

# Intermolecular Potential Energy and Intermolecular Forces of Nanostructures to Identify Asphaltene

S. Sabbaghi<sup>1</sup>, A. Jahanmiri<sup>1</sup>, M. Shariaty-Niassar<sup>2</sup>,  
Sh. Ayatollahi<sup>1</sup>, A. Boushehri<sup>3</sup>

1- Shiraz University, Department of Chemical Engineering

2- Tehran University, Department of Chemical Engineering

3- Shiraz University, Department of Chemistry

sabbaghi@shirazu.ac.ir

## Abstract

Remediation of the heavy organic deposits in the course of petroleum production has been a costly process and it has hampered the production activities in many parts of the world. Precipitation of asphaltene in wells and reservoirs has detrimental effects on the economics of oil production as it reduces well production. On the other hand, using the knowledge of exact intermolecular interactions between molecules and the development of accurate nanoscale phase separations/transition models, it will be possible to increase our fundamental understanding of organic nanostructures. The basics of quantum mechanics and statistical thermodynamics are used to predict the potential energy and intermolecular forces of asphaltene molecules. The functional forms for potential energy and intermolecular force are evaluated. Calculated data are graphically compared with proposed models. A dimensionless intermolecular potential energy function and forces are also proposed. A set of real data is used to check the validity of the calculated results. A well achieved agreement between one of the proposed models and the calculated data is promising.

**Keywords:** Asphaltene, Intermolecular potential energy, Intermolecular forces, Quantum Mechanics and Statistical thermodynamics.

## 1. INTRODUCTION

Asphaltene aggregation is a phenomenon of considerable importance in oil industry. An increase in aggregation results in enhanced oil viscosity. This, however, causes undesirable stability of water/oil emulsions, flock formation and low solubility. These eventually have a significant negative effect on production, transportation and processing of crude oil. Asphaltene bitumens are a product of crude oil and sometimes appear in a concentrated form as a residue of petroleum deposits. Asphaltene is the crude oil constituent with highest molar mass, aromaticity and hydrogen content. They are defined as the solubility class of a crude oil that precipitates upon the addition of a non-polar solvent (like n-alkanes) but dissolve in polar solvents (like aromatics such as toluene). Asphaltenes may also precipitate upon a change in pressure, temperature and/or composition. Generally, precipitation and

deposition of asphaltenes are reported to have caused operational problems ranging from plugging of tubulars and flow lines to clogging production separators. Despite the impact of asphaltenes in many technologies, some of their most fundamental properties have remained unresolved. So, the structural characterization of asphaltene is considered to be an important topic.

### 1.1. Asphaltene Structure

The investigation of the chemical constitution of petroleum heavy fractions such as asphaltene is hindered by their complex nature. The need for understanding the nature of heavy organics present in the crude oil and their role in the production and processing of petroleum is well recognized around the world as manifested by the extensive, related researches while the experimental activities are still underway at various research centers [1- 4]. Since 1980s, many models of asphaltene precipitation

have been developed to predict the onset and the amount of asphaltene precipitation. These predicting models can be divided into five groups (solubility, solidarity, equation of state, colloidal and micellization model) [5-11].

The models will be improved very well if the structure of asphaltene is known. However, the asphaltene structures are hardly known. There have been considerable efforts by analytical chemists to characterize asphaltene in terms of its chemical structure, elemental analysis as well as by the carbonaceous sources. A number of investigators have attempted to postulate model structures for asphaltenes based on physical and chemical methods for local oils. Figure (1) shows the molecular structure of asphaltene proposed for residue of Venezuelan Crude by Carbognan [12].

### 1.2. Computational details of proposed model

The importance of forces between macroscale molecules is so critical that it cannot be ignored. The systems are so dense and molecules are so close to each other that most of their properties are governed by interaction forces. It has been tried to relate measurable macroscopic quantities to microscopic interactions between molecules. Such relations are of essential objects in statistical mechanics. The potential energy of interactions between particles can be estimated using quantum mechanics. To determine the chemical potential, complicated numerical calculations are needed which can be evaluated by quantum mechanics. A rather general function which is used for interaction potential energy is that of the Mie potential function [13,14].

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

$U(r)$ : Potential energy,  $\left[\frac{\text{Kcal}}{\text{mol}}\right]$

$\varepsilon$ : Well depth (Minimum potential energy,  $\left[\frac{\text{Kcal}}{\text{mol}}\right]$ )

$\sigma$ : The intermolecular distance at which the potential is zero,  $[\text{\AA}]$

$r$ : Intermolecular distance,  $[\text{\AA}]$

$n, m$ : Dimensionless constants [-]

The constants  $\varepsilon$  and  $\sigma$  are obtained from intermolecular potential energy data. The curve of intermolecular potentials ( $U$ ) versus the distance ( $r$ ) is drawn in Figure (2) by using the proposed function of intermolecular pair potential. The method of semi-empirical equations such as PM3 is used for calculating the real data. It solves an approximate form of the Schrodinger equation that depends on having appropriate parameters available for the type of chemical system in question. In this work, two models (1) and (2) are suitable for the potential function of asphaltene. They are in different forms and will be discussed later within the scope of this work.

In order to determine the constants of potential function, the calculated data have been fitted. The results are as follows:

$$n=18$$

$$m=9$$

$$\sigma = 16.0399 (\text{\AA})$$

$$\varepsilon = 23.057 (\text{kcal/mol})$$

Then, model (1) is defined by equation (2) as follows:

$$U(r) = 92.228 \times \left[ \left(\frac{16.0399}{r}\right)^{18} - \left(\frac{16.0399}{r}\right)^9 \right] \quad (2)$$

For many purposes, the equation suffices to distinguish two principal forces: The first term; a repulsive force which is primarily due to the electrostatic repulsions between outer electron clouds of the molecular structure, and the second term; an attractive force which relates to the positions of the electrons in one molecule with respect to those in the other, which occur in such a way that cause a net electrical attraction. Either of the terms (repulsive, attractive) in equation (2), as well as the total intermolecular potential energy are separately plotted in Figure(3) [15,16,17].

### 1.3. Intermolecular Forces

It should be clearly understood that all forces between atoms and molecules are electrostatic in origin. They are ultimately based on Coulomb's law of attraction between unlike, and repulsion between

like, charges. The interparticle interaction potential energy between molecules is generally denoted by [13,14]:

$$U(r) = U_{rep.} + U_{att.} \quad (3)$$

where

r: Intermolecular distance

$U_{rep.}$ : The repulsive interaction energy

$U_{att.}$ : The attractive interaction energy

Interparticle energies are known to be orientation dependent and are the sum of repulsive, London dispersion, hydrogen bonding as well as electrostatic energies. For natural and spherically symmetric molecules when the separation distance(r) is large, the London dispersion forces dominate. Then, all these forces may be represented as gradients of potential energies [13].

$$F = -\frac{\partial U}{\partial r} = F_{rep.} + F_{att.} \quad (4)$$

Total force is calculated by equation (4) and then a plot of dimensionless force ( $\frac{F \sigma}{\epsilon}$ ) versus distance is shown in Figure (4).

#### 1.4. Computational details of model(2)

Similar to model (1), a second model is proposed for calculation data. In order to determine the constants of potential energy in model (2), the calculated data have been fitted. The results are as follows:

n=12

m= 6

$\sigma = 16.0399$  (°A)

$\epsilon = 23.057$  (kcal/mol)

Then, model (2) is defined by equation (5) as follows:

$$U(r) = 92.228 \times \left[ \left( \frac{16.0399}{r} \right)^{12} - \left( \frac{16.0399}{r} \right)^6 \right] \quad (5)$$

Likewise, in model(1), Figure(6), each of the terms (repulsive, attractive) as well as the summation (that is, the total potential energy), U(r), are plotted. The total force is calculated by equation (4) and then a dimensionless plot of force versus distance is shown in Figure (7).

#### 1.5. Shifted-Force Potential

For testing purposes, the step change in U(r) and F(r) can be removed by shifting F(r) vertically. So, the force goes smoothly to zero at  $r_c$ . Hence, it defines a shifted force  $F_{S(r)}$  by [18]:

$$F_{S(r)} = \begin{cases} -\frac{du}{dr} + \Delta F & r \subseteq r_c \\ 0 & r \supset r_c \end{cases} \quad (6)$$

where  $\Delta F$  is the magnitude of the shift.

$$\Delta F = -F(r_c) = \left( \frac{du}{dr} \right)_{r_c} \quad (7)$$

The shifted- force potential ( $u_{s(r)}$ ) corresponding to  $F_{S(r)}$  can be derived from:

$$F_{S(r)} = -\frac{du_{s(r)}}{dr} \quad (8)$$

$$\int_0^{u_s} du_s = -\int_{\infty}^r F_{S(r)} . dr \quad (9)$$

Substituting equation (6) into equation (9) and integrating gives:

$$u_{s(r)} = \begin{cases} u_{(r)} - u_{(r_c)} - (r-r_c) \left( \frac{du}{dr} \right) & r \subseteq r_c \\ 0 & r \supset r_c \end{cases} \quad (10)$$

Equations (11,12) and Figures (8,9) compares this shift force potential with proposed models (1,2).

$$u_{S(r)} = u_{(r)} - (-.0512) - (r - 40.1) \times (-.0125) \quad (11)$$

$$u_{S(r)} = u_{(r)} - (-.376) - (r - .10964) \times (-.0561) \quad (12)$$

## 2. Results

The validity of the results has been checked by comparing the results predicted by the model with the calculated data. It showed a good agreement which was promising. Then, the results were used to investigate the behavior of asphaltene. The numerical results are shown in Table(1).

A comparison was made between models (1) and (2) the real data. This comparison is shown in Figure (10). It revealed that model (1) was suitable for our work. A dimensionless potential function was proposed for the sake of generality of the results. The comparison between dimensionless intermolecular forces and the potential function is shown in Figures (11) and (12). So, dimensionless shifted-potential energy ( $U^*$ ) and dimensionless distance ( $r^*$ ) was expressed to facilitate making a comparison between the results shown in this paper. Therefore, dimensionless potential and distance are defined by equations(13) & (14) and the results are graphically shown in Figures(13) and (14).

$$U^* = \frac{U_s}{\varepsilon} \quad (13)$$

$$r^* = \frac{r}{\sigma} \quad (14)$$

If intermolecular structure of a particle is known, then technically,one can predict its size by taking the bond lengths into account. It is understood that formidable challenges remain in the fundamental understanding of various phenomena in organic nanostructures before their impact on nanotechnology

becomes a reality. Using the knowledge of exact intermolecular interactions between molecules and the development of accurate nanoscale phase separation/transition models, it will be possible to increase our fundamental understanding of organic nanostructures. The essence of nanotechnology is the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. Asphaltene which is in this category of molecular level of structure can have interesting and useful applications in nanotechnology. Our primary focus is to establish all details of nanostructure asphaltene for future nanotechnology application.

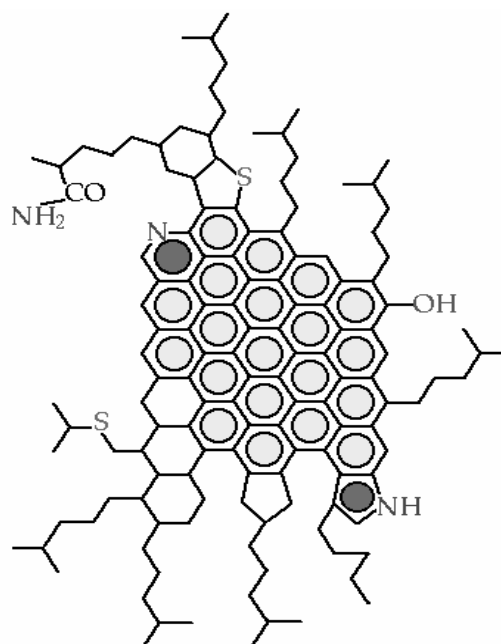
## References

1. David, A., 1973. *Asphaltene flocculation during solvent stimulation of heavy oils. AIChE(Am. Inst. Chem. Eng.) Symp. Ser.*, 69(127):56-61.
2. 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.
3. Mansoori, G.A.,1988. *Asphaltene deposition: An economic challenge in heavy petroleum crude utilization and processing. OPEC Rev.*, pp.103-113.
4. Mansoori, G.A. and Jiang, T.S., 1985. *Asphaltene deposition and its role in enhanced oil recovery miscible gas flooding. Proc. 3rd Eur. Conf. On Enhanced Oil Recovery, Rome, Apr. 1985.*
5. Mansoori, G.A., 1999. *Modeling and Asphaltene and Other Heavy Organic Compound. J. of Petroleum Science Engineering*, 16,101.
6. Andersen, S.I., Speight, 1999. *Thermodynamic Models for Asphaltene Solubility and Precipitation. J. of Petroleum Science and Engineering*, 22, 53-66.
7. Thomas, F.R, Bennion, D.W., Hunter, RE., 1992. *Experimental and Theoretical Studies of Solids Precipitation from Reservoir Fluid. Can. Pet. Tech.*,31, pp.22-31.
8. Alexander, G.L., Creagh, A.L., Prausnitz, J.M., 1985. *Phase Equilibria for High Boiling Fossil-Fuel Distillates:1. Characterization. Ind. Eng. Chem. Fund.*, 24, p.301.
9. Akbarzadeh, K., Sh. Ayatollahi, M., Moshfeghian, H. Alboudwarej, H.W. Yarranton,2004. *Estimation of SARA Fraction Properties With the SRK EOS, Journal of Canadian Petroleum Technology, Volume43, No.9.*

10. Akbarzadeh, K., Sh. Ayatollahi, Kh. Nasrifar, M., Moshfeghian, H.W. Yarranton, 2002. Equations lead to Asphaltene Deposition Prediction, *Oil & Gas Journal*, Volume 100, Issue 44, Oct. 28.
11. Akbarzadeh, K., Sh. Ayatollahi, M., Moshfeghian, M., Alboudwarej, H., Svrcek, H.W. Yarranton, 2004. Prediction of Asphaltene Precipitation with a Modified SRK EOS, *5th International Symposium on Thermodynamic of Heavy Oils and Asphaltenes*,
12. Carbognani, 1992. INTEVEP S.A., Tech. Rept.
13. Mc Quarrie, D.A. , 1976. *Statistical Mechanics*, Harper Collines Publishers.
14. Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., 1964. *Molecular Theory of gases and Liquids*, 2nd Printing, Wiley, New York.
15. Cark Nyeland, 2003. Gradient expansions in density functional calculations of intermolecular potentials, *Chemical physics letters*, pp.353-359.
16. Akiyoshi S., Satimi K., Nobuaki M., Kenro H., 2004. Potential energy surface and intermolecular vibrations of  $O_2 - H_2O$ , *Chem. Phys. letters*, pp.101-105.
17. Yu Zhang, Hong-Yun Shi, 2002. An ab initio study of intermolecular potential for the He-Hcl complex, *J. of molecular structure(Theochem)*, pp.89-93.
18. J.J. Nicolas, K.E. Gabbin, W.B. Streett and D.J. Tildesley, 1979. Equation of state for the Lennard-Jones fluid. *Mol. Phys.* 37,142

**Table 1:** Contributions to calculated potential energy of asphaltene for proposal models (1,2)

| r (Å) | U(r)<br>Calculated | U(r)<br>Model(1) | U(r)<br>Model(2) |
|-------|--------------------|------------------|------------------|
| 16    | 5                  | 2.138129         | 1.409515         |
| 16.04 | -.006              | -.00532834       | -.003562         |
| 16.05 | -.637              | -.5182515        | -.3464736        |
| 16.1  | -1.644             | -2.951863        | -2.001274        |
| 16.2  | -5.68              | -7.212301        | -5.027039        |
| 16.3  | -9.425             | -10.75559        | -7.704967        |
| 16.5  | -16.55             | -16.06854        | -12.14805        |
| 16.6  | -20.455            | -17.99689        | -13.97104        |
| 16.7  | -21.532            | -19.52859        | -15.56238        |
| 17    | -24.323            | -22.26625        | -19.16133        |
| 18    | -19.4              | -21.09931        | -23.05735        |
| 18.5  | -17.5              | -18.46506        | -22.53565        |
| 19    | -13.315            | -15.71186        | -21.30055        |
| 20    | -12.395            | -10.92182        | -18.01119        |
| 21    | -4.699             | -7.438375        | -14.67692        |
| 22    | -2.133             | -5.056317        | -11.77227        |
| 25    | -2.115             | -1.667821        | -5.984638        |
| 28    | -1.221             | -.6086506        | -3.144173        |
| 31    | -.165              | -.2444973        | -1.735784        |
| 33    | -.0695             | -.1394446        | -1.200139        |



**Figure 1:** Molecular structure of asphaltene [12]

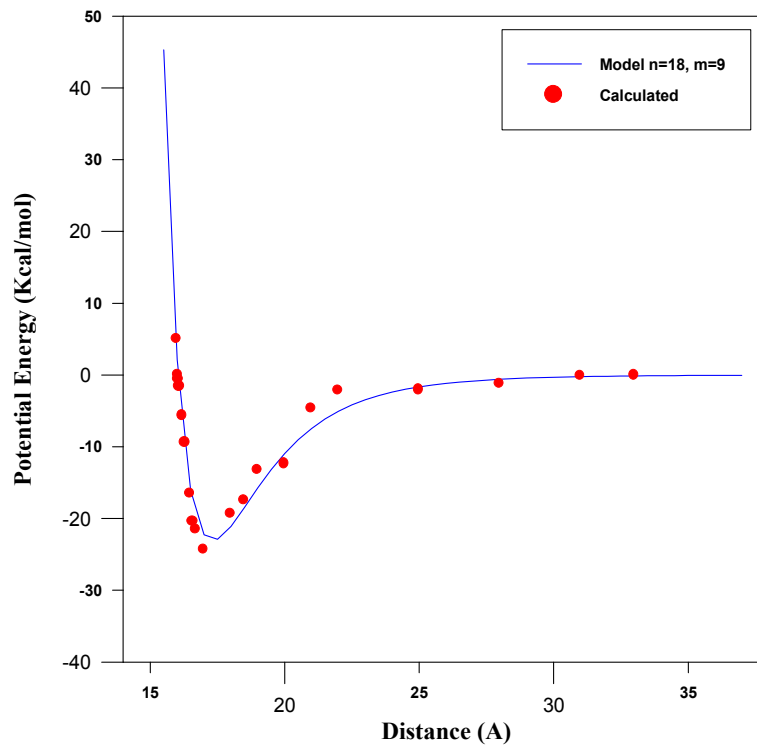


Figure 2: Intermolecular potential of asphaltene formode

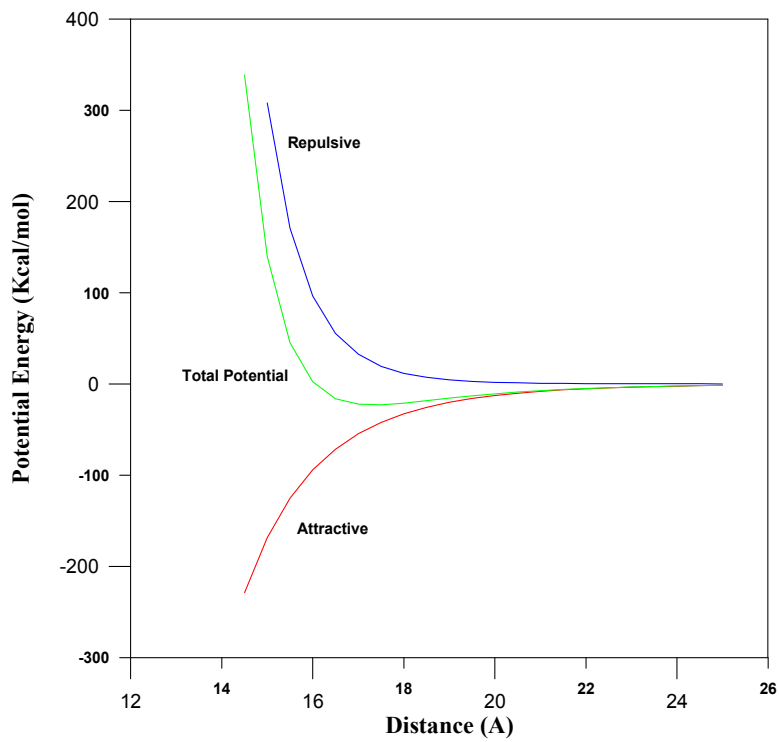


Figure 3: Intermolecular separation of asphaltene for model (1)

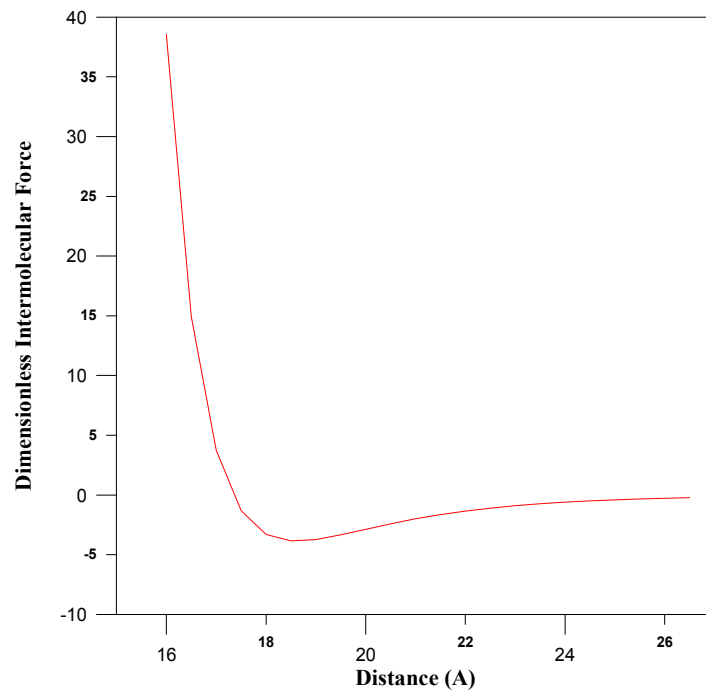


Figure 4: Dimensionless force versus distance for model (1)

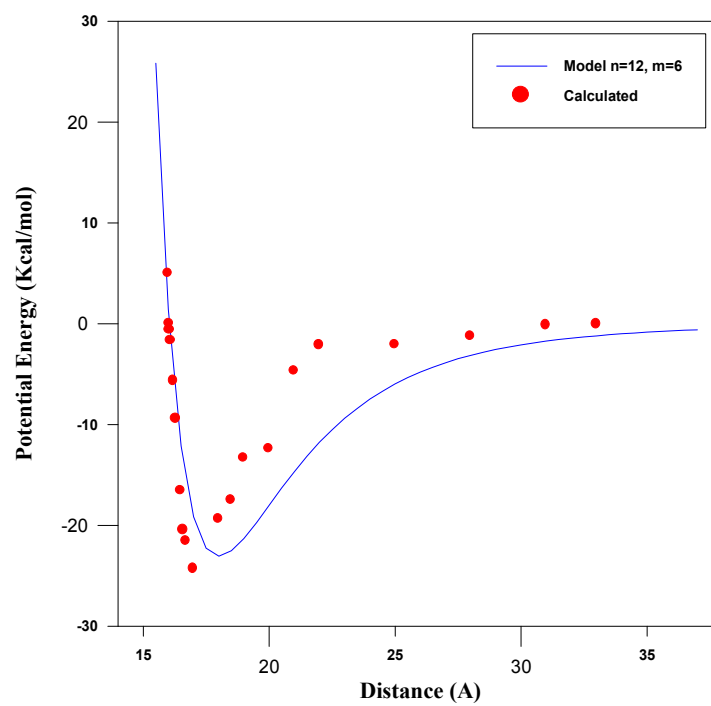
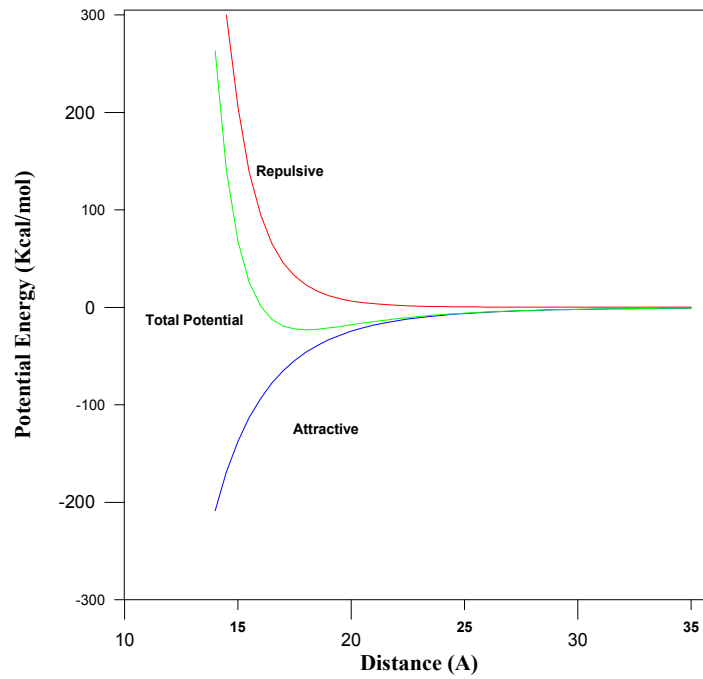
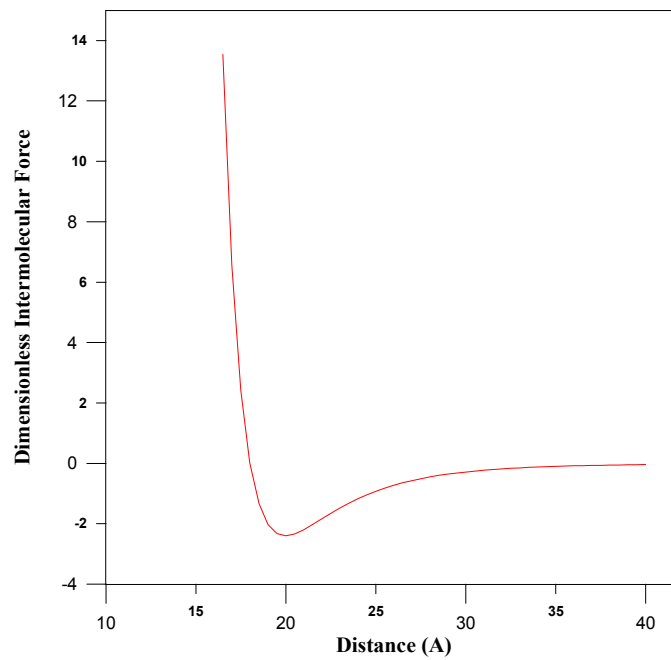


Figure 5: Intermolecular potential of asphaltene for model (2)





**Figure 6:** Intermolecular separation of asphaltene for model (2)



**Figure 7:** Dimensionless force versus distance for model (2)

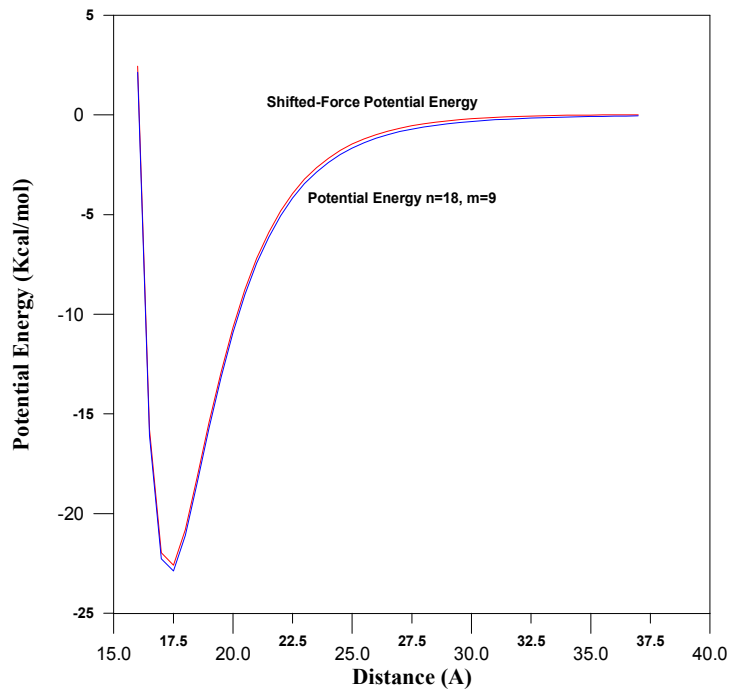


Figure 8: Comparison of model(1) with that of shifted-force potential {11}.

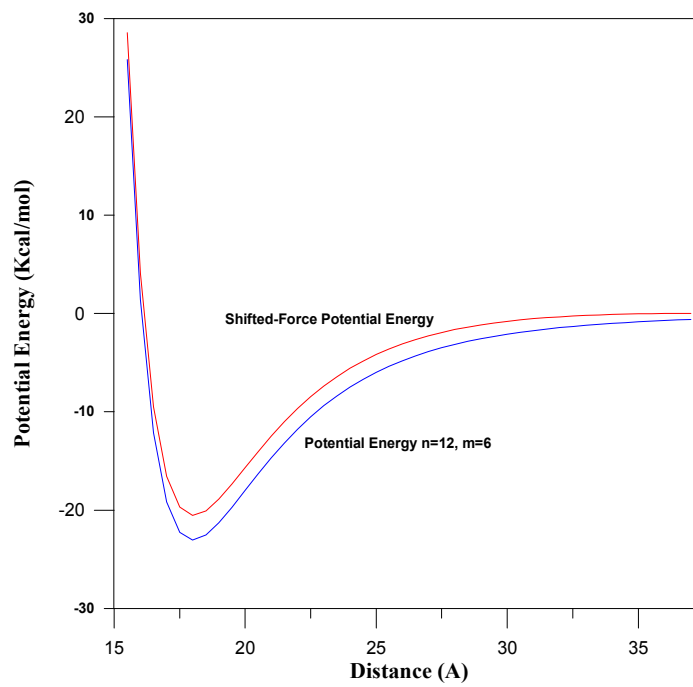


Figure 9: Comparison of model(2) with that of shifted-force potential {12}

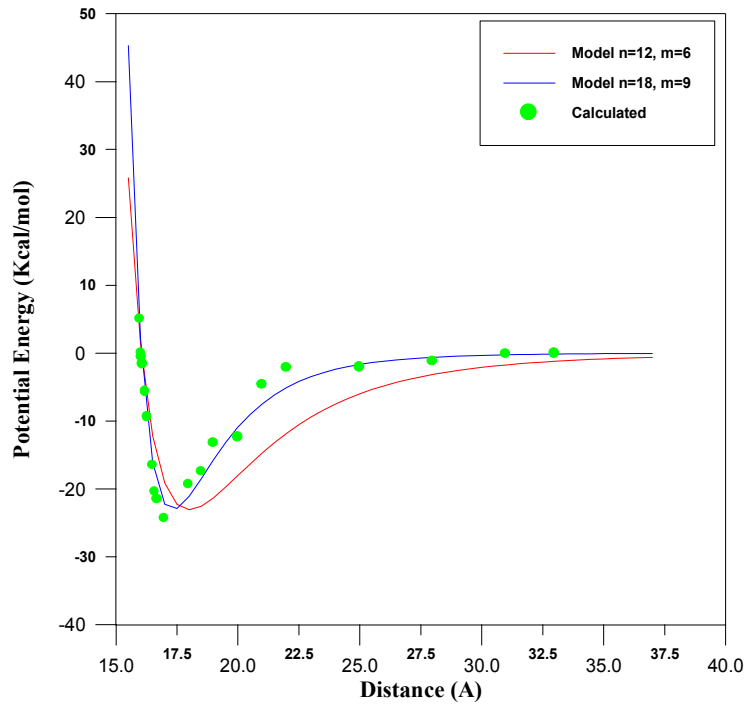


Figure 10: Comparison of the models (1&2) with real data

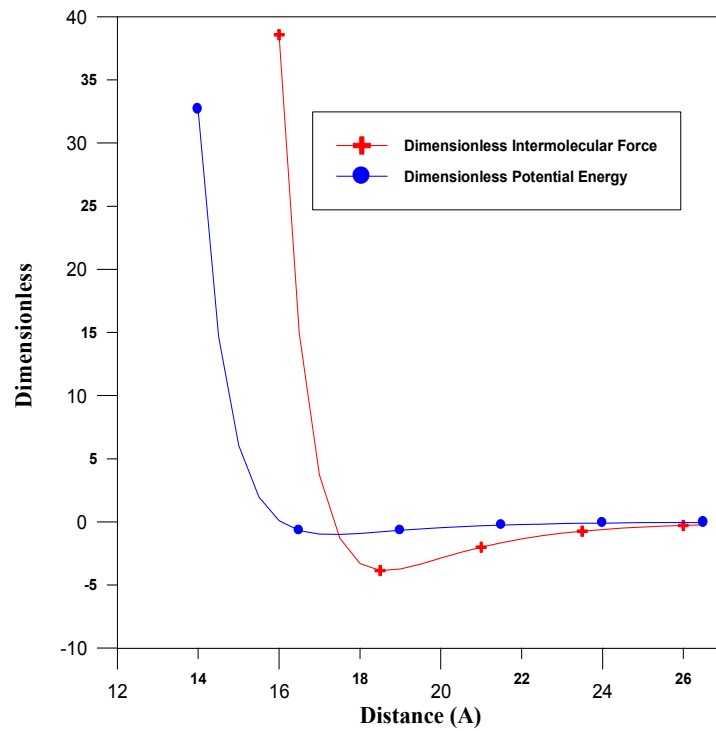


Figure 11: Dimensionless intermolecular force and potential energy versus distance for proposed model (1)

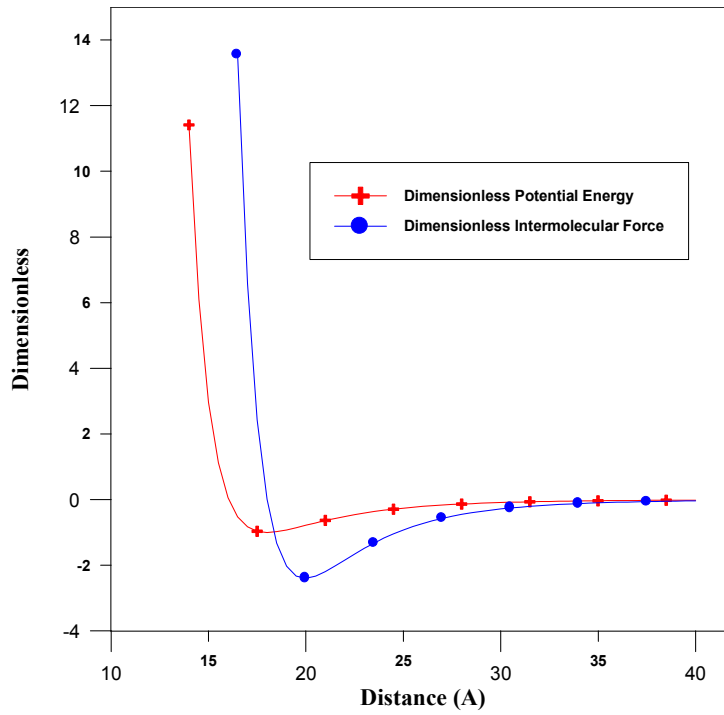


Figure 12: Dimensionless intermolecular force and potential energy versus distance for proposed model (2)

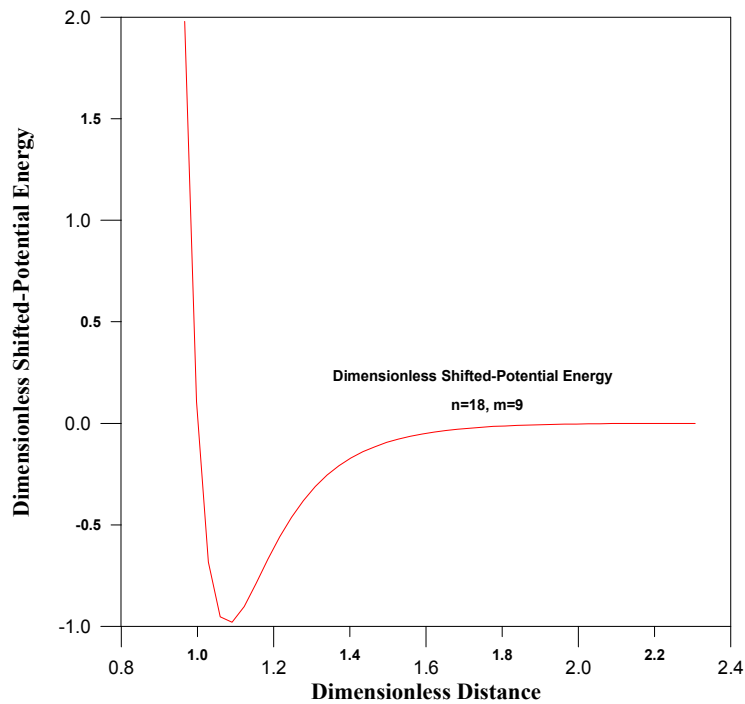
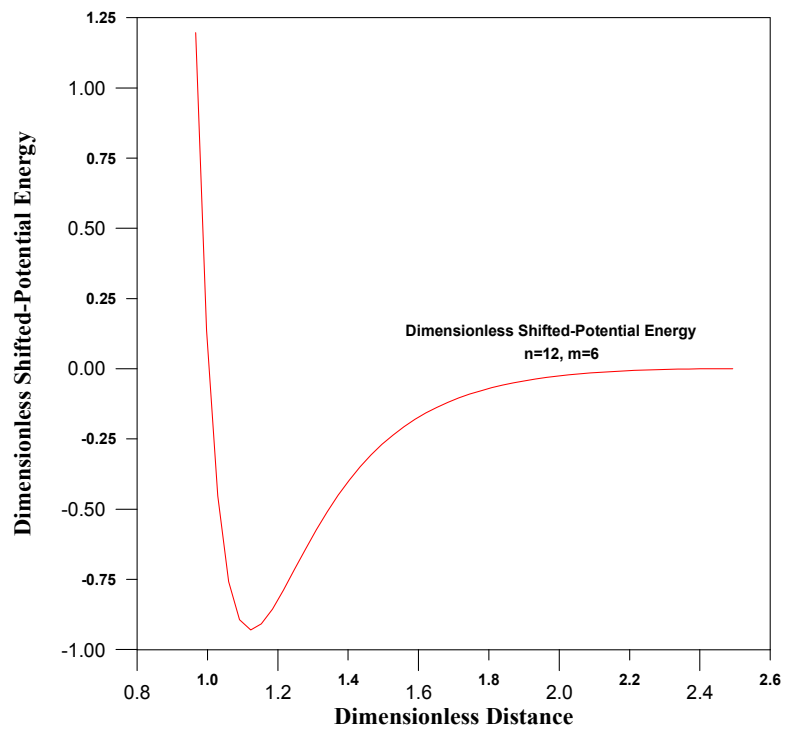


Figure 13: Dimensionless plot of potential energy with distance for proposed model (1)



**Figure 14:** Dimensionless potential energy versus dimensionless distance for proposed model (2)

