Predicting The Onset of Asphaltene Precipitation by Virial EOS

S. Sabbaghi[1], M. Shariaty-Niassar[2], Sh. Ayatollahi[1] and A. Jahanmiri[1]

Abstract: In this study, the Onset of Asphaltene Precipitation is predicted by a modified Virial equation of state. The bases of quantum mechanics and statistical thermodynamics are used to evaluate the potential energy and intermolecular forces related to asphaltene molecules. The Virial equation of state is modified using group-contribution-methods for asphaltenes, which are assumed to be polymeric-like compounds consisting of aggregates of monodisperse asphaltene monomers. It is shown how the modified Virial equation of state with the Peneloux correction leads to estimate the molar volume and solubility parameter. These parameters are also compared successfully with results provided by the Soave-Redlich-Kwong equation of state. The proposed model clearly shows that the asphaltene density and solubility parameters depend on molecular weight and temperature. Some useful correlations among these parameters are introduced.

Keyword: Potential energy; Equation of state; Asphaltene Precipitation

1 Introduction

The structure and stability of petroleum depend on the way by which the asphaltene and resin constituents interact. Hence, these interactions play a major role in the formation of sediment and deposition of asphaltenic material.

Asphaltene precipitation in reservoirs has proven to be a problem in oil production, as it can occur in surface facilities and pipelines. Since treatment of the deposited solids increases operating costs, it is desirable to prevent or mitigate asphaltene deposition. As a first step, it is necessary to predict the onset and amount of asphaltene precipitation.

Knowing the mechanism of asphaltene precipitation is a key element for developing a realistic model in predicting asphaltene aggregates.

Since the 1980's many models of asphaltene precipitations have been developed (David, 1973; Lichaa, 1977; Mansoori, 1999). The use of cubic equations of state (CEOS) such as those of Soave Redlich Kwong (SRK) and Peng Robinson (PR) has enjoyed a widespread use for calculating phase equilibrium values (temperature-pressure-composition relationships), as they are simple and convenient (Andersen, 1999). These models are very successful for vapor-liquid, as well as liquid-liquid equilibrium calculations (Pedersen, 1991).

In 1986, Gupta used a combination of the SRK and PR equations to calculate asphaltene solubility. The SRK EOS was used in combination with a structural correlation for the estimation of both critical properties and the acentric factor of asphaltenes. These properties were then introduced into the PR EOS and a solid-liquid-equilibrium calculation was then performed for a non-associating single component with a fixed molar mass (Alexander, 1985).

In an other model, the precipitated asphaltenes were considered pure solid, while the oil and gas phases were modeled with a CEOS. A correlation including eight parameters was introduced for calculating the fugacity of an asphaltene fraction. Thomas' model, however, employed a large number of parameters (Thomas, 1992).

In the year 2000, Wu et al. used their thermodynamic model to predict asphaltene precipitation in reservoir fluids (Wu, 2000). The calculated results were in good agreement with the experimental measurements. Akbarzadeh developed a

[1] Department of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran

[2] Corresponding Author. Tel.: +98-21-66957785; Fax: +98-21-66957785. E-Mail address: mshariat@ut.ac.ir. Department of Chemical Engineering, Tehran University, Iran.

new thermodynamic model for predicting asphaltene precipitation at various conditions. Correlations were developed for the critical properties and the acentric factor of each solubility class (Akbarzadeh, 2002; 2004).

The aim of this article is to present a correlation for solubility, density and structure coefficients. It is important to note that in the previous studies, the structure coefficient was evaluated by trial and error methods, and also the density and solubility parameters were evaluated as a function of molecular weight only. In this study, these parameters are evaluated as a function of temperature and molecular weight, using a specific molecular structure model for asphaltene.

2 Computational details of the proposed model

The interaction of forces between molecules in macromolecules is very critical and can not be ignored. These systems are dense and the molecules are very close to each other such that most of their properties are governed by the aforementioned interaction forces.

Fig. 1 shows the molecular structure of asphaltene proposed for 510°C residue of Venezuelan Crude by Carbognani (Carbognani, 1992).

It has been shown that the measurable macro-

scopic quantities are related to microscopic interactions between the molecules. For the calculation of the intermolecular potential, complicated numerical calculations are needed (they are somewhat linked to quantum mechanics). A quite general function used for the interaction potential energy is the Mie potential function (Mc Quarrie, 1976; Hirschfelder, 1964).

$$U(r) = \frac{n\varepsilon}{n-m} \left(\frac{n}{m}\right)^{\frac{m}{n-m}} \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right] \quad (1)$$

The constants ε and σ are typically obtained from intermolecular potential energy data. The curve of intermolecular pair potentials (U) versus distance (r) is drawn in Fig. 2 by using the proposed function in eq. (1).
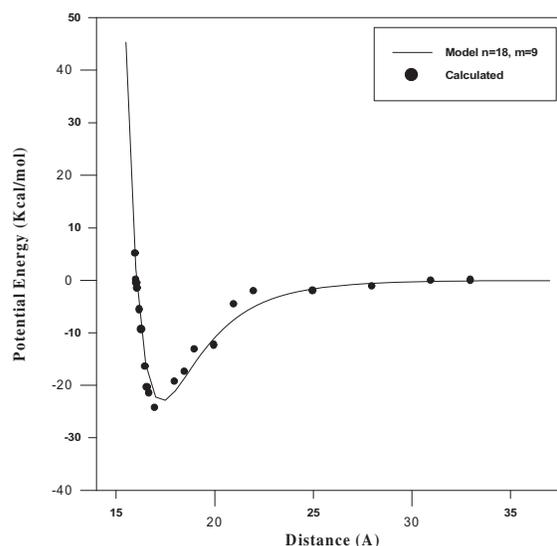
Figure 2: Intermolecular potential of asphaltene vs. distance using Eq. (1) compared to calculated data from quantum mechanics (Sabbaghi 2005; 2006).

Since the well-known Schrodinger equation cannot be solved exactly, there are various methods to solve this equation numerically. The most used method for molecular systems is Hartree-Fock method in the Born-Oppenheimer approximation framework. According to the Born-Oppenheimer approximation, the nuclei are assumed to move much slower than the electrons (this can be regarded as a reasonable approximation). For systems of high size such as asphaltene, even when

Figure 1: Molecular structure of asphaltene (Carbognani, 1992).

applying approximations, the computation time and storage, however, are very demanding. Therefore, semi-empirical methods are often used in order to simplify the system. In this research we have used the PM3 semi-empirical method which provides a reasonable wave function for large systems (Carl Nyeland, 2003; Akiyoshi, 2004; Yu Zhang, 2002).

Our previous works have shown that the proposed model for the potential energy of asphaltene can result in good agreement with the calculated parameters from EOS (Sabbaghi 2005; 2006). The validity of the results has been checked by comparing the results predicted by the model with the calculated data. These results can be then used to investigate the behavior of asphaltene. In order to determine the constants of the potential function, the calculated data have been fitted. The results are shown in Table 1.

Table 1: Parameters of Eq. (1)

aConstant	Value
n	18
m	9
σ	16.0399
ε	23.057

3 Second-Virial coefficient

Eq. (2) shows a general form of the Virial equation:

$$\frac{PV}{RT} = 1 + \frac{B_2(T)}{V} \tag{2}$$

Here the second-Virial coefficient $B_2(T)$ is a function of temperature that can be obtained by the interaction between pairs of molecules. Previous works using the statistical mechanics showed that the second-Virial coefficient for intermolecular pair potential can be calculated as (Mc Quarrie, 1976; Hirschfelder, 1964):

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta u} - 1 \right) r^2 dr \tag{3}$$

Where;

$$\beta = \frac{1}{KT} \tag{4}$$

that is a parameter to determine the shape of distribution. Figure 3 shows the second-Virial coefficient as a function of temperature (based on Eq. 3). These results have been fitted using an exponential model with Eq. (5) and the constant values shown in Table 2.

$$B_2(T) = xe^{yT} \tag{5}$$
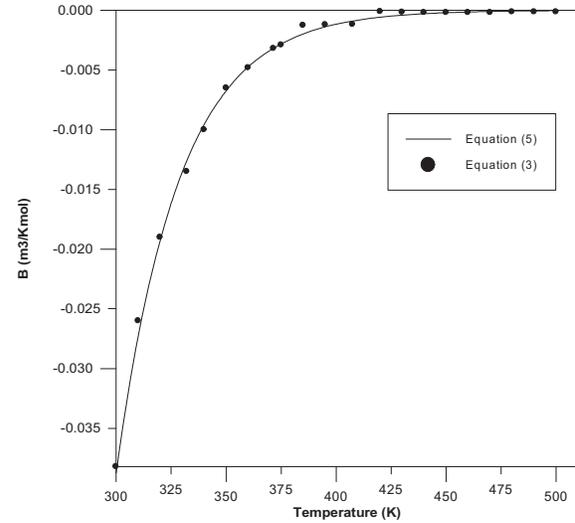
Figure 3: Second-Virial coefficient vs. temperature for asphaltene using Eq. (5) compared to calculated data from Eq. (3).

Table 2: Parameters of Eq. (5)

Constant	Value	Unit
x	-1407.7807	$m^3 \cdot Kmol^{-1}$
y	-.035	K^{-1}

4 A modified form of the Virial equation of state (VEOS) for asphaltene

It is known that the VEOS, with a Peneloux correction gives the best estimates of the liquid molar volume (Peneloux, 1982):

$$V^L = V^{Virrial} - C \tag{6}$$

Where C is the Peneloux correction term which can be estimated by (Peneloux, 1982):

$$C = 1.374 \left(MW \right)^{1.27} \left(.29 - Z_{RA} \right) \tag{7}$$

Where Z_{RA} is the Racket compressibility factor proposed by Spencer and Danner for saturated liquid molar volumes and is reported for 200 hydrocarbons (Spencer, 1972). If this parameter is not available, it may be estimated from Reid (Reid, 1989).

$$Z_{RA} = 0.29 - 0.088\omega \qquad (8)$$

Where w is the acentric factor. This parameter can be calculated using the following correlations, presented by Akbarzadeh (Akbarzadeh, 2002).

$$w = C_f [0.584 \ln(MW) - 2.54] \qquad (9)$$

Replacing V in Eq. (2) by $V^{Virrial}$ of Eq. (6) will result in the following form of the EOS:

$$P = \frac{RT}{(V^L + C)} \left(1 + \frac{B_2(T)}{(V^L + C)} \right) \qquad (10)$$

If $\overline{r}$ is defined as the average number of monomers in a given aggregate, then the parameters of Eq. (10) for the aggregates related to the monomer parameter will be (Akbarzadeh, 2002):

$$\overline{r} = \frac{\overline{MW}^{agg}}{MW^{mon}} \qquad (11)$$

$\overline{MW}^{agg}$ and MW^{mon} are the average molar mass of the asphaltene aggregate and the monomer molar mass, respectively.

$$C = \overline{r} C_m \qquad (12)$$
$$B = \overline{r} B_m \qquad (13)$$
$$V^L = \overline{r} v^L \qquad (14)$$

Where C_m and B_m are the monomer parameters. This idea was first suggested by Sy-Siong-Kiao (Sy-Siong-Kiao, 1996) and later applied by Akbarzadeh and Moshfeghian (Akbarzadeh, 2004; 2002; 2001). The modified VEOS is obtained by replacing C in Eq. (10):

$$P = \frac{RT}{\overline{r}(v^L + C_m)} \left(1 + \frac{B_m}{(v^L + C_m)} \right) \qquad (15)$$

The density of asphaltene can be calculated using the modified VEOS (Eq. 15). The temperature effects on the predicted density of asphaltene for different molecular weights are shown in Fig. 4.
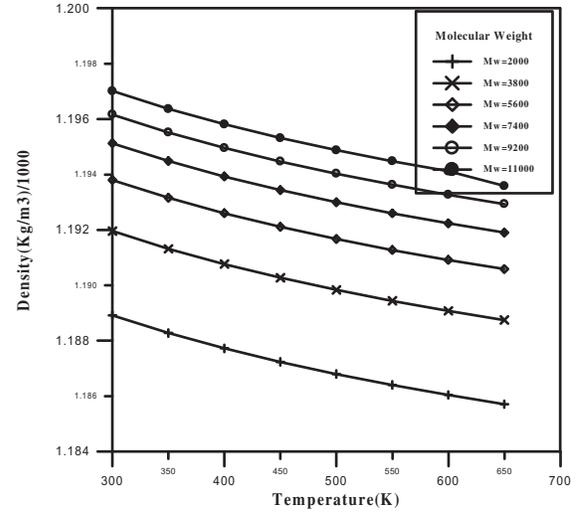
Figure 4: Density vs. temperature for asphaltene using Eq. (15) compared to SRK EOS (Akbarzadeh, 2002); (Lines Eq. (2), symbols SRK EOS).

It is shown that, as the temperature increases, the density of asphaltene decreases. The results in Fig. 4 include the effects of the molecular weight.

The calculated density of asphaltene using SRK EOS (Akbarzadeh, 2002) is also added to Fig. 4 for the sake of comparison. The measured densities of different asphaltenes are also compared with the results of SRK EOS (Akbarzadeh, 2002).

Basically, the results shown in Fig. 4 indicate the good ability of the VEOS for the prediction of asphaltene density at different temperatures and molecular weights. To check the accuracy of the proposed model, the density measurements at different samples are also calculated.

5 EOS calculation of solubility parameter

The solubility parameter, one of the key parameters in modeling asphaltene behavior, in principle, may be estimated either by a correlation or an EOS. Here, we have used the modified form of the VEOS

Hildebrand, et al. correlated the liquid solubility 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 (Hilde-

brand, 1949):

$$\delta^L = \left(\frac{\Delta U^{LV}}{v^L}\right)^{\frac{1}{2}} \tag{16}$$

The internal energy of vaporization was calculated using the following equation (Reid, 1989):

$$\Delta U^{LV} = \int_{v^l}^{v^v} \left[\left(T\frac{\partial P}{\partial T}\right)_v - P\right] dv \tag{17}$$

Therefore, the solubility parameter can be obtained by Eqs. (16) and (17), that is:

$$\delta^L = \frac{T}{v^l}\left[R\frac{dB}{dT}\right]^{1/2} \tag{18}$$

Note that the number of monomers $(\bar{r})$ indirectly affects the solubility parameter (Eq. (18)) as the monomer molar volume, $\left(v^L\right)$ determined from Eq. (15), is a function of $(\bar{r})$. The calculated solubility parameters by VEOS using Eq. (18) are plotted in Fig. 5, where the predicted solubility parameter of asphaltene is plotted versus the molar mass for different temperature. As shown there, the molar mass has little effect on the solubility parameter of asphaltene.

For liquids, temperature affects both the internal energy of vaporization and density. The changes in these properties result in a decrease in the solubility parameter of asphaltene. Fig. 5 also compares the calculated solubility of asphaltene from the proposed model with the results of SRK EOS (Akbarzadeh, 2002). To clearly show the compatibility between these two EOS in predicting solubility parameters, Fig. 6 compares the solubility parameter calculated from the model (VEOS) with SRK EOS (Akbarzadeh, 2002). According to this figure, all the points scatter around the 45-degree line, which means a good agreement has been achieved.

6 Mixing rules

To calculate the properties of oils from their solubility classes (SARA fraction), mixing rules are required. In this work molar mass, density, molar volume and solubility parameter of bitumens have
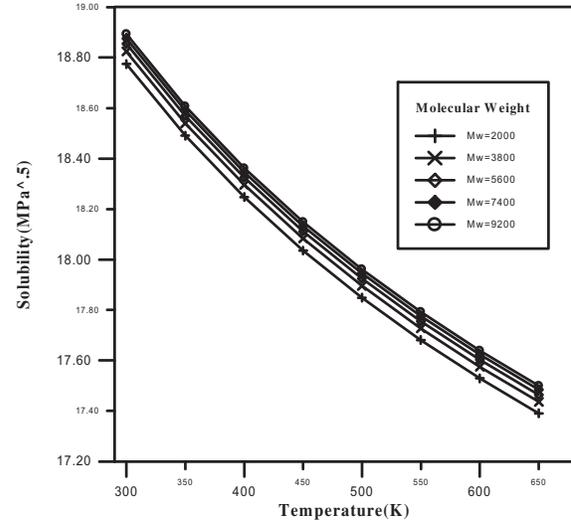
Figure 5: Solubility parameter vs. temperature for asphaltene using Eq. (18) compared to SRK EOS (Akbarzadeh, 2002); (Lines Eq. (18), symbols SRK EOS).
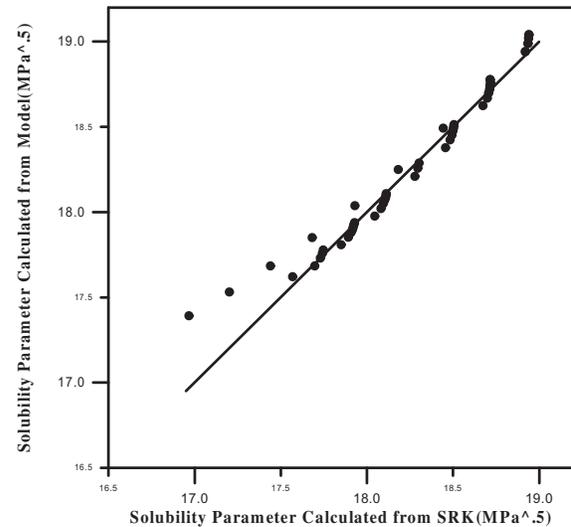
Figure 6: Comparison of the solubility parameter calculated and the results of SRK EOS (Akbarzadeh, 2002).

been estimated from the following well-known mixing rules:

$$Mw_B = \sum_{i=SARA} x_i Mw_i \tag{19}$$

$$\frac{1}{\rho_B} = \sum_{i=SARA} \frac{w_i}{\rho_i} \tag{20}$$

$$\delta_B = \sum_{i=SARA} \frac{x_i V_i \delta_i}{V_B} \tag{21}$$

$$V_B = \sum_{i=SARA} x_i V_i \tag{22}$$

$$V_a = r v_a^L \tag{23}$$

Where x_i, w_i are the mole fraction and mass fraction of constituent i in the bitumen, respectively. The mass fraction of asphaltene in bitumen is considered to be the C5-asphaltene fraction. Note that the non-asphaltenic solids less than 2% of the heavy oils/bitumens have been neglected in these calculations.

The following mixing rules are used for calculating the monomeric parameters of the mixture from its individual components.

$$B_m^{mix} = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \sqrt{B_{mi} B_{mj}} \left(1 - k_{ij}\right) \tag{24}$$

$$C_m^{mix} = \sum_{i=1}^{N} x_i C_{mi} \tag{25}$$

$$\bar{r}_{mix} = \sum_{i=1}^{N} x_i \bar{r}_i \tag{26}$$

Where N is the number of components in the mixture, x_i the mole fraction of component i, k_{ij} the binary interaction parameter between components i, j. In this work, the binary interaction parameter between the precipitation and other components available in the system is estimated from (Nghiem et. al. 1993; Kohse et. al. 2000):

$$k_{ij} = 1 - \left(\frac{2 V_{ci}^{1/6} V_{cj}^{1/6}}{V_{ci}^{1/3} + V_{cj}^{1/3}} \right)^{\theta} \tag{27}$$

Where V_{ci} is the critical volume of component i, and the exponent θ is a regression parameter found by matching some data points.

7   Onset of asphaltene precipitation

An attempt has been made to predict the onset with regular solution theory using the molar volumes and solubility parameters generated with the modified Virial EOS. To obtain an accurate prediction of the onset and amount of prediction, the molar mass distribution of the asphaltene in bitumen is required.

To determine the onset of prediction, it is sufficient to estimate the molar mass of the first asphaltene to precipitate.

These experiments were based on direct gravimetric measurements of precipitated asphaltenes at various solvent-to-bitumen ratios. For each experiment, 20 g of bitumen and a given mass of *n*-heptane were placed in an Erlenmeyer flask. The mixture was sonicated for 30 minutes and then left to settle for 24 hours. The precipitated asphaltenes were separated from the solution using a centrifuge at 3500 rpm for 6 minutes and dried until the mass remained constant. Fig. 7 compares the predicted onset points with the SRK EOS. According to this figure, the points scatter near the 45-degree line which means low error. The accuracy of the onset prediction depends on the accuracy of the asphaltene molar mass, an estimated quantity. A method for predicting asphaltene molar mass in pure solvents has already been developed (Hildebrand, 1949).
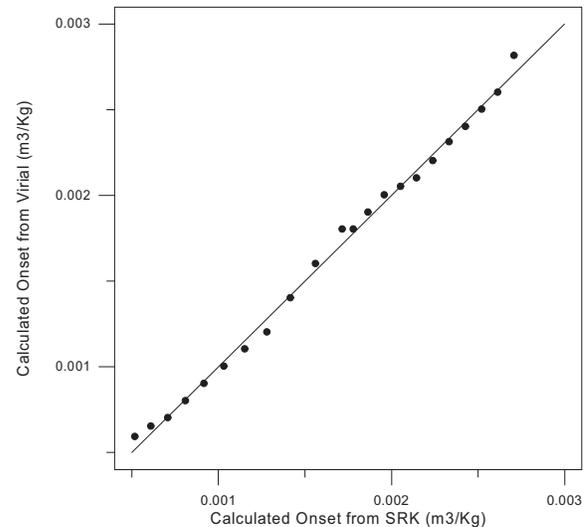
Figure 7: Calculated onset from model vs. SRK EOS (Akbarzadeh, 2002).

8   Asphalten molar mass distribution

The final step in fluid characterization is to determine the asphaltene molar mass distribution;

that is, the distribution of r. Asphaltenes self-associations can be considered as a polymerization step in which monomers react in such a way that groups of them which are already linked together can be coupled with other groups (Strobl, 1997). 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 then the molar mass. It is given by the following equation:

$$f(r) = \frac{1}{\eta(\beta)} \left(\frac{\beta}{\bar{r}}\right)^{\beta} r^{\beta-1} \exp\left(-\frac{\beta r}{\bar{r}}\right) \qquad (28)$$

Where β is as stated in equation 3, $\bar{r}$ is the average number of monomers per aggregate or degree of association which is estimated from Eq. (11) and η is the gamma function. In most cases $\beta \approx 2$ provides a good data fit and when $\beta = 2$ equation simplifies to:

$$f(r) = \frac{4r}{\bar{r}^2} \exp\left(-\frac{2r}{\bar{r}}\right) \qquad (29)$$

9 Regular solution theory

Regular solution solubility 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 regarded as a liquid-liquid equilibrium (LLE) or liquid-solid equilibrium (SLE) (Andersen, 1999; Hirschberg, 1984; Chung, 1992; Yang, 1999; Kohse, 2000; Kawanaka, 1989). To perform the equilibrium calculation and estimate the amount of precipitate, the equilibrium ratios for each component are required.

For an asphaltene species in a LLE or an SLE where the solid phase activity is unity and the heat of fusion term is negligible (Yarranton, 1996), the following expression for the equilibrium ratio, K_i, can be derived:

$$K_i = \frac{x_i^s}{x_i^l}$$

$$= \exp\left[1 - \frac{V_i^l}{V_{mix}} + \ln\left(\frac{V_i^l}{V_{mix}}\right) + \frac{V_i^l}{RT}(\delta_i - \delta_{mix})^2\right]$$

$$(30)$$

Where x_i^s and x_i^l are the solid and liquid-phase mole fractions of component i, respectively. V_i^l and V_{mix} 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. Once the values of K_i are known details of the solution procedure can be found in the literature (Hirschberg, 1984; Chung, 1992).

10 The effects of temperature and pressure on the onset point

In order to investigate the effects of temperature and pressure on the onset point from a modeling point of view, we have plotted the calculated onset versus temperature and pressure at a constant dilution ratio (solvent to bitumen ratio). This is shown in Figs. 8 and 9.
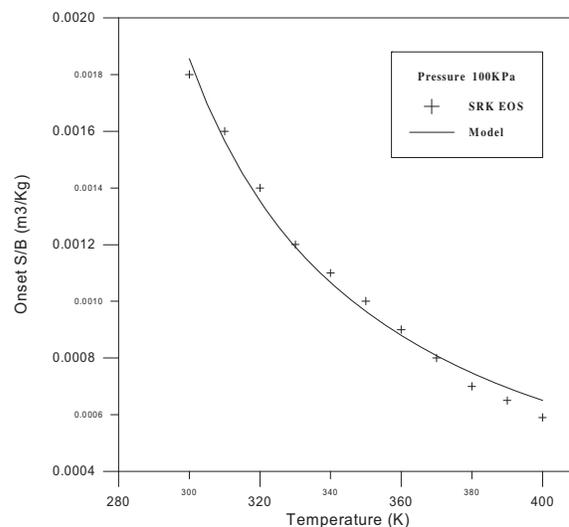
Figure 8: The effect of temperature on the onset solvent to bitumen ratio (at 100 Kpa).

In Fig. 8 it is shown that as the temperature increases, the onset dilution ratio of asphaltene decreases. The reasons for such predictions should be searched in the changes of the solubility parameter of heavy fractions especially asphaltenes
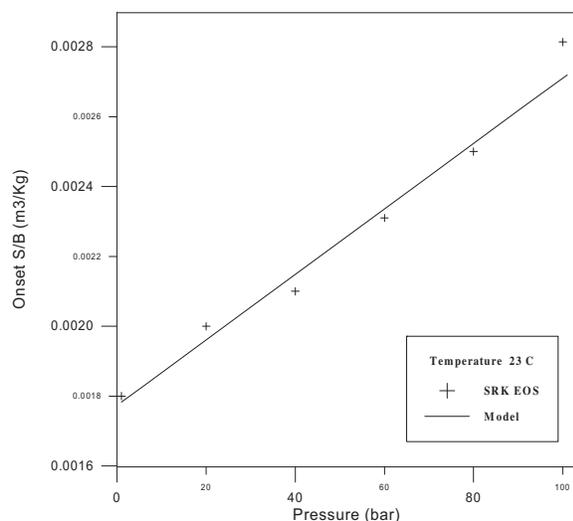
Figure 9: The effect of pressure on the onset solvent to bitumen ratio (at 23°C).

and resins with temperature. Also, in Fig. 9 it is shown that as the pressure increases, the onset dilution ratio of asphaltene increases.

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. In this case the onset dilution ratio increases, i.e. more precipitant is required for starting asphaltene precipitation. Secondly, an increase in temperature also reduces liquid density and this effect decreases the solvent power (Wu, 2000).

11 Results and discussion

The validity of the model has been checked by comparing the experimental data with calculated data. Tables 3 and 4 show such a comparison. As expected, the predicted results are in good agreement with the measured density within the range of experiments. As a consequence, these results can be used to investigate the behavior of asphaltene. The calculated key parameters of asphaltene presented in Fig. 4 and 5 clearly indicate the effects of molar mass and temperature on density and solubility.

Table 3: Comparison of data calculated from the model with experimental results

Sample	Measured Density $\left(\frac{\text{gr}}{\text{cm}^3}\right)$	Calculated Density $\left(\frac{\text{gr}}{\text{cm}^3}\right)$	%AAD (calc.– meas.) /meas.
Atabasca	1.25	1.229722	1.62
Cold Lake	1	1.103824	10.38
Lioydminster	1.05	1.165	9.87
Peace River	.95	1.080868	12.1

Table 4: Measured and calculated onset of asphaltene precipitation at 23°C: heptane-to-bitumen ratio (H/B) versus $\left(\frac{\text{m}^3}{\text{Kg}}\right)$

Sample	Measured Onset	Calculated Onset
Atabasca	.0019	.001915
Cold Lake	.00175	.001792
Lioydminster	.00165	.001641
Peace River	.00175	.001739

Accordingly, we developed three correlations for the prediction of density, the solubility parameter and the structure coefficient, respectively. The structure coefficient, as a key parameter in the VEOS, has been predicted through the back calculation of the densities from SRK EOS. This scenario proceeds from Eqs. (6-9) towards Eq. (15), resulting in the C_f calculation at different temperatures, as well as asphaltene molecular weight.

To summarize, three new correlations are presented here to estimate the structure coefficient, density and the solubility parameter of asphaltene. The developed correlations are presented in Eqs. (31-33) as functions of temperature and molecular weight.

$$C_f = 77.3 \, (MW)^{-1.1677} \, (T)^{1.13} \tag{31}$$

$$\delta = 32.02 \, (MW)^{.0041} \, (T)^{-.0991} \tag{32}$$

$$\rho = 1.1767 \, (MW)^{.00398} \, (T)^{-.0035} \tag{33}$$

Figs. 10-12 show the density, solubility parameters and structure coefficient as functions of molecular weight and temperature calculated from eqs.(31-33) respectively. According to these

results, density increases sharply with the increase in molecular weight, before approaching a constant value at very high molecular weight. The solubility parameter of asphaltene is not sensitive to the molecular weight value; however, its value decreases as the temperature increases as shown in Fig. 11.
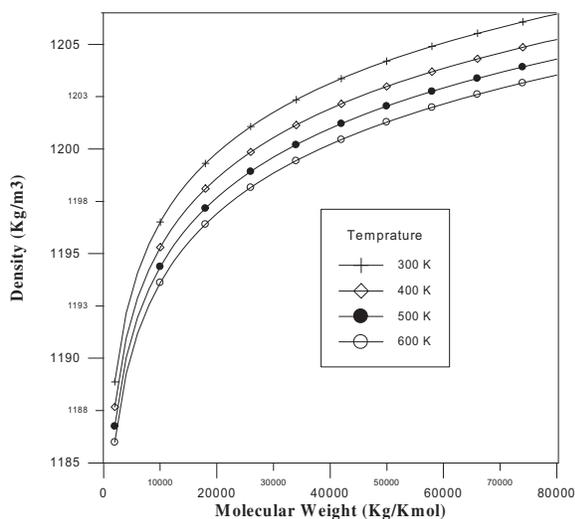
Figure 10: Density vs. molar mass for asphaltene using Eq. (22) compared to model; (Lines Eq. (22), symbols model (VEOS)).
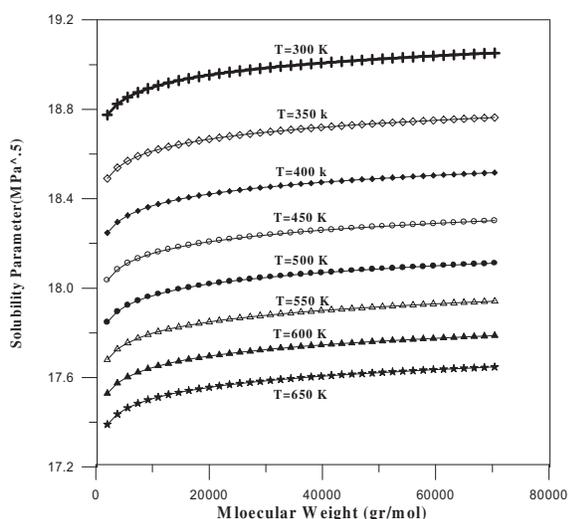
Figure 11: Solubility parameter vs. molar mass for asphaltene using Eq. (21) compared to model; (Lines Eq. (21), symbols model (VEOS)).
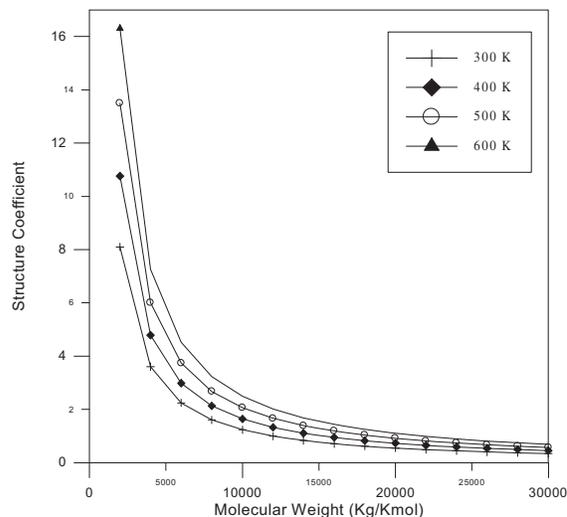
Figure 12: Structure coefficient vs. molar mass of asphaltene using Eq.(20) at different temperatures.

12   Conclusions

This work has been focused on the characterization of the structure of heavy petroleum molecules (and related dynamics and thermodynamics) to establish a relationship between these properties and petroleum fluid behavior.

The basics of quantum mechanics and statistical thermodynamics have been used to predict the potential energy and intermolecular forces of asphaltene molecules. The parameters associated with the chemical structure have been also estimated to define the Mie potential function.

According to the structural results, a new form of the Virial EOS with Peneloux correction has been introduced that allows evaluation of the density, the solubility parameter and a correction factor accounting for the asphaltene structural effect.

Finally, three new correlations have been developed relating the key parameters of asphaltenes (namely the structural coefficient, density and solubility) to temperature and molecular weight.

List of symbols

$B_2(T)$ second-Virial coefficient ($m^3 \cdot Kmol^{-1}$)
B aggregate parameter
B_m monomer parameter

C	Peneloux correction
C_m	monomer parameter
C_f	a correction factor that accounts for structural effect
K	Boltzmann constant (Kcal·mol^{-1}·K^{-1})
$\overline{MW}^{agg}$	average molar mass of the asphaltene aggregate (Kg.Kmol^{-1})
MW^{mon}	monomer molar mass (Kg·Kmol^{-1})
MW	molar mass of asphaltene (Kg·Kmol^{-1})
m	dimensionless constant of Eq. (1)
n	dimensionless constant of Eq. (1)
p	pressure (bar)
R	universal gas constant (KPa·m^3·Kmol^{-1}·K^{-1})
r	Distance ($\dot{A}$)
$\overline{r}$	average number of monomer
T	temperature (K)
$U(r)$	potential energy (Kcal·mol^{-1})
ΔU^{LV}	energy of vaporization (j·mol^{-1})
V	volume (m^3)
V^L	molar volume of liquid (m^3·Kmol^{-1})
v^L	monomer molar volume of liquid (m^3·Kmol^{-1})
V^{Virial}	molar volume calculated by Virial Eq. (m^3·Kmol^{-1})
x	parameter of Eq. (5) (m^3·Kmol^{-1})
y	parameter of Eq. (5) (K^{-1})
Z_{RA}	Racket compressibility factor

Greek letters

β	=1/KT
ε	well depth (Kcal·mol^{-1})
σ	intermolecular distance at which the potential is zero ($\dot{A}$)
η	gamma function
w	acentric factor
δ	solubility parameter (MPa$^{.5}$)
Δ	represents a change

Subscript

m	monomer

Superscripts

L	liquid

agg	Aggregate
mon	monomer
Virial	Virial equation of state

Reference

Akbarzadeh, K.; Ayatollahi, Sh.; Moshfeghian, M.; Alboudwarej, H.; Yarranton, H.W. (2004): Estimation of SARA Fraction Properties With the SRK EOS, *J. of Can. Pet. Technol.*, v.43, no. 9, pp. 85-97.

Akbarzadeh, K.; Ayatollahi, Sh.; Nasrifar, Kh.; Moshfeghian, M.; Yarranton, H.W. (2002): Equations lead to Asphaltene Deposition Prediction, *Oil & Gas J.*, v. 100, Issue 44, Oct. 28.

Akbarzadeh, K. (2002): Ph.D. Dissertation, Dept. of Chem. Eng., Shiraz University, Iran, January.

Akbarzadeh, K.; Moshfeghian, M. (2001): Application of the polymer chain-of-rotator (PCOR) equation of state and its extension to polymer blends, *Fluid Phase Equl.*, No. 187-188, pp. 347-361.

Akiyoshi S.; Satimi K.; Nobuaki M.; Kenro H. (2004): Potential energy surface and intermolecular vibrations of $O_2 - H_2O$, *Chem. Phys. Lett.*, no. 391, pp.101-105.

Alexander, G.L.; Creagh, A.L.; Prausnitz, lM. (1985): Phase Equilibria for HighBoiling Fossil-Fuel Distillates: 1. Characterization, *Ind. Eng. Chem. Fund.*, no. 24, pp. 301-312.

Andersen, S.l., Speight, lG. (1999): Thermodynamic Models for Asphaltene Solubility and Precipitation, *J. of Pet. Sci. and Eng.*, no. 22, pp. 53-66.

Carbognani, S.A. (1992): INTEVEP, Tech. Rept.

Carl Nyeland (2003): Gradient expansions in density functional calculations of intermolecular potentials: *Chem. Phys. Lett.*, v. 370, pp. 353-359.

Chung, T.H. (1992): Thermodynamic Modeling for Organic Solid Precipitation, *Presented at the 1992 SPE Annual Technical Conference and Exhibition, Washington*, DC, Oct. 4-7, SPE 24851.

David, A. (1973): Asphaltene flocculation during solvent stimulation of heavy oils: *A. I. Ch. E. (Am. Inst. Chem. Eng.) Symp. Ser.*, vol. 69, no. 127, pp. 56-61.

Gupta, A.K. (1986): A model for asphaltene Flocculation Using an Equation of State, M.Sc. Thesis, Department of Chemical and Petroleum Engineering, University of Calgary, June.

Hildebrand, H.; Scott, R. (1949): *Solubility of Non-Electrolytes*, 3rd ed., Reinhold, New York.

Hirschberg, A.; deJong, LN.J.; Schipper, R.A.; Meijers, J.G. (1984): Influence of Temperature and Pressure on Asphaltene Flocculation, *SPE J.*, no. 24, pp. 283-295.

Hirschfelder, J.O.; Curtiss, C.F.; Bird, R.B. (1964): *Molecular Theory of gases and Liquids*, 2nd Printing, Wiley, New York.

Kawanaka, S.; Leontaritis, K.J.; Park, S.J.; Mansoori, G.A. (1989): Thermodynamic and Colloidal Models of Asphaltene, flocculation in Oil Field Chemistry, *ACS Symposium Series* No. 396, Chapter 24, American Chemical Society, Washington, D.C.

Kohse, B.F.; Nghiem, Lx.; Madea, H.; Ohno, K. (2000): Modeling Phase Behavior Including the Effect of Pressure and Temperature on Asphaltene Precipitation, *SPE 64465*, pp. 1-13.

Lichaa, P.M. (1977): Asphaltene deposition problem in Venezuela crudes-usage of asphaltenes in emulsion stability. In: Oil and sands: *Can.Pet.Technol. J.*, (Jun), pp. 609-624.

Mansoori, G.A. (1999): Modeling and Asphaltene and Other Heavy Organic Compound: *J. of Pet. Sci. Eng.*, no. 16, pp. 101-111.

Mc Quarrie, D.A. (1976): *Statistical Mechanics*, Harper Collines Publishers.

Nghiem, Lx.; Kohse, RF.; Farouq Ali, S.M.; Doan, Q. (2000): Asphaltene Precipitation: Phase Behavior Modelling and Compositional Simulation, *SPE 59432*, Proc. 2000 SPE Asia Pacific Conference on Integrated Modeling for Asset Management, Yokohama, Japan, April, pp. 25-26.

Pedersen, K.S.; Skovberg, P.; Ronningsen, H.P. (1991): Wax Precipitation from North Sea Crude Oils: 4. Thermodynamic Modeling, *Energy & Fules*, no. 5, pp. 924-932.

Peneloux, A.; Rauzy, E.; Freeze, R. (1982): A Consistent Correction for RedlichKwong-Soave Volumes: *Fluid Phase Equilibria*, no. 8, pp. 7-23.

Reid, RC.; Prausnitz, lM.; Poling, B.E. (1989): *The Properties of Gases & Liquids*, 4th edition., Mc Graw-Hill, New York.

Sabbaghi S.; A. Jahanmiri, M.; Shariaty-Niassar, Sh.; Ayatollahi, A. (2007): Characterization of Asphaltene Structure Using Atomic Force Microscopy, *J. of Microscopy*, printed manuscript.

Sabbaghi S.; Jahanmiri, A.; Shariaty-Niassar, M.; Ayatollahi, Sh.; Boushehri A. (2005): Theoretical Study of Potential Energy and Intermolecular Forces of Asphaltene Using a Quantum Mechanics, *Intl. J. Nanosci.&Nanotech.(IJNN)*, no. 1, pp. 31-43.

Sabbaghi, S.; Shariaty-Niassar, M.; Mansoori, G.Ali; Ayatollahi, Sh.; Jahanmiri, A. (2006): Study of nanostructures to identify asphaltene with atomic force microscopy, *Energy Nanotechnology Intenational Conference*. Massachusetts Institute of Technology (MIT), Cambridge, MA.

Sabbaghi, S.; Shariaty-Niassar, M.; Mansoori, G.Ali; Ayatollahi, Sh.; Jahanmiri, A. (2006): Characterization of Complexe System of Heavy Organic Compounds by Use of Nanotechnology Case Study: Asphaltene Deposition: *NanoEurope fair & conference, September 12-14, Switzerland, Olma Messen St.Gallen.*

Sabbaghi, S.; Shariaty-Niassar, M.; Mansoori, G.Ali; Ayatollahi, Sh.; Jahanmiri, A. (2006): Identification of Nanostructures with Nanotechnology Science Case Study: Asphaltene Deposition, *International Congress Nanoscience & nanotechnology (ICNN2006)* – 18 to 20 December, Iran, Tehran.

Spencer, C.F.; Danner, R.P. (1972): Improved Equation for Prediction of Saturated Liquid Density, *Chem. Eng. Data*, no. 17, 236-241.

Strobl, O.R. (1997): *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*, 2nd corrected edition, Springer.

Sy-Siong-Kiao, R.; Caruthers, l.M.; Chao, K.C. (1996): Polymer Chain-of-Rotators Equation of State: *Ind. Eng. Chem. Res.*, no. 35, pp. 1446-1455.

Thomas, F.R.; Bennion, D.W.; Hunter, R.E. (1992): Experimental and Theoretical Studies of Solids Precipitation from Reservoir Fluid, *Can. Pet. Tech.*, no. 31, pp. 22-31.

Wu, L.; Prausnitz, lM.; Firoozabadi, A. (2000): Molecular Thermodynamics of Asphaltene Precipitation in Reservoir Fluids, *AIChE J.*, no. 46, pp. 197-209.

Yang, Z.; Ma, C.-F.; Lin, X.-S.; Yang, l-T.; Guo, T.-M. (1999): Experimental and Modeling Studies on the Asphaltene Precipitation in Degassed and Gas-Injected Reservoir Oils, *Fluid Phase Equ.*, no. 157, pp. 143-158.

Yarranton, H.W.; Masliyah, J.H. (1996): Molar Mass Distribution and Solubility Modeling of Asphaltenes: *AIChE J.*, no. 42, pp. 3533-3543.

Zhang, Y.; Shi, H.-Y.; (2002): An ab initio study of intermolecular potential for the He-Hcl complex, *J. of molecular structure(Theochem)*, no. 589-590, pp. 89-93.