



# Modeling Asphaltene Precipitation in Reservoir Oils by CPA EoS via a new Approach based on the Asphaltene Molecular Structure

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## INTRODUCTION

Asphaltenes are the most complex constituent of a crude oil. Moreover, they are defined as a solubility fraction which is insoluble in n-pentane or n-heptane but soluble in toluene [1]. Asphaltenes strong self-association tendency causes asphaltenes aggregation, flocculation and finally precipitation. In order to control and prevent asphaltene precipitation and its subsequent deleterious effects, it is crucial to model and predict asphaltene phase behavior. Over the past years, a large variety of models have been proposed for modeling thermodynamic behavior of asphaltene precipitation. Among the proposed methods, cubic plus association equation of state (CPA EoS) has gained a lot of application and attention through its high accuracy and lower complexity in comparison with the other methods. Considering the high

capability of the CPA EoS in modeling the phase behavior of complex systems including heavy components, self-associating and cross-associating components, it has been applied for modeling asphaltene phase behavior [2, 3]. The aim of this study is to introduce a new simple and easily applicable approach according to asphaltene molecular structure for modeling the asphaltene phase behavior in live oils. Finally, the accuracy of the model is analyzed by applying it to two different live oil samples and comparing the results with other available models.

## MODELING

In order to model asphaltene precipitation, a liquid-liquid phase separation between two liquid phases, the asphaltene-rich phase which is a pure liquid-dense phase and the oil-rich phase which behaves as a solvent for asphaltenes is

assumed. In order to characterize the investigated live oil samples [4, 5], the composition of reservoir oils and SARA test results are used. In the reservoir fluid compositions, those components heavier than pentane are lumped as a  $C_{6+}$ . Then it is assumed that the quantity of the components lighter than hexane in the stock tank oil is negligible. In order to reduce the complexity and number of tuning parameters of the model, the saturates, aromatics and resins fractions are lumped into a pseudo-component termed as heavy component (HC) or maltene. Moreover, in this study, all binary interaction coefficients are assumed to be equal to zero. Experimental investigation by Hosseinpour et al [6] revealed that in the asphaltene structure, the concentration of basic functional groups is 4.5 times of that of the acidic functional groups. In other words, for each acidic site of asphaltene, there are four basic sites. Therefore, it is assumed by us that each asphaltene molecule has five association sites, which is consistent with its molecular structure. Also, two association sites are assigned for the heavy component. In our approach, self-association between asphaltene molecules and cross-association between asphaltene and heavy component are taken into account. The critical pressure of the heavy component is tuned with respect to one experimental point to match the bubble point pressure of the asphaltene. The cross-association energy between asphaltene and heavy component ( $\epsilon^{AH}/R$ ) is considered as the only tuning parameter for modeling asphaltene onset point. Moreover, it is assumed to be temperature dependent and obtained by using at least two experimental data of onset pressure. Three different forms of temperature-dependency are considered for the  $\epsilon^{AH}/R$

(Equations 1-3).

$$\epsilon^{AH}/R = A + BT \quad (1)$$

$$\epsilon^{AH}/R = A + B/T \quad (2)$$

$$\epsilon^{AH}/R = A + BT + C/T \quad (3)$$

where, in the above equations, A, B and C are constants obtained by regressing of experimental data.

## RESULTS AND DISCUSSION

As it was mentioned in previous section, in this study, the critical properties of the heavy component are tuned based on a single experimental bubble point pressure. Our obtained results show that the tuned values of the critical pressure for the sample 1 [4] and sample 2 [5] are equal to 21.98 bar and 20.36 bar respectively. These tuned values are used to predict the bubble point pressure of the samples over the whole range of the temperature, and the results are compared with the experimental data. The obtained results indicate that the proposed approach is able to predict the bubble point pressure of the sample 1 [4] and sample 2 [5] with an average absolute relative error (AARE) equal to 1.54% and 0.93%, respectively, demonstrating the high accuracy of the proposed approach.

In order to apply the CPA EoS to model asphaltene onset point, the  $\epsilon^{AH}/R$  is considered as the only tuning parameter of the model and adjusted with respect to two experimental data point (using Equations 1 and 2) and three experimental data point (using Equation 3). After tuning the  $\epsilon^{AH}/R$ , the CPA EoS is applied to predict the onset point over the broad range of temperature. Figures 1 and 2 show the precipitation envelope

(APE) for the sample 1 [4] and sample 2 [5] respectively. These findings indicate that  $\epsilon^{AH}/R=A+BT+C/T$  although gives the lowest AARE, it cannot predict the actual trend of the asphaltene precipitation with respect to temperature. The asphaltene aggregate size decreases with temperature since the asphaltene solubility increases, as stated by Hemmati et al [1]. Therefore, from Figures 1 and 2, it can be concluded that  $\epsilon^{AH}/R=A+B/T$  is the best choice, which models the asphaltene onset point of the sample 1 [4] and sample 2 [5] with AARE of 5.37% and 5.50% respectively. As well as

providing precise prediction of asphaltene onset point, the actual trend of asphaltene onset point with variation of temperature can be accurately predicted by considering the  $\epsilon^{AH}/R=A+B/T$ . Comparison of the results of the developed approach in this work with previously available one, e.g. the Zhang et al [3], verifies more the accuracy of the proposed approach. Both of the investigated samples in this study were studied by Zhang et al [3]. Their obtained results indicate that with increasing the temperature, asphaltene stability decreases and then increases, which is beyond the actual phase behavior of asphaltene.

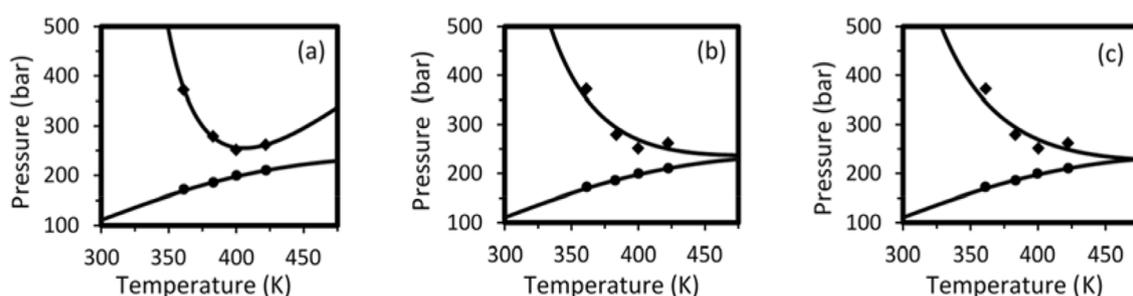


Figure 1: APE for the sample 1 [4], (a):  $\epsilon^{AH}/R=A+BT+C/T$  (b):  $\epsilon^{AH}/R=A+B/T$  (c):  $\epsilon^{AH}/R=A+BT$ .

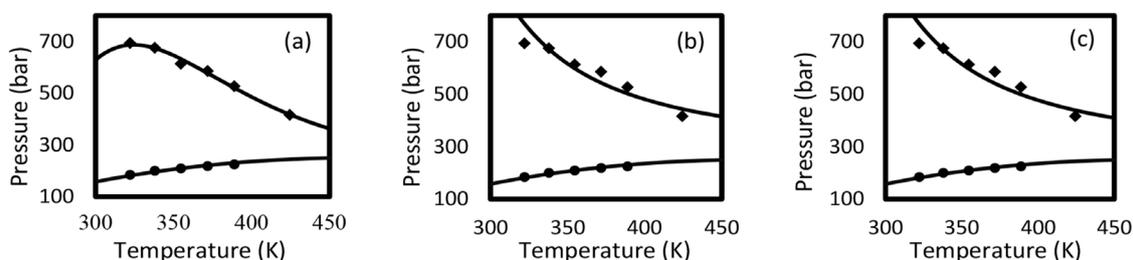


Figure 2: APE for the sample 2 [5], (a):  $\epsilon^{AH}/R=A+BT+C/T$  (b):  $\epsilon^{AH}/R=A+B/T$  (c):  $\epsilon^{AH}/R=A+BT$ .

## CONCLUSIONS

The CPA EoS was applied to model the asphaltene precipitation in live oil samples with a new modeling approach based on the asphaltene molecular structure. Five association sites were assigned to the asphaltene molecules, while two association sites were considered for the heavy component. The dependency of the asphaltene-heavy component cross-association energy ( $\varepsilon^{AH}/R$ ) was modeled with three different equations. It is found out that considering  $\varepsilon^{AH}/R = A + BT + C/T$  provides the best results.

The model predicts not only the bubble point pressure curve with a high accuracy but also the asphaltene precipitation onset with temperature. Finally, the trend of the asphaltene onset curve with temperature is consistent with the natural behavior of asphaltene.

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