x_a^L V_a^L}{V_{\text{mix}}} \right) + \frac{V_a^L}{RT} (\delta_a - \delta_{\text{mix}})^2 \right] = 0 \quad (26)$$

When $F < 0$, asphaltenes are stable in solution and no precipitation occurs; $F > 0$, asphaltenes are unstable and precipitation occurs; $F = 0$, onset of asphaltene precipitation.

RESULTS AND DISCUSSION

The heptane- to- bitumen ratios at which precipitation occurred for different oils are given in table 2. An attempt was made to predict the onset with regular solution theory

Table 2: Measured and calculated onset of asphaltene precipitation at 23 °C. a) heptane- to- bitumen ratio (H/B) and b) mass fraction of heptane (wH).

	Onset H/B (cm ³ /g)			Onset w _H		
	Measured	Predicted	%RD	Measured	Predicted	%RD
Oil1	1.90	1.92	+1.05	0.565	0.568	+0.53
Oil2	1.75	1.82	+4.00	0.545	0.554	+0.65
Oil3	1.65	1.66	+0.61	0.530	0.532	+0.38
Oil4	1.75	1.70	-2.86	0.545	0.538	-1.28
%AAD ^b			+2.13			+0.96

$$a) \%RD = \frac{calc - exp}{exp} \times 100, \quad b) \%AAD = \frac{\sum_i \frac{| \%RD |}{N}}{N}$$

using the molar volumes and solubility parameters generated with the modified PR EOS. To obtain an accurate prediction of the onset and amount of precipitation, the molar mass distribution of the asphaltenes in bitumen is required. To determine the onset of precipitation, it is sufficient to estimate the molar mass of the first asphaltenes to precipitate. Previous work (Agrawala, 2001) [13] with asphaltene-resin mixtures indicates that at asphaltene-to-resin ratios similar to bitumen the degree of association is quite low with average molar masses in the order of 2500 g/mol. In this work, the molar mass of the first asphaltenes to precipitate from bitumen was estimated by trial and error so that the calculated onset point for one of the systems (Oil1) matches with the measured onset. The approximated value is 2000 g/mol. This value was used to predict the onset of precipitation in all of the other bitumens, as reported in table 1. The predicted onsets are within 4% of the measured values.

The accuracy of the onset prediction depends on the accuracy of the molar mass in pure solvents has already been developed (Agrawala, 2001) [13].

THE EFFECTS OF TEMPERATURE AND PRESSURE ON THE ONSET POINT

A change in temperature may result in two consequences: First, a rise in temperature improves miscibility; in the absence of specific intermolecular forces, two fluids mix more easily at high temperatures because the negative contribution of the entropy of mixing to the Gibbs energy of mixing increases with temperature, favoring mixing (Wu *et al.*, 1998) [8]. In this case, the onset dilution ratio increases; that is,

more precipitant is required for starting asphaltene precipitation. Secondly, however, an increase in temperature also reduces liquid density, and that reduction decreases solvent power (Wu *et al.*, 1998) [8]. At constant temperature, the solubility of asphaltenes decrease as the density of solvent falls.

Therefore, due to these two opposing trends, in some cases, raising the temperature increases the solubility while in other cases, it decreases solubility (Wu *et al.*, 1998) [8].

At constant temperature, the liquid density increases as pressure increases. Thus, an increase in pressure raises asphaltene solubility that in turn increases the onset dilution ratio.

In order to investigate the effects of temperature and pressure on the onset point from the modeling point of view, we have plotted the changes of F (Eq. (3)) with temperature and pressure at a constant dilution ratio (solvent-to-bitumen ratio) shown in Figs.1 and 2. Also, the effects of temperature and pressure on the calculated onset can be seen in Figs. 3 and 4, respectively.

Based on Fig. 1, at constant pressure and solvent- to-bitumen ratio, the model predicts lower asphaltene solubility as temperature increases. This means that the onset dilution ratio decreases with an increase in temperature (Fig. 3) which is opposite to what we expect. The reasons for such predictions should be searched in the changes of solubility parameters of heavy fractions especially asphaltenes and resins with temperature.

Comparing the changes of asphaltene solubility parameter with temperature calculated from the modified PR EOS with the temperature functionality of asphaltenes presented by Hirschberg *et al.*, (1984) [17] shows that the

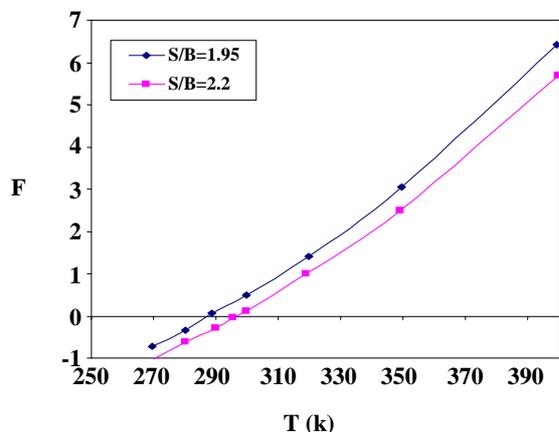


Fig. 1: The temperature effect on the asphaltene stability and solubility.

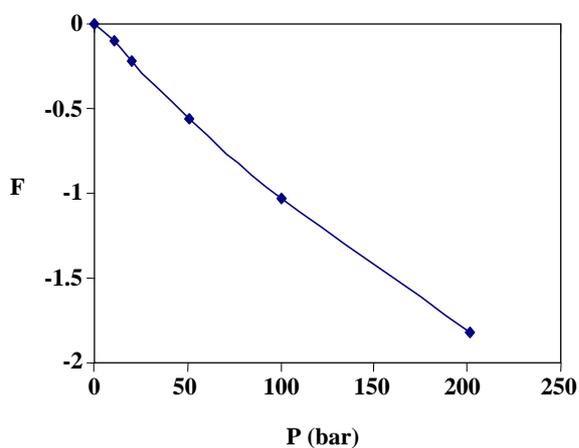


Fig. 2: The effect of pressure on the stability and solubility of asphaltenes.

asphaltene solubility parameter estimated from the model changes a little with temperature while the slope in temperature functionality is higher (Fig. 5). The small changes of the solubility parameter of asphaltenes and resins can be due to two factors: First, the temperature dependency of a parameter in the PR EOS and therefore solubility parameter relation; and secondly, the calculated molar volumes or densities of these heavy fractions from the modified PR EOS.

Gasem *et al.*, (2001) [18] developed a modified temperature dependency for the parameter of the PR EOS for heavy paraffin. To develop such a dependency for the modified PR EOS for SARA fractions, some density measurements and onset measurements at various temperatures are required.

Based on Fig. 2, at constant temperature and solvent-to-bitumen ratios, increasing pressure increases asphaltene

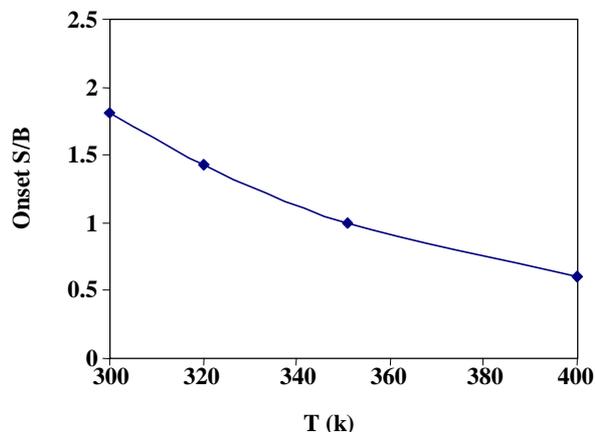


Fig. 3: The effect of temperature on the onset solvent-to-bitumen ratio.

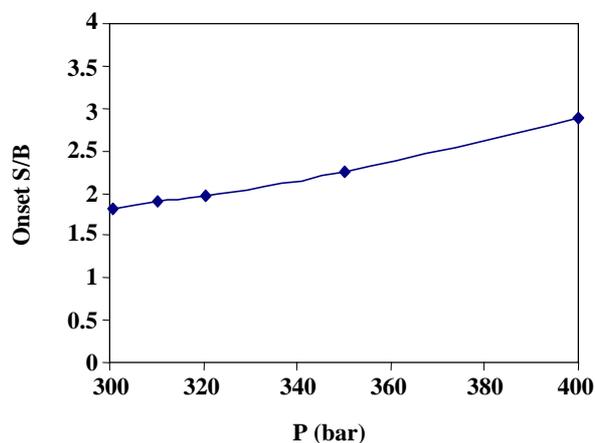


Fig. 4: The effect of pressure on the onset solvent-to-bitumen ratio.

solubility (more negative F) which in turn raises onset dilution ratio (Fig. 4). Thus, the model predicts the pressure effect correctly but qualitatively. In the absence of experimental data, we can not investigate the model predictions quantitatively. Some onset measurements at various pressures are required to check the accuracy of the model predictions.

CONCLUSIONS

A new form of the PR-EOS with Peneloux correction was developed to estimate the molar volumes and solubility parameters of the four solubility classes (SARA fractions) of bitumen. In this ways asphaltenes were considered as polymer-like compounds consisting of aggregates of monodisperse asphaltene monomers.

The onset heptane- to- bitumen ratios were predicted with the regular solution theory using the molar volumes

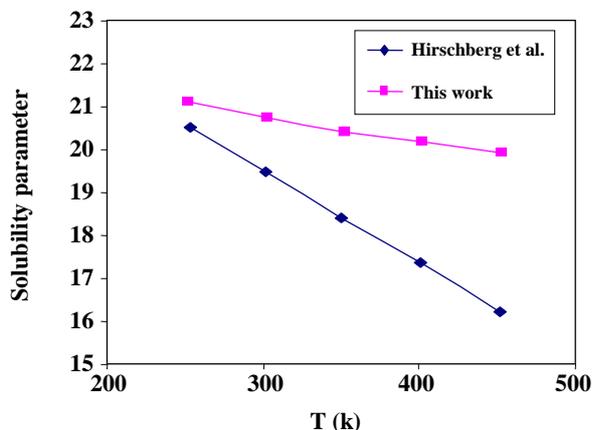


Fig. 5: The effect of temperature on the asphaltene solubility parameter calculated by the modified PR EOS and by Hirschberg et al.'s correlation.

and solubility parameters generated with the modified PR- EOS. When temperature is increased, the onset dilution ratio increases; that is, more precipitant is required for starting asphaltene precipitation and increasing the pressure increases asphaltene solubility which in turn raises onset dilution ratio. The agreement between the predicted and measured onsets is very good.

Nomenclatures

a	Parameter in Peng- Robinson EOS, $\text{KPa} \cdot (\text{m}^3/\text{kmol})^2$
b	Parameter in Peng- Robinson EOS, (m^3/kmol)
c	Constant (function of ω)
M	Molar mass, (kg/mol)
P	Pressure, (kPa)
r	Aggregation parameter
R	Universal gas constant, $(\text{m}^3 \cdot \text{kPa}/\text{kmol} \cdot \text{K})$
T	Temperature, (K)
V	Molar volume

Greek Symbols

μ	Chemical potential
δ	Solubility parameter
ω	A centric factor

Subscripts

i	Component
m	Monomer
RA	Racket
c	Critical property
mix	Mixture
a	Asphaltene

Superscripts

L	Liquid
agg	Aggregate
mon	Monomer

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REFERENCES

- [1] Anderson, S.I., Speight, J.G., *Journal of Petroleum Science and Engineering*, **22**, 53 (1999)
- [2] Rassamdana, H., Dabir, B., Nematy, M., Farahani, M., Sahimi, M., *AICHE J.*, **42**, 10 (1996).
- [3] Gupta, A.K, M.Sc Thesis, Department of Chemical and Petroleum Engineering, University of Calgary, Canada (1986).
- [4] Alexander, G.L., Creagh, A.L., Prausnitz, J.M., *Ind. Eng. Chem. Fund.*, **24**, 301 (1985).
- [5] Speight, J.G., Preprints Americans Chemical Society, *Div. Pet. Chem.*, 825 (1981).
- [6] Thomas, F.B., Bennion, D.W., Hunter, B.E., *J. Can. Pet. Tech.*, **31**, 22 (1992).
- [7] Nghiem, L.X., Hassam, M.S., Nutakki, R., George, E.D., *SPE*, **26642**, 375 (1993).
- [8] Wu, J., Prausnitz, J. M. and Firoozabadi, A., *AICHE Journal*, **44**, 1188 (1998).
- [9] Wu, J., Prausnitz, J. M. and Firoozabadi, A., *AICHE Journal*, **46**, 197 (2000).
- [10] Szewczyk, V., Behar, E., *Fluid Phase Equilibria*, **454**, 158 (1999).
- [11] Avaullee, L. PhD Thesis University of Aix-Marseille III, France (1996).
- [12] Rogalski, M., Neau, E., *Fluid Phase Equilibria*, **56**, 59 (1990).
- [13] Agrawala, M., MSc Thesis, Department of Petroleum and Chemical Engineering, University of Calgary, Canada (2001).
- [14] Peneloux, A., Rauzy, E., Freeze, R., *Fluid Phase Equilibria*, **8**, 7 (1982)
- [15] Akbarzadeh, K., Alboudvarej, H., Beck, J., Svrcek, Y.W., Yarranton, H.W., *AICHE J.*, 2948, 2956 (2003).
- [16] Yang, ZMa, C.F., Lin, X.S., Yang, J.T., Guo, T.M., *Fluid Phase Equilibria*, **157**, 143 (1999).
- [17] Hirschberg, A., deJong, L. N. J., Schipper, B. A., Meijers, J.G., *SPE J.*, **24**, 283 (1984).
- [18] Gasem, K. A. M., Gao, W., Pan, Z., Robinson Jr., R.L., *Fluid Phase Equilibria*, **181**, 131 (2001).

- [19] Avaulle, L., Trassy, L., Neav, E., Jaubert, J.N., *Fluid Phase Equilibria*, **139**, 155 (1997).
- [20] Strobl, G. R., *The Physics of Polymer: Concepts for Understanding Their Structures and Behavior*, 2th Corrected Edition, Springer (1997).
- [21] Reid, T. C., Prausnitz, J. M., Poling, B. E., *The Properties of Gases & Liquids*, 4th Edition., Mc Graw-Hill, New York, 67 (1989).