

Chapter 5

THERMODYNAMIC PROPERTIES OF ASPHALTENES: A PREDICTIVE APPROACH BASED ON COMPUTER ASSISTED STRUCTURE ELUCIDATION AND ATOMISTIC SIMULATIONS

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INTRODUCTION

Crude oil is a complex mixture of hydrocarbons and heteroatomic organic compounds of varying molecular weight and polarity [1]. A common practice in the petroleum industry is to separate crude oil into four chemically distinct fractions: saturates, aromatics, asphaltenes and resins [1–4]. Asphaltenes are operationally defined as the non-volatile and polar fraction of petroleum that is insoluble in *n*-alkanes (i.e., pentane). Conversely, resins are defined as the non-volatile and polar fraction of crude oil that is soluble in *n*-alkanes (i.e., pentane) and aromatic solvents (i.e., toluene) and insoluble in ethyl acetate. A commonly accepted view in petroleum chemistry is that asphaltenes form micelles which are stabilized by adsorbed resins kept in solution by aromatics [5,6]. Two key parameters that control the stability of asphaltene micelles in a crude oil are the ratio of aromatics to saturates and that of resins to asphaltenes. When these ratios decrease, asphaltene micelles will flocculate and form larger aggregates [7,8]. The precipitation of asphaltene aggregates can cause such severe problems as reservoir plugging and wettability reversal [9,10]. The adsorption of asphaltene aggregates at oil–water interfaces has been shown to cause the steric stabilization of (W/O) petroleum emulsions [11,12]. Consequently, the oil industry is in critical need of quantitative tools and thermodynamic data to predict asphaltene solubility and aggregation as a function of crude oil composition and reservoir temperature and pressure.

Asphaltene aggregation and solubility in crude oil have been the subject of several theoretical investigations. Hirschberg et al. [13] combined Hildebrand regular solution theory with a Flory-Huggins entropy of mixing to express asphaltene solubility in crude oil as a function of molar volume and solubility parameter. Brandt et al. [14] combined a mean field energy of mixing with a modified Flory-Huggins entropy of mixing to describe asphaltene aggregation in a given solvent. They model asphaltene molecules as flat hard discs called ‘unit sheets’ that can ‘stack’ to any arbitrary degree in the solvent. They express the volume fraction of asphaltene ‘stacks’ as a function of asphaltene concentration, asphaltene cohesive/‘stacking’ energy, asphaltene-solvent interaction energy, and asphaltene ‘unit sheet’/‘stack’ excluded volume. Victorov and Firoozabadi [15] have extended the free energy models of amphiphile micellization of Nagarajan and Ruckenstein [16] and Puvvada and Blankshtein [17] to petroleum fluids. Their new thermodynamic model combines a free energy model of micellization with the Peng–Robinson equation of state [18] and express asphaltene solubility

in a crude oil as a function of temperature, pressure, asphaltene–resin concentration, resin–asphaltene interaction energy, resin–crude oil interaction energy and a ‘molecular geometric’ parameter that accounts for resin packing constraints at the surface asphaltene micelles. Rogel [19] has carried out molecular dynamics (MD) simulations of asphaltene aggregation in *n*-heptane, toluene and their mixtures. He reported that the stability of asphaltene aggregates in the mixtures increase with the ratio of *n*-heptane to toluene. Murgich et al. [20] have carried out molecular mechanics calculations of the energies of model asphaltene and resin molecules. They reported that the interactions between the ‘aromatic planes’ of asphaltene molecules was the main driving of their aggregation.

Although these thermodynamic models have resulted in a better understanding of the phase behavior of asphaltic crude oil, the lack of accurate data are major impediments to the utilization of these models in field applications. Because of this lack of thermodynamic data, Hirschberg et al. [13] determined their model input data (solubility parameter and molar volume) by fitting the results of asphaltene solubility measurements to a thermodynamic model of asphaltene precipitation. They assumed an asphaltene molar volume of 4 m³/kmol to get “an optimal fit between calculated and experimental data” [13]. Because of the lack of a suitable structural model of asphaltene, Brandt et al. [14] employed a “polycyclic aromatic compound with saturated substituents” to evaluate two input parameters of their thermodynamic model of asphaltene aggregation. The lack of molecular and thermodynamic data on asphaltenes and resins has also led Victorov and Firoozabadi [15] to make several simplifying assumptions including the use of ‘guessed’ values for the interaction energy of a ‘resin molecule head’ with asphaltene. Such ‘guessed’ values may increase the uncertainties in the predicted solubility of asphaltenes in crude oil.

The petroleum industry is in critical need of experimental and theoretical estimates of asphaltene thermodynamic properties. In this chapter, we describe a new methodology for predicting the thermodynamic properties of petroleum geomacromolecules (asphaltenes and resins). This methodology (Fig. 5-1) combines computer assisted structure elucidation (CASE) with atomistic simulations (molecular mechanics and molecular dynamics and statistical mechanics). To illustrate this new approach, we use quantitative and qualitative structural data as input to a CASE program (SIGNATURE) to generate a sample of ten asphaltene model structures for a Saudi crude oil (Arab Berri). We then carry out MM calculations and MD simulations to estimate selected volumetric and thermal properties of the model structures. We find that the estimated values are in good agreement with the available experimental data.

This chapter is organized as follows. In COMPUTER ASSISTED STRUCTURE ELUCIDATION OF PETROLEUM GEOMACROMOLECULES, we highlight the state-of-the art of CASE. We show that the CASE program SIGNATURE can be used to generate a sample of structural model of asphaltenes that statistically represents the entire population of all the possible structures that can be built from a given set of analytical data. In ESTIMATION OF THERMODYNAMIC PROPERTIES OF CONDENSED PHASE SYSTEMS FROM ATOMISTIC SIMULATIONS, we briefly discuss the estimation of the thermodynamic properties of condensed phase systems from Monte Carlo (MC) and molecular dynamics (MD) simulations. In COMPUTER ASSISTED STRUCTURE ELUCIDATION OF ARAB BERRI

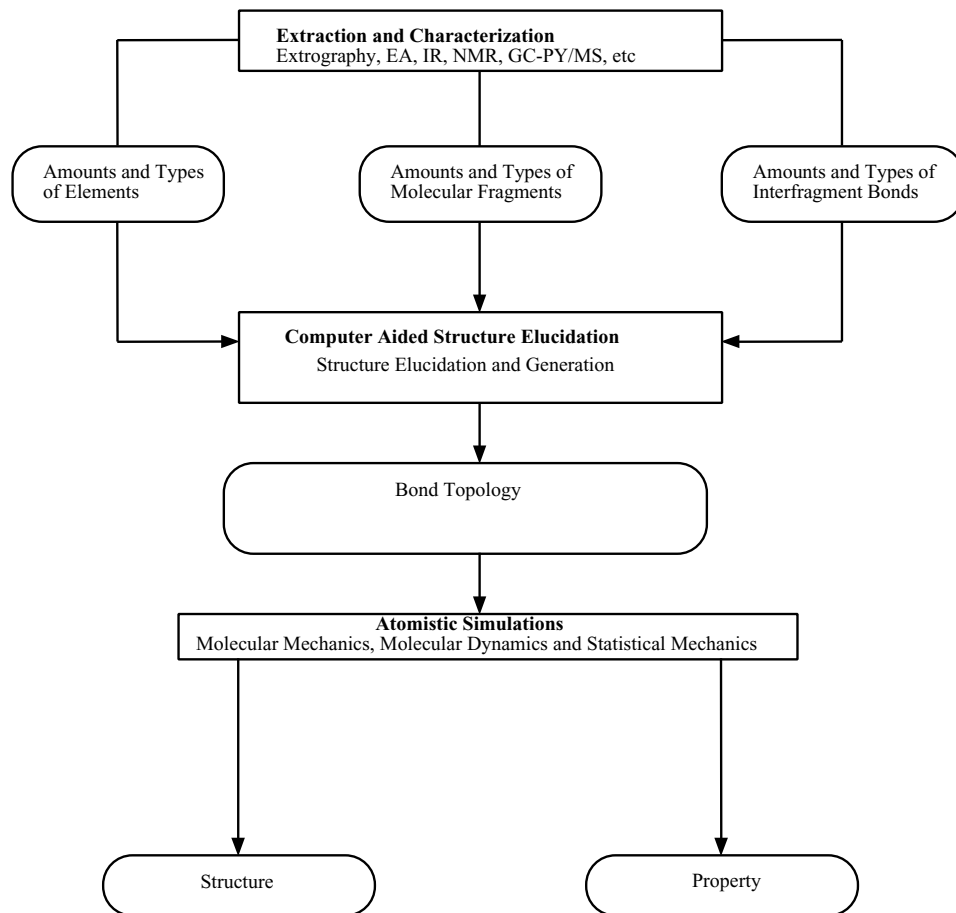


Fig. 5-1. Hierarchical approach for predicting the structures and properties of petroleum geomacromolecules.

ASPHALTENES, we input quantitative and qualitative structural data into SIGNATURE to generate a sample of ten structural models of asphaltene from a Saudi crude oil (Arab Berri). We then use molecular mechanics (MM) calculations and MD simulations to estimate the molar volume, density, cohesive energy, solubility parameter, enthalpy, thermal expansion coefficient and specific heat at constant pressure of the model asphaltene structures in VOLUMETRIC AND THERMAL PROPERTIES OF ARAB BERRI ASPHALTENES FROM MOLECULAR DYNAMIC SIMULATIONS. Finally, we summarize the main results of this work.

COMPUTER ASSISTED STRUCTURE ELUCIDATION OF PETROLEUM GEOMACROMOLECULES

Because petroleum geomacromolecules such as asphaltenes are operationally defined as a 'solubility class' of compounds precipitated from crude oil by addition of an excess

amount of aliphatic solvents [1], accurate structural models for these compounds are not currently available. Three approaches may be used to elucidate the structures of complex petroleum geomacromolecules: *conventional*, *deterministic* and *stochastic*.

Conventional approach

The conventional approach to structure elucidation is the traditional means by which chemists infer a structural formula from a set of analytical data. This is essentially a trial-and-error process of manually matching the candidate structure with analytical data. Virtually, all the chemical structures of the compounds known to date have been elucidated using the conventional approach. There are, however, two major impediments to the systematic application of the conventional approach to petroleum geomacromolecules. First, the structure elucidation process is carried out by manual fitting. Thus, it is prohibitively time-consuming for large molecules such as asphaltenes. Second, when several isomers can be built from the same analytical data set, the conventional approach does not provide any means of selecting the 'appropriate' isomer. Consequently, it is often difficult to draw definite conclusions regarding geomacromolecules (i.e., lignin, coal and asphaltene) generated with the conventional approach because of arbitrary isomer selection [21–24].

Deterministic approach

The deterministic approach is predicated upon the retrieval of all the structural models of a compound from a given set of structural data. For the past 25 years, there has been many attempts to automate the deterministic approach. Several techniques and computer programs have been proposed under the generic name *computer assisted structure elucidation* (CASE). The first CASE program capable of enumerating all the acyclic structures from a molecular formula is believed to be that of Lederberg et al. [25]. This program, which evolved out of the DENDRAL project, was the precursor of CONGEN [26] and GENOA [27], the first CASE expert systems ever published. CONGEN and GENOA can handle any structure and enumerate the isomers of a molecular formula. These can also be used to generate structures with more restrictive constraints, e.g. isomers with specified molecular fragments. However, both GENOA and CONGEN use more heuristic than systematic algorithms. Moreover, the proof of irredundancy and exhaustivity of the structure generation process was never published, and differences between the structures generated by GENOA/CONGEN and CASE programs have been reported [28]. Several CASE programs based on a more systematic structure generation protocol have been developed as alternatives to GENOA and CONGEN including the structure generators CHEMICS [29–33], ASSEMBLE [34,35] and COMBINE [36]. These programs are based on the concept of the connectivity stack, which allows an exhaustive and unique enumeration [28]. The basic building block of these programs is a set of segments (a segment is a small molecular fragment containing one, two or three atoms) representing the unknown compound. To enumerate the isomers, an exhaustive permutation of all segments is carried out. With the concept of the connectivity stack, redundancies can be avoided without cross-checking the solutions. Using this method,

exhaustivity and irredundancy of the solutions can be easily proven; in fact, all the permutations are considered and all redundant structures are rejected.

The ability of a CASE program to treat redundant information is a central issue in structure elucidation. Because chemical structural data tend to be highly redundant, the molecular fragments used as input to CASE programs generally overlap. The problem of overlapping fragments was studied by Dubois et al. [37,38]. They developed the program DARC-EPIOS [39], which can retrieve structural formulas from overlapping ^{13}C NMR data. Similar techniques have also been applied with the COMBINE program, while GENOA uses a more general technique based on the determination of all possible combinations of non-overlapping molecular fragments. All the CASE programs described above generate chemical structure by assembling atoms and/or molecular fragments together. More recently, a new strategy based on structure generation by reduction has been proposed to deal with the problem of overlapping fragments [44]. Structure generation by reduction does not create bonds but removes bonds from a *hyperstructure*. Initially, the *hyperstructure* contains all the possible bonds between all the required atoms and molecular fragments. The fragments can overlap. As bonds are removed, the continued containment of each fragment is tested until a valid chemical structure is obtained. Examples of CASE programs based on the concept of structure generation by reduction include COCOA [40] and GEN [41].

Computational complexity is another critical issue in CASE. Because the treatment of overlapping fragments usually results in an exponential increase of computational time as the number of input atoms increase, current CASE programs are ill suited for large systems. In order to limit the number of combinations that generate duplicate structures, several investigators have attempted to optimize existing CASE programs [28,42–45]. The largest reported structure that has been resolved with these optimized CASE programs is a fragment of lignin ($\text{C}_{116}\text{H}_{126}\text{O}_6$) that contains 122 non-hydrogen atoms [28]. Although these optimized programs can handle relatively large structures, the number of atoms or molecular fragments that can be processed by any deterministic CASE program is still limited due to the exponential complexity of the problem of structure elucidation. Consequently, the deterministic approach to structure elucidation is ill suited for large petroleum geomacromolecules such as asphaltenes and kerogen.

Stochastic approach

The stochastic approach to structure elucidation is very similar in approach to the search of the conformational space of a chemical compound by Monte Carlo simulations or simulated annealing to find its lowest energy conformations. However, in the case of structure elucidation, the search space is the finite number of all possible structural isomers that can be constructed from a given set of analytical data. Faulon has shown that by using a stochastic approach [46], it is possible to: (1) generate the total number of model structures that match a given set of analytical data in a reasonable computational time; (2) generate a sample of model structures that statistically represents the entire population of all the possible structures that can be built from a given set of analytical data

The new CASE program based on this approach, SIGNATURE (Fig. 5-2), (1) determines the best list of molecular fragments and interfragment bonds that best match the

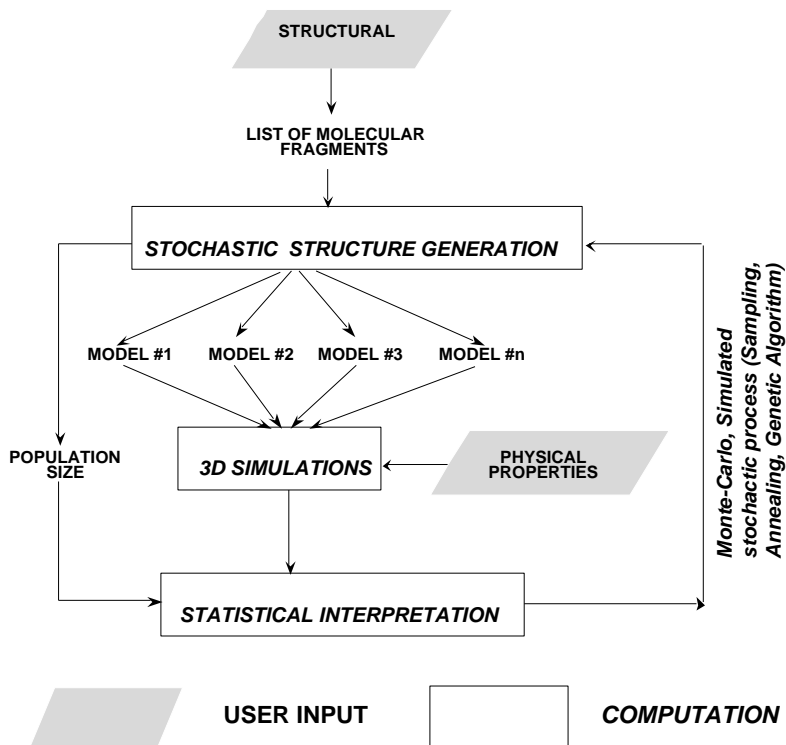


Fig. 5-2. Stochastic generator of chemical structure (SIGNATURE): general program scheme.

experimental data, (2) evaluates the total number of possible structural models that can be generated from (1), and (3) generates a sample of structural formulas that statistically represent the entire population of model structures that can be generated from (1).

SIGNATURE input data can be derived from experimental techniques as diverse as elemental analysis, UV, IR and NMR spectroscopy, GC-MS, vapor pressure osmometry and small angle X-ray/neutron scattering [46]. Thus, SIGNATURE has the inherent capability to generate molecular models of asphaltenes that take into account the properties of a specific crude oil. Kowalewski et al. [47] have recently reported the first utilization of two stochastically based CASE programs (XMOL and SIGNATURE) to generate a sample of ten model structures of asphaltenes from Boscan crude oil, a Venezuelan crude of high asphaltene content.

ESTIMATION OF THERMODYNAMIC PROPERTIES OF CONDENSED PHASE SYSTEMS FROM ATOMISTIC SIMULATIONS

Molecular dynamics (MD) and Monte Carlo (MC) simulations have become the most widely used theoretical methods of investigations of condensed phase systems since their inception in the late 1950's [48,49]. These two methods represent two alternatives

but equivalent approaches to the statistical mechanics of N -body systems. The original form of the Monte Carlo method was developed to model an N -body system in the canonical (NVT) ensemble. The probability distribution of states (ρ) for this ensemble is given by:

$$\rho = \frac{e^{-E/kT}}{Z} \quad (5-1)$$

where E is the energy of the system, T is its temperature and k is the Boltzmann constant. The partition function, Z , is given by:

$$Z = \frac{1}{C} \int e^{-E/kT} d\tau \quad (5-2)$$

where $d\tau = (dpdr)^{3N}$ is the differential element in the $6N$ dimensional phase space of coordinates (r) and momenta ($p = mv$) of the N -body systems, m and v are the particle mass and velocity and C is a normalization constant. A microscopic variable, for instance internal pressure $\pi(r, p)$, may therefore be expressed in terms of phase space variables as:

$$\pi(r, p) = \frac{p^2}{mv} - W \quad (5-3)$$

where $W = \delta U / \delta V$ is the virial, i.e. the volume (V) derivative of the potential energy. Conversely, the macroscopic pressure is given by the ensemble average:

$$P = \frac{\int \pi(r, p) e^{-E/kT} d\tau}{\int e^{-E/kT} d\tau} \quad (5-4)$$

In actual MC simulations the kinetic degrees of freedom are not explicitly considered and the statistical mechanics is carried out in the configuration space. Thus, the full partition function is replaced by the configuration partition function and microscopic definitions for state variables are expressed only in terms of configuration variables.

In an MD simulation, a finite number of molecules are allowed to interact via prescribed intermolecular forces in a finite domain. The molecular motions caused by these force fields are deterministic; thus, the positions and energies of the molecules can be determined by solving the corresponding Newton's equations of motion. In the MD simulation methodology, a macroscopic observable A corresponding to a microscopic descriptor, $A[p(t), r(t)]$ is given by:

$$A = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A[p(t), r(t)] dt \quad (5-5)$$

Because an infinite sampling time of phase space is not feasible, current MD simulation codes implement a step-by-step strategy to solve the equations of motion for N -body systems. For a finite number of time steps N_t of duration $\Delta\tau = T/N_t$, A may then be expressed as:

$$A = \frac{1}{N_t} \sum_{\tau=1}^{N_t} A(\tau) \quad (5-6)$$

where τ is an index running over the succession of time steps.

MD simulation methodology was initially developed to model an N -body condensed phase system in the microcanonical (NVE) ensemble. Then in the early 1980s practitioners of the field, recognizing the importance of simulating physical systems under different conditions of temperature, pressure, etc, began developing extended forms of MC and MD for other ensembles (NPT, NVT, NPH, etc.). These advances have resulted in the development a number of theoretical framework for estimating the thermodynamic and structural properties of condensed phase systems from MC and MD simulations [50,51].

The connection between MC/MD simulations and equilibrium thermodynamics is made through statistical mechanics. First-order properties such as internal pressure, internal energy, density are directly obtainable by ensemble/time averaging of the corresponding microscopic quantities. Second-order properties, i.e. thermodynamic and mechanical response functions such as specific heat, isothermal compressibility, thermal expansion etc., may be obtained either using the finite difference approach or by using the appropriate statistical fluctuation formulae corresponding to these properties. To illustrate these two different approaches, consider three commonly used response functions in the isothermal isobaric ensemble (NPT): specific heat at constant pressure (C_p), isothermal compressibility (K_T) and volumetric thermal expansion coefficient (α_p). The finite difference method of estimation of these properties is based on their thermodynamic definitions:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (5-7)$$

$$K_T = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (5-8)$$

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (5-9)$$

where H is the enthalpy of the system. The statistical fluctuation formulae for estimating these properties are given by [52]:

$$C_p = \frac{\langle H^2 \rangle - \langle H \rangle^2}{kT^2} \quad (5-10)$$

$$K_T = \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle kT^2} \quad (5-11)$$

$$\alpha_p = \frac{\langle VH \rangle - \langle V \rangle \langle H \rangle}{\langle V \rangle kT^2} \quad (5-12)$$

where the angular brackets represent a time average of the corresponding system property. Eqs. 5-10–5-12 are rigorously valid in the thermodynamic limit of an infinite size system. Derivations for the finite N case have been made and the exact and thermodynamic limit formulae were compared to Eqs. 5-10–5-12; differences were found to be less significant than the other systematic and random errors for systems of size N as low as 200–300 particles [52].

COMPUTER ASSISTED STRUCTURE ELUCIDATION OF ARAB BERRI ASPHALTENES

Structural input data

The starting point of any property estimation by atomistic simulations is the bond topology of the compound of interest, that is, a list of connections between all its atoms. Because asphaltene is operationally defined as a 'solubility class' of compounds precipitated from crude oil by addition of an excess amount of aliphatic solvents [1], the assignment of a precise and definite molecular structure to asphaltene has been a major challenge to petroleum chemists. Although a precise molecular structure of asphaltene is not currently available, elemental analysis, IR, UV and NMR spectroscopic studies have indicated that asphaltene consists primarily of naphthenic and naphthenoaromatic rings linked by alkyl side chains [53]. The degree of condensation of the polynuclear aromatic systems of asphaltene is still not precisely known despite several investigations [54]. However, indirect evidence from pyrolysis studies of asphaltene indicates a small degree of condensation (less than five) of their polynuclear aromatic systems [53]. Speight [53] in his recent review of the 'molecular nature of petroleum asphaltene' cited several studies of pyrolysis and 'transalkylation chemistry' showing that asphaltene contains substantial amounts of alkanes. Strausz and co-workers have used the ability of Ru ion catalyzed oxidation (RICO) to remove aromatics "while leaving aliphatics and naphthenics essentially unaffected" to determine the distribution and number of carbons of *n*-alkyl groups attached to aromatic rings of asphaltene isolated from Athabasca bitumen [54]. They reported that the alkyl side chains consisted of *n*-alkyl groups with *n* ranging from 1 to 22.

There is ample experimental evidence showing that the heteroatoms of asphaltene consist primarily of oxygen, sulfur and nitrogen [53]. Oxygen in crude oil asphaltic fractions has been primarily found as carboxylic, phenolic and ketonic groups [53]. Sulfur, on the other hand, has been found as benzothiophenes, naphthenobenzothiophenes, alkyl-alkyl sulfides, alkyl-aryl sulfides and aryl-aryl sulfides, whereas nitrogen is found scattered at various heterocyclic positions [53]. Metals such as vanadium and nickel have also been found in crude oil asphaltic fractions [53]. However, their exact locations in the structural framework of asphaltene remain to be determined [53]. Because asphaltene tends to aggregate in various solvents, reported molecular weights of asphaltene vary considerably throughout the literature [54]. However, Speight has found that the average molecular weights of crude oil asphaltic fractions "fall into a range centered around 2000 daltons" when these were measured by vapor pressure osmometry in highly polar solvents that prevent asphaltene association [53].

As stated in the Introduction, several structural models of asphaltene have been developed and used for various purposes. Brandt et al. [14], Rogel [19] and Murgich et al. [20] used model asphaltene in their theoretical investigations of asphaltene aggregation. Yen and co-workers [55-57] also employed a model asphaltene to describe the stacking and flocculation of asphaltene in crude oil. Similarly, Speight has used a 'low-molecular-weight-high polarity' model asphaltene to gain insight into the chemistry of coking [53]. Although these models have led to some significant insights into the chemistry and phase behavior of asphaltene, their ability to describe the

TABLE 5-1

SIGNATURE input parameters for Arab Berri crude oil^a — atomic ratios

| Element | % Weight | Atomic ratios | SIGNATURE parameters | |
|------------------------------------|----------|---------------|----------------------|---------|
| | | | minimum | maximum |
| H ^b | 7.49 | 109.60 | 106.50 | 110.50 |
| S ^b | 5.15 | 2.35 | 2.14 | 4.14 |
| O ^b | 2.97 | 2.71 | 1.12 | 3.12 |
| N ^c | 0.67 | 0.80 | | |
| C ^d _{aromatic} | 50 | | 48.00 | 52.00 |

^a Elemental analysis data were taken from Mclean and Kilpatrick [58]. The molecular weight was assumed to be greater than 1224 daltons and less than 2052 daltons.

^b Atomic ratios normalized per 100 C atoms.

^c Because the amount of nitrogen is low (<1%), the incorporation of nitrogen in the asphaltene structural framework was not taken into account.

^d ¹³C NMR data were taken from Mclean and Kilpatrick [58].

specific asphaltene chemistry of a given crude oil remain to be established. In this work, we used SIGNATURE to generate a sample of ten structural models of asphaltenes for a Saudi crude (Arab Berri). The elemental analysis and ¹³C NMR input data for SIGNATURE were taken from Mclean and Kilpatrick [58] and are given in Table 5-1. The conceptual framework for asphaltene model development was provided by the results of FITR studies of Arab Berri asphaltenes by Mclean and Kilpatrick [58], RICO characterization of Athabasca asphaltenes by Strausz et al. [54] and Speight's recent review of asphaltene chemistry [53]. Thus, in our development of a molecular model for Arab Berri asphaltenes, we have assumed that: (1) the degree of condensation of the naphthenic and/or naphtheno-aromatic rings is less than six; (2) the number of carbon atoms of the alkyl side chains range from four to twenty; (3) oxygen is present predominantly as carboxylic, carbonyl and phenolic groups; (4) sulfur occurs as dibenzopyrene, dibenzothiophene, sulfide and sulfoxide; (5) the molecular weight of asphaltenes is greater than 1000 daltons and less than 2500 daltons.

Because the amount of nitrogen in Arab Berri asphaltenes is relatively low, less than 1% [58], we have not accounted for the possible incorporation of nitrogen into the asphaltene molecular framework. A complete list of the molecular fragments and interfragment bonds used to generate the model asphaltenes from Arab Berri crude oil is given in Table 5-2.

Model generation

The generation of the asphaltene models for Arab Berri crude oil consisted of two steps: (1) determination of the set of molecular fragments and interfragment bonds that best match the quantitative and qualitative data given in Tables 5-1 and 5-2; (2) generation of a sample of structural models of asphaltenes from fragments found in step (1).

The set of fragments that best match the analytical data (Tables 5-1 and 5-2) was generated by the SIGNATURE program. A simulated annealing search of five

TABLE 5-2

SIGNATURE input parameters for Arab Berri crude oil — list of molecular fragments and interfragment bonds

| Linear alkanes | Aromatics | Elements and functional groups | Interfragment bonds |
|------------------|-------------------|--------------------------------|-----------------------|
| sl4 ^a | sn1 ^b | H | ali_ali ^d |
| sl5 | sn2 | O | ali_h |
| sl6 | sn3 | S | ali_o |
| sl7 | sn4 | CO | ali_s |
| sl8 | sn5 | COOH | aro_ali ^e |
| sl9 | a1n0 ^c | OH | aro_aro |
| sl10 | a1n1 | SO | aro_csp2 ^f |
| sl11 | a1n2 | | aro_h |
| sl12 | a1n3 | | aro_h |
| sl13 | a1n4 | | aro_o |
| sl14 | a1n5 | | h_o ^g |
| sl15 | a2n0 | | o_h |
| sl16 | a2n1 | | |
| sl17 | a2n2 | | |
| sl18 | a2n3 | | |
| sl19 | a3n0 | | |
| sl20 | a3n1 | | |
| | a3n2 | | |
| | a4n0 | | |
| | a4n1 | | |
| | Dibenzopyrene | | |
| | Dibenzothiophene | | |

^a sli is a saturated linear alkane containing *i* carbon atoms [59].

^b sni is a saturated naphthenic ring containing *i* rings [59].

^c ainj is a naphtheno-aromatic group containing *i* aromatic rings and *j* naphthenic rings [59].

^d ali_*i* is an sp³ carbon bonded to atom *i* [59].

^e aro_*i* is a resonance carbon bonded to atom *i* [59].

^f csp2 is an sp² carbon [59].

^g i_*j* is an element *i* singly bonded to element *j*. [59]

annealing cycles was employed to determine this list. The initial and final annealing temperatures were respectively set equal to 10 and 1000 K. The SIGNATURE output list of molecular fragments is given in Table 5-3. It consists of two aromatics (a3n0 and a4n0), 3 naphtheno-aromatics (a2n2, a2n3 and a3n2), two aliphatic chains (sl7 and sl9), an ether oxygen (O), a carboxylic group (COOH), a sulfide sulfur (S), a heteroaromatic (dibenzothiophene) and 21 hydrogen atoms. The SIGNATURE output list of interfragment bonds is also given in Table 5-3. It consists of fifteen C–H bonds (ali_h), six C_R–H bonds (aro_h), seven C_R–C_R (aro_aro), four C–S bonds (ali_s), four C–O bonds (ali_o) and one C_R–C_{sp2} (aro_csp2) bond. The combination of these molecular fragments and interfragment bonds yield a model asphaltene with a molecular formula C₁₄₄H₁₅₆O₄S₃. The average molecular weight of the corresponding model asphaltene molecule is equal to 2044 daltons (Table 5-3). This value compares very favorably with the average molecular weight of 2000 daltons reported in Speight's recent

TABLE 5-3

SIGNATURE output: best list of molecular fragments and interfragment bonds for Arab Berri^a

| Molecular fragments | Number of molecular fragments | Interfragment bonds | Number of interfragment bonds |
|---------------------|-------------------------------|---------------------|-------------------------------|
| a2n2 | 1 | ali_s | 4 |
| a2n3 | 1 | ali_o | 4 |
| a3n0 | 1 | aro_csp2 | 1 |
| a3n2 | 1 | ali_h | 15 |
| a4n0 | 1 | aro_h | 6 |
| s17 | 2 | aro_aro | 7 |
| s19 | 1 | | |
| O | 2 | | |
| COOH | 1 | | |
| S | 2 | | |
| Dibenzothiophene | 1 | | |
| H | 21 | | |

^a The model Arab Berri asphaltene molecule obtained from SIGNATURE's best solution has the molecular formula $C_{144}H_{156}O_4S_3$. Its average molecular weight is 2044 daltons.

review of the 'molecular nature of petroleum asphaltenes' [53]. However, as shown in Table 5-4, the match between the best list of molecular fragments and interfragment bonds is not perfect. For every 100 carbons of the model asphaltene molecule, 0.17 hydrogen atoms and 0.04 oxygen atoms are missing. Similarly, 1.06 sulfur atoms are missing. The average matching between the SIGNATURE solution and the data is approximately to 1.32 atoms missing or in excess for every 100 carbon atoms.

Two isomer construction modes were used to generate a sample of ten model asphaltene isomers that is statistically representative of the entire population of isomers that can be built from the set of molecular fragments and interfragment bonds given in Table 5-3. In the first mode, two samples of ten isomers were generated by directly connecting these fragments. The resulting structures were highly reticulated and thus had very high potential energies. A high degree of reticulation may be the reason why a

TABLE 5-4

SIGNATURE output atomic ratio: model predictions vs. experimental data^a

| Element | SIGNATURE parameters | | SIGNATURE solution | Deviation |
|----------------|----------------------|---------|--------------------|-----------|
| | minimum | maximum | | |
| H ^b | 106.50 | 110.50 | 108.33 | 0.17 |
| S ^b | 2.14 | 4.14 | 2.77 | 1.06 |
| O ^b | 1.12 | 3.12 | 2.08 | 0.04 |

^a The model Arab Berri asphaltene molecule obtained from SIGNATURE's best solution has the molecular formula $C_{144}H_{156}O_4S_3$. Its average molecular weight is 2044 daltons. The average matching between SIGNATURE solution and quantitative/qualitative data is 1.319 atoms missing or in excess.

^b Number of atoms per 100 carbon atoms.

TABLE 5-5

Molar volume, density, cohesive energy and solubility parameter of SIGNATURE model asphaltene isomers

| Isomer # | E^a (kcal/mol) | E_c^b (kcal/mol) | V_m^c (cm ³ /mol) | ρ^d (g/cm ³) | δ^e (cal ^{1/2} /cm ^{3/2}) |
|------------|---------------------|-----------------------|-----------------------------------|----------------------------------|--|
| 1 | 293.23 | 148.52 | 1755.83 | 1.16 | 9.20 |
| 2 | 445.82 | 178.35 | 1863.26 | 1.10 | 9.78 |
| 3 | 625.19 | 192.62 | 1730.78 | 1.18 | 10.55 |
| 4 | 806.70 | 146.99 | 1990.57 | 1.03 | 8.59 |
| 5 | 349.17 | 149.61 | 1808.77 | 1.13 | 9.09 |
| 6 | 350.61 | 195.04 | 1919.21 | 1.06 | 10.08 |
| 7 | 370.33 | 171.63 | 1741.62 | 1.17 | 9.93 |
| 8 | 386.01 | 154.84 | 1747.94 | 1.17 | 9.41 |
| 9 | 457.29 | 139.92 | 1863.93 | 1.10 | 8.66 |
| 10 | 597.02 | 149.95 | 1820.63 | 1.12 | 9.07 |
| Average | | | | 1.12 | 9.44 |
| Experiment | | | | 1.158 ^f | 9.50 ^g |

^a Energy by gas phase minimization.^b Cohesive energy estimated from NPT molecular dynamics simulations followed by energy minimization.^c Molar volume estimated from NPT molecular dynamics simulations followed by energy minimization.^d Density estimated from NPT molecular dynamics simulations followed by energy minimization.^e Solubility parameter estimated from NPT molecular dynamics simulations followed by energy minimization.^f Experimental density for Wafra crude oil taken from Yen et al. [65]. This crude oil originates from the Kuwait–Saudi Arabia Neutral Territory.^g Experimental solubility parameter estimated by fitting asphaltene precipitation data to a thermodynamic model of asphaltene precipitation [13].

stochastically generated model of Boscan asphaltene recently developed by Kowalewski et al. [47] had a very high energy (7000 kcal/mol) even though it was annealed through a series of MD simulations for a total of 150 ps followed by energy minimizations. To reduce the degree of reticulation of the model asphaltenes, the molecular fragments and interfragment bonds from Table 5-3 were combined into segments having an average of 13 carbon atoms prior to model construction. A sample of 10 model asphaltene isomers were generated by direct linkage of these fragments. Each of the ten model isomers was then minimized (rms force of 0.1 kcal mol⁻¹ Å⁻¹) using the Cerius2 molecular modeling software [60]. A Dreiding II force field (EXP-6 potential for the van der Waals interactions and $\epsilon = 1$) were used in all calculations [61]. The charge equilibration procedure (Q_{eq}) of Rappe and Goddard was used to determine all partial atomic charges [62]. All non-bond interactions were treated directly using a cutoff distance of 50 Å. The strain energies of the ten model asphaltene isomers are given in Table 5-5. These range from a low value of 293 kcal/mol for model asphaltene isomer #1 to a high value of 806 kcal/mol for model asphaltene isomer #4 and are approximately one order of magnitude lower than that of the most ‘stable’ conformation of Boscan model asphaltene of Kowalewski et al. [47]. The three dimensional structures of the ten Arab model asphaltene molecules are shown in Figs. 5-3 and 5-4.

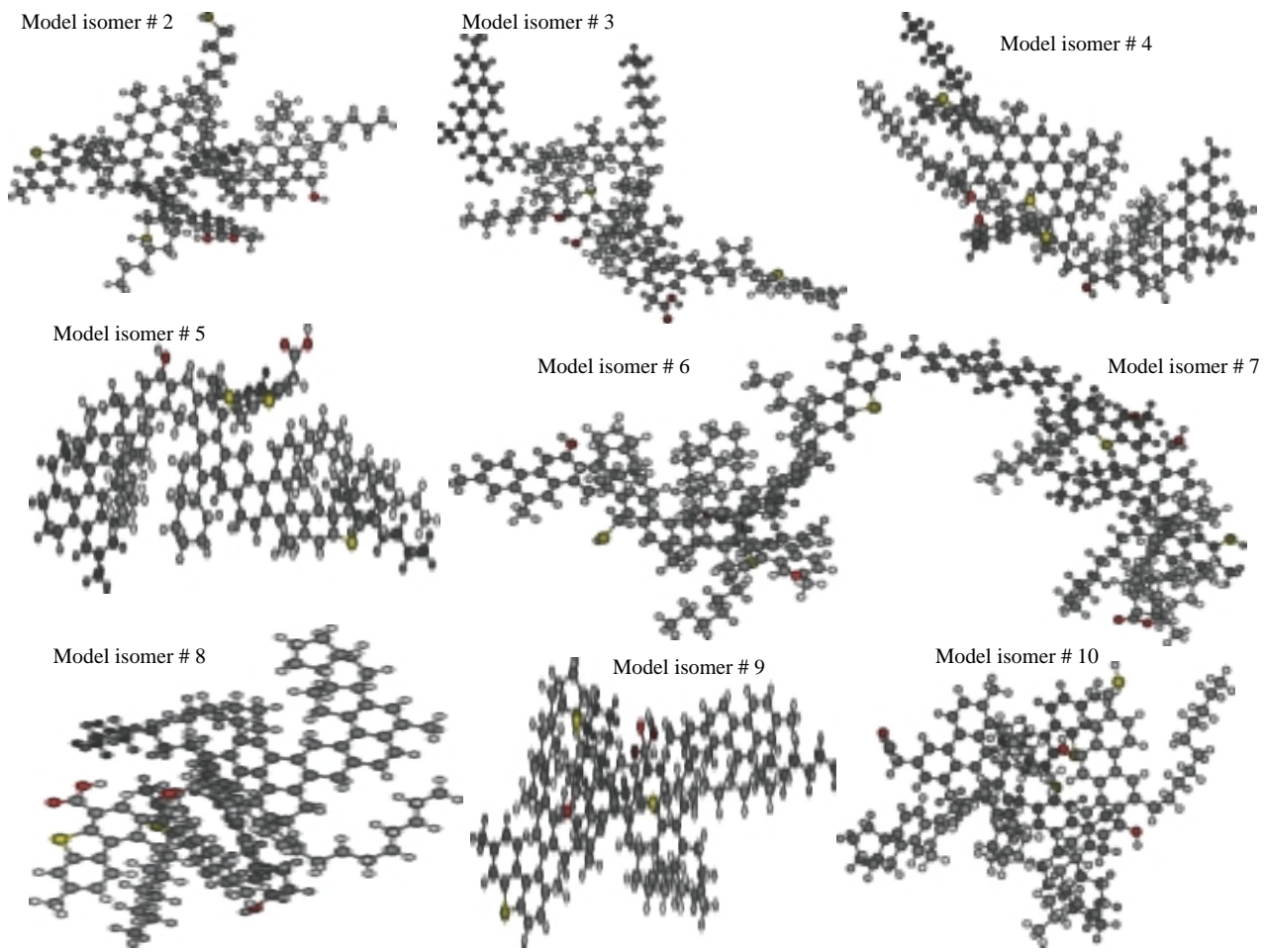


Fig. 5-3. SIGNATURE Arab Berri model asphaltenes.

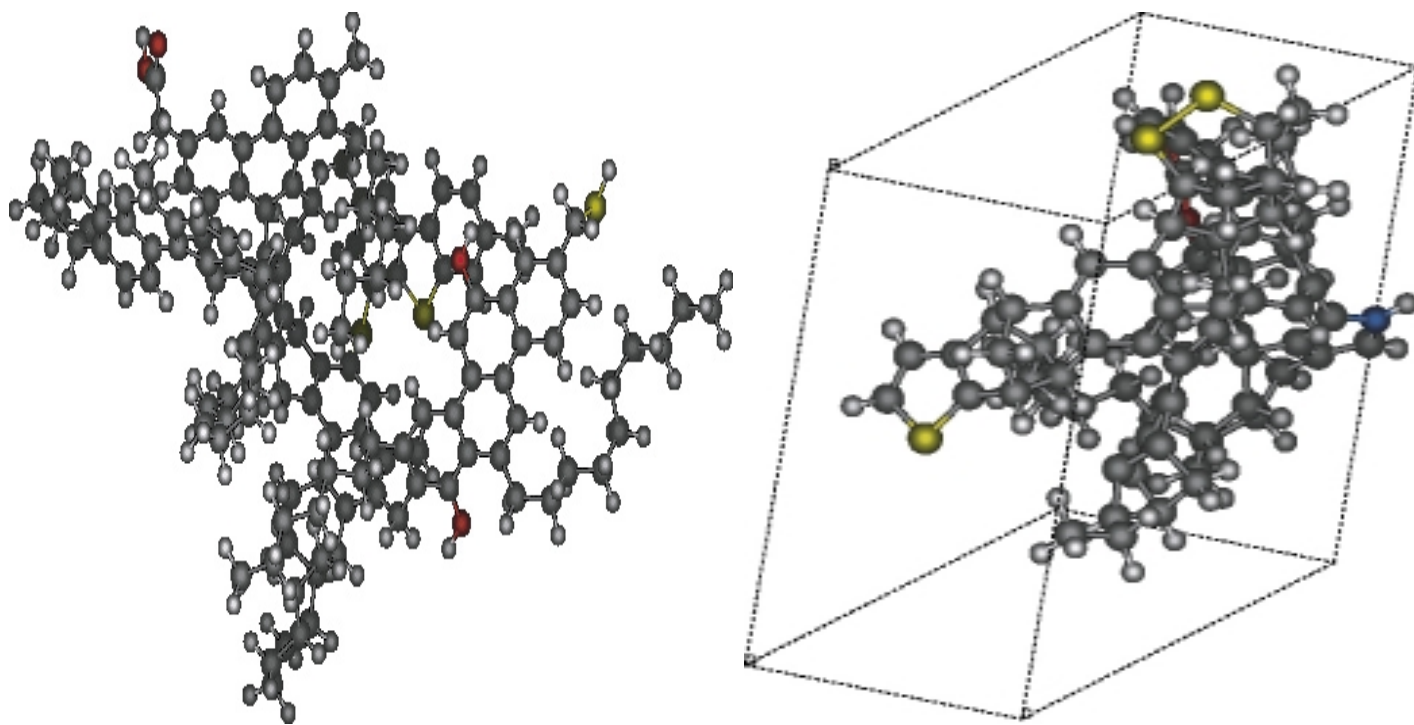


Fig. 5-4. In vacuo and periodic models for SIGNATURE Arab Barri asphaltene isomer #1.

VOLUMETRIC AND THERMAL PROPERTIES OF ARAB BERRI ASPHALTENES FROM MOLECULAR DYNAMIC SIMULATIONS

Molar volume, density, cohesive energy and solubility parameter at 0 K

Constant-pressure and constant-temperature (NPT) MD simulations followed by energy minimization were carried out to determine selected thermodynamic properties of the ten model asphaltene isomers using Cerius2 [60]. For the isolated molecules (gas phase simulations), the procedures used to treat the non-bond interactions were similar to those employed in the minimization of the ten model asphaltene isomers. For the bulk phase simulations, periodic boundary conditions were applied to each model asphaltene isomer. Ewald summation was used to calculate the long range interactions in all bulk phase MD simulations [63]. The Berendsen–Gunsteren thermal coupling method (cell mass prefactor of 0.04 and time constant of 0.1) and the Maxwell–Boltzman distribution method of assignment of initial velocities were employed in all MD simulations [60]. Each model was first minimized (rms force of $0.1 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$) and then placed into a 3-D cell with periodic boundary conditions. The resulting periodic structure was then minimized using Cerius2's Crystal Packer module [60]. Following this, each model was annealed by 10 ps of NPT dynamics at 300 K followed by minimization. The cell volume V_p and the strain energy E_p/E_{np} in the periodic cell/vacuum were then calculated. The molar volume (V_m), density (ρ) and cohesive energy (E_c) of each model asphaltene were expressed as:

$$V_m = N_a V_p \quad (5-13)$$

$$\rho = \frac{M_w}{V_m} \quad (5-14)$$

$$E_c = -(E_p - E_{np}) \quad (5-15)$$

where N_a is Avagadro's number and M_w is the molecular weight of the SIGNATURE model asphaltene isomer estimated to 2044 daltons (Table 5-3).

Following Barton [64], the solubility parameter (δ) was expressed as:

$$\delta = \left(\frac{E_c}{V_m} \right)^{0.5} \quad (5-16)$$

The molar volumes, densities, cohesive energies and solubility parameters of the model asphaltene isomers at 0 K are given in Table 5-5. The densities vary from a minimum value of 1.08 g/cm^3 for asphaltene model # 4 to a maximum value of 1.18 g/cm^3 for asphaltene model # 3. Except for asphaltene model #4, the estimated densities compare favorably with the measured density of asphaltenes (1.158 g/cm^3) for Wafra crude oil reported by Yen et al. [65]. This crude oil originates from a reservoir located at the Kuwait Saudi Neutral Territory. Similarly, the estimated solubility parameters, which range from a minimum value of $8.66 \text{ cal}^{1/2}/\text{cm}^{3/2}$ for asphaltene model #4 to a maximum value of $10.55 \text{ cal}^{1/2}/\text{cm}^{3/2}$, compare favorably with the experimental value of $9.50 \text{ cal}^{1/2}/\text{cm}^{3/2}$ reported by Hirschberg et al. [13].

Effects of temperature and pressure on molar volume, solubility parameters and enthalpy

NPT MD simulations were carried out to assess the effects of temperature and pressure on the molar volume, solubility parameter and enthalpy of model asphaltene isomer #1 (Fig. 5-4). This isomer was selected because it has the lowest energy (293 kcal/mol, see Table 5-5). The annealed and minimized 3-D periodic structure of the model asphaltene was first equilibrated for 20 ps at the specified temperatures and pressures. This was followed by 25 ps of NPT dynamics during which a trajectory frame was saved every 100 fs. The values of the cell volume (V_p), strain energy (E_p) in the periodic cell and enthalpy (H_p) at each time step and those of the strain energy in vacuum (E_{np}) at every time step of 100 fs were averaged to compute the molar volume (V_m), solubility parameter (δ) and enthalpy (H) of asphaltene model # 1. The results of these calculations are summarized in Tables 5-6 and 5-7.

TABLE 5-6

Molar volume, solubility parameter and enthalpy of SIGNATURE model asphaltene isomer #1 as a function of temperature for $P = 100$ bar

| Temperature (K) | V_m^a (cm ³ /mol) | δ^b (cal ^{1/2} /cm ^{3/2}) | H^c (kcal/mol) |
|-----------------|--------------------------------|---|------------------|
| 200 | 1808.50 | 8.67 | 517.21 |
| 250 | 1798.45 | 8.66 | 600.52 |
| 350 | 1869.54 | 8.15 | 785.27 |
| 400 | 1863.25 | 8.15 | 877.71 |
| 500 | 1874.94 | 8.00 | 1092.21 |

^a Molar volume estimated from lattice NPT molecular dynamics simulations.

^b Solubility parameter estimated from lattice NPT molecular dynamics simulations.

^c Enthalpy estimated from lattice NPT molecular dynamics simulations.

TABLE 5-7

Molar volume and solubility parameter of SIGNATURE model asphaltene isomer #1 as a function of pressure at $T = 300$ K

| Pressure (bar) | V_m^a (cm ³ /mol) | δ^b (cal ^{1/2} /cm ^{3/2}) | H^c (kcal/mol) |
|----------------|--------------------------------|---|------------------|
| 200 | 1886.46 | 8.09 | 699.00 |
| 400 | 1870.37 | 8.20 | 703.67 |
| 600 | 1868.24 | 8.22 | 699.41 |
| 800 | 1865.76 | 8.18 | 699.09 |
| 1000 | 1893.32 | 8.15 | 699.15 |

^a Molar volume estimated from lattice NPT molecular dynamics simulations.

^b Solubility parameter estimated from lattice NPT molecular dynamics simulations.

^c Enthalpy estimated from lattice NPT molecular dynamics simulations.

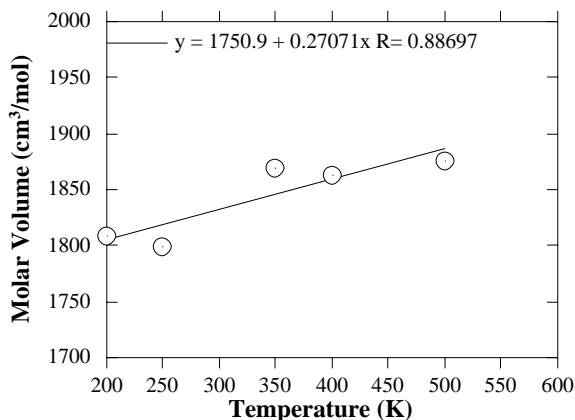


Fig. 5-5. Molar volume of asphaltene model isomer #1 as a function of temperature for $P = 100$ bar.

TABLE 5-8

Volumetric and thermal properties of SIGNATURE asphaltene model 1 and selected hydrocarbons at $T = 300$ K

| Compounds | ρ (g/cm ³) | δ (cal ^{1/2} /cm ^{3/2}) | C_p (J g ⁻¹ K ⁻¹) | α_p (K ⁻¹) |
|--------------------|--------------------------------|--|---|------------------------------------|
| Asphaltene model 1 | 1.12 ^a | 8.97 ^a | 3.71 ^a | 1.49×10^{-4} ^a |
| Decane | 0.72 ^b | 7.72 ^c | 2.20 ^d | 1.02×10^{-3} ^d |
| Benzene | 0.88 ^b | 9.17 ^c | 1.74 ^d | 1.14×10^{-3} ^d |
| Toluene | 0.86 ^b | 8.88 ^c | 1.70 ^d | 1.05×10^{-3} ^d |
| Naphthalene | 1.20 ^b | 9.91 ^c | 1.12 ^d | 0.28×10^{-4} ^e |
| Anthracene | 1.19 ^b | 9.91 ^c | 1.19 ^d | 1.57×10^{-4} ^e |
| Phenanthrene | 1.13 ^b | 9.76 ^c | 1.24 ^d | 2.56×10^{-4} ^e |

^a Estimated from NPT molecular dynamics simulations at $P = 100$ bar.

^b Estimated from molar volume ($P = 1$ bar) data taken from Ref. [64].

^c Experimental solubility parameter at $P = 1$ bar taken from Ref. [64].

^d Experimental data ($P = 1$ bar) taken from Ref. [66].

^e Experimental data from Ref. [67].

The effect of temperature on the molar volume V_m of asphaltene model # 1 for a pressure $P = 100$ bar is depicted in Fig. 5-5. The symbols represent calculated molar volumes; the solid line is a linear regression line through the data points. Fig. 5-5 clearly shows that the molar volume of asphaltene model # 1 increases linearly with temperature. From the slope of Fig. 5-5, we estimate the thermal expansion coefficient α_p (Eq. 5-9) for Arab Berri model asphaltene isomer # 1 ($T = 300$ K and $P = 100$ bar) to be approximately equal to 1.49×10^{-4} K⁻¹. This value is approximately one order of magnitude smaller than those of the liquid hydrocarbons (decane, benzene and toluene) given in Table 5-8. However, it is of the same order of magnitude as those of the polycyclic aromatic hydrocarbons (PAHs) and is approximately equal to that of anthracene (1.57×10^{-4} K⁻¹). Using the molar volume data of Table 5-6,

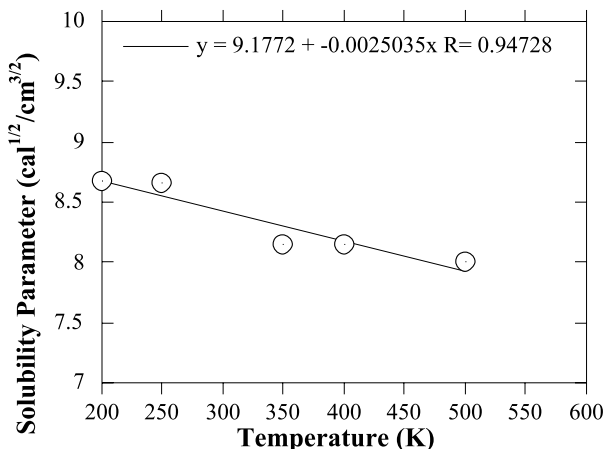


Fig. 5-6. Solubility parameter of asphaltene model isomer #1 as a function of temperature for $P = 100$ bar.

we estimate the density of SIGNATURE model asphaltene # 1 ($T = 300$ K, $P = 100$ bar) to be equal to 1.12 g/cm³. This value is substantially higher than those of decane (0.72 g/cm³), benzene (0.88 g/cm³) and toluene (0.86 g/cm³) given in Table 5-8. It is, however, slightly lower than those of naphthalene (1.20 g/cm³), and anthracene (1.19 g/cm³) and approximately equal to that of phenanthrene (1.13 g/cm³). This closeness between the values of the molar volume, density and thermal expansion coefficient for Arab Berri model asphaltene isomer # 1 and the PAHs is not surprising. It is consistent with the presence of aromatic rings of small degree of condensation (less than 5) in the structural framework of Arab Berri asphaltene model #1 (Fig. 5-4).

The effect of temperature on the solubility parameter of model asphaltene isomer #1 at $P = 100$ bar is shown in Fig. 5-6. The symbols are calculated solubility parameters; the solid line represents a linear regression line through the data points. Despite the scattering of the data, Fig. 5-6 clearly indicates that the solubility parameter of model asphaltene # 1 decreases linearly with temperature. A linear decrease of the asphaltene and naphthalene solubility parameter with temperature has also been reported by Hirschberg et al. [13]. The effect of temperature on the enthalpy of model asphaltene isomer #1 for $P = 100$ bar is shown in Fig. 5-7. The symbols are calculated enthalpies; the solid line is a linear regression curve through the data points. Fig. 5-7 indicates that the enthalpy of model asphaltene isomer #1 increases linearly with temperature. Because of this linear relationship, we can use Eq. 5-7 to express the specific heat at constant pressure ($P = 100$ bar) as:

$$C_p = \frac{\int_{T_0}^T dH}{\int_{T_0}^T dT} = \frac{H - H_0}{T - T_0} \quad (5-17)$$

where T_0 is a reference temperature. If we choose $T_0 = 200$ K, we estimate the value of C_p to be equal to 3.72 J g⁻¹ K⁻¹. In this case, however, the estimated specific heat of the model asphaltene is closer to that of decane (Table 5-8). This

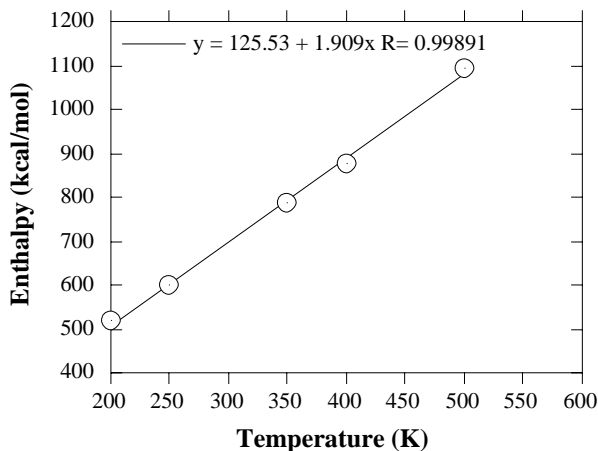


Fig. 5-7. Enthalpy of asphaltene model isomer #1 as a function of temperature for $P = 100$ bar.

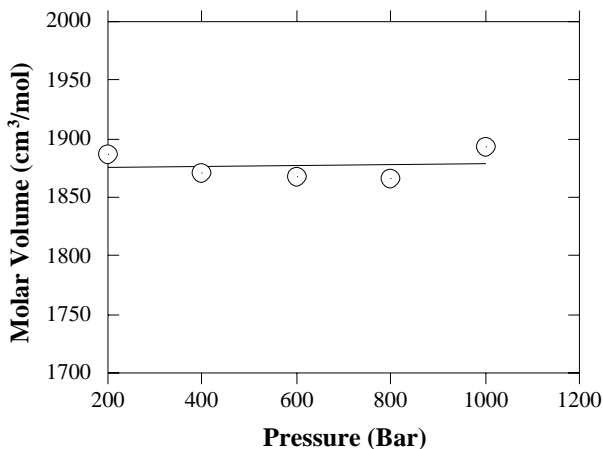


Fig. 5-8. Molar volume of asphaltene model isomer #1 as a function of pressure for $T = 300$ K.

behavior, which sharply contrasts with those of the molar volume and thermal expansion coefficient, may be attributed for the most part to the flexibility of SIGNATURE model asphaltene isomer #1 and decane. This flexibility is expected to significantly increase the number of vibrational modes of these molecules. Consequently, heating the more flexible asphaltene model isomer # 1 and decane will require more energy. Thus, the specific heat at constant pressure of Arab Berri model asphaltene isomer #1 (Fig. 5-4) is expected to be higher than those of the less flexible PAHs.

The effects of pressure on the molar volume, solubility and enthalpy of model asphaltene isomer # 1 are depicted in Figs. 5-8 to 5-10. The symbols are calculated values; the solid lines are linear regression lines fitted to the data points. Not surprisingly,

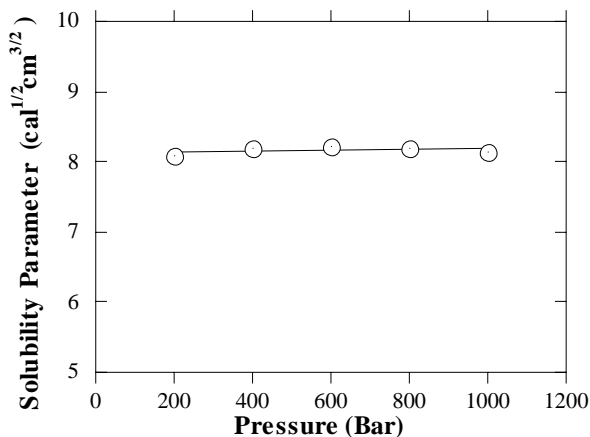


Fig. 5-9. Solubility parameter of asphaltene model isomer #1 as a function of pressure for $T = 300$ K.

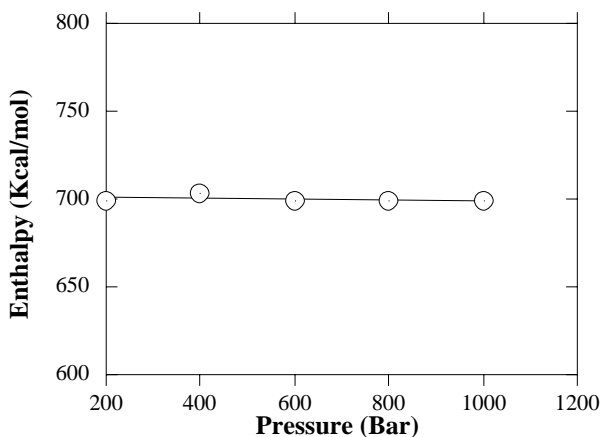


Fig. 5-10. Enthalpy of asphaltene model isomer #1 as a function of pressure for $T = 300$ K.

Figs. 5-8 to 5-10 indicate that pressure does not very much affect the molar volume, solubility parameter and enthalpy of asphaltene model #1. These results are consistent with a number of observations showing that the molar volume, solubility parameter and enthalpy of liquids and solids are not significantly affected by changes in pressure [64].

SUMMARY AND CONCLUSIONS

The precipitation of asphaltene aggregates can cause such severe problems as reservoir plugging and wettability reversal. The adsorption of asphaltene aggregates at oil-water interfaces has been shown to cause the steric stabilization of (W/O) petroleum emulsions. Consequently, the oil industry is in critical need of quantitative tools and

thermodynamic data to predict asphaltene solubility and aggregation as a function of crude oil composition and reservoir temperature and pressure.

This chapter describes a new methodology used in the estimation of the thermodynamic properties of asphaltenes. This methodology combines computer assisted structure elucidation (CASE) with atomistic simulations. To illustrate this new approach, we used quantitative and qualitative structural data as input to a CASE program (SIGNATURE) to generate a sample of ten model asphaltene structures for a Saudi crude oil (Arab Berri). We then carried out molecular mechanics (MM) calculations and molecular dynamics (MD) simulations to estimate selected volumetric and thermal properties of the model structures. We found that the estimated values are in good agreement with the available experimental data. The results of this study suggest that CASE can be combined with atomistic simulations to obtain adequate estimates of the thermodynamic properties of petroleum geomacromolecules such as asphaltenes.

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