

## Effect of inhibitors on asphaltene aggregation

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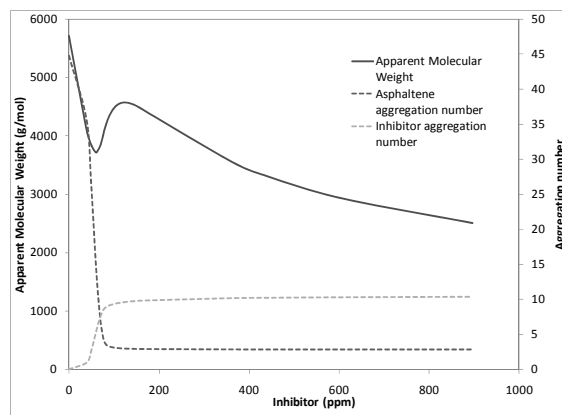
The use of chemical additives containing inhibitors to prevent asphaltene precipitation has been a regular practice in the petroleum industry during many years. It is known that the efficiency of the additives is associated to several variables including asphaltene characteristics[1], inhibitor solubility in the media[1] and inhibitor characteristics[2]. It has also been reported that additive efficiency correlates well with the maximum amount of inhibitor adsorbed on asphaltenes[3]. In terms of mechanism, it is accepted that inhibitors adsorb on asphaltenes decreasing the size of aggregates and/or hindering further aggregation[4]. However, recent measurements using Vapour Pressure Osmometry (VPO) have indicated that this is not always the case[2].

The main goal of this work is to shed some light on the possible mechanism that rules inhibitor activity on asphaltene aggregation. To this end, a model is proposed based on a molecular thermodynamic approach successfully used for asphaltene aggregation[5]. In this model, asphaltene aggregates are described as composed of an aromatic core formed by stacked aromatic sheets surrounded by aliphatic chains. According to the model the driving force for the aggregation is the low solubility of the polyaromatic rings in the solvent due to the strong  $\pi$ - $\pi$  interactions.

In the proposed model, inhibitors interact with active sites in the core of the asphaltene aggregates and their energetic contribution to the formation of a complex aggregate-inhibitor is incorporated in the aggregation model. The incorporation of inhibitors induces changes in several free energy contributions to the formation of the asphaltene aggregates. In particular, it affects the interactions between solvent and aggregates and induces new steric interactions in which can be considered as the aliphatic crown of the aggregates. The effect of the self aggregation of inhibitors in the solvent is also taking into account in the model.

Several parameters were evaluating using the model including: active site number, active site-inhibitor interactions, driving force to inhibitor's self aggregation, inhibitor concentration, etc

It was found that the model can reproduce recent findings related to VPO results[2]. Figure 1 shows the effect of inhibitor's concentration on VPO measurements as well as on the number of asphaltenes and additives present in an average aggregate change. In the case, inhibitor-asphaltene interaction energy was considered slightly larger than the inhibitor-inhibitor interaction energy.



**Fig. 1.** Effect of inhibitor concentration on the apparent molecular weight observed using VPO, asphaltene aggregation number and number of inhibitor molecules incorporate in the aggregate.

According to the model, the incorporation of inhibitors in the aggregates correlates very well with the deagglomeration of the asphaltenes as can be seen in Figure 1. Once the active sites in the asphaltenes are occupied by inhibitors, the deagglomeration stops and additional inhibitor remains in solution and depending on its micellization energy might start to aggregate at larger concentrations. In terms of the apparent molecular weight, the sharp decrease observed at the beginning in the curve corresponds to the deagglomeration effect on the inhibitor in the asphaltenes up to the point in which the incorporation of inhibitors in the aggregate doesn't induce significant deagglomeration but increases molecular weight of the aggregates. Once all the active sites are occupied, the molecular weight observed decreases as more inhibitors are free in the solvent in monomeric form or in small aggregates.

The proposed model can successfully reproduce experimental trends observed for the effect of inhibitors on asphaltene aggregation. It also provides a plausible mechanism for inhibitors activity.

### References

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