

Flocculation of asphaltenes by chemicals

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Asphaltene have a tendency to agglomerate and may undergo phase separation owing to their greater polarity, which causes them to be less hydrophobic than others petroleum fractions. Variations in crude oil temperature, pressure and/or composition during the extraction, transport or refining can compromise stability and result in phase transitions.¹ Due to the several problems caused by asphaltene deposition, it is very important to understand the stabilization process of the asphaltene dispersions induced by additives. In this work, chemically modified polystyrene presenting different sulfonate groups content (PSS), obtained previously, are used as asphaltene flocculant.

Asphaltene flocculation by polymers has not been studied before by the simple reason that it does not present interest to the petroleum industry. However these studies may be useful to obtain some insight on the mechanism of asphaltene precipitation and redispersion and the mechanisms involved in these processes. Furthermore asphaltene flocculants may find application in processes such as deasphalting in which asphaltic material is removed from petroleum residues as part of some petroleum derivatives such as wax or lubricating oils. Another potential application of asphaltene flocculants may be heavy oil upgrade in which a partial reduction of the asphaltic fraction would improve the crude oil market price.

The influence of the additives on the asphaltene stabilization was evaluated in an ultraviolet Varian Cary 50. Each system was constituted of asphaltene dispersed in toluene, in which polymer dissolved in a solvent (toluene or acetone or isopropanol or mixtures) was added. We used a polymer solvent volume equal to the minimum amount that was enough to dissolve the polymer in all used concentrations (0.1 to 1.0 wt%). The asphaltene concentration was 0.5 wt% based on the total solvent volume (toluene + polymer solvent). The evaluation at additive concentration equal to zero is related to the asphaltene/toluene/polymer solvent system. The concentration of dispersed asphaltene was gotten by measuring the absorbance, using a calibration plot.

In order to guarantee the complete solubilization of the polymers, the effect of the PSS on asphaltene solubility was studied in solvent mixtures. Asphaltene are insoluble in acetone and isopropanol and present a limited solubility in toluene/acetone or

isopropanol mixtures. In this solvent mixtures there is a critical point from what asphaltene precipitate.

Polymers with sulfonation levels between 5 and 10% initially reduce the asphaltene concentration in solution and subsequently increase it again for polymer concentrations beyond 0.5%. The first branch of the curves, ascribed to flocculation, becomes less important for 12% sulfonation and disappears completely for 13% sulfonation, which presents a moderate dispersant effect. The results obtained for PSS showed that the flocculation behavior depends on sulfonation degree and polymer concentration. In a previous work, it was observed that for polycardanol samples, flocculation initially increases with concentration, goes through a maximum and decreases at higher concentrations. This behavior was ascribed to the amount of phenol groups available to interact with the asphaltene polar groups. A large number of asphaltene-polymer interactions results in less asphaltene-asphaltene interactions to form aggregates susceptible to flocculate. The considerations asserted for polycardanol in relation to interaction between the polymer and the asphaltene polar groups may be considered applicable to PSS. In comparison to both sets of polymers, some PSS samples were more effective as flocculants. In principle it may be assumed that this difference correlates with the distribution of the polar group in the polymer. For polycardanol these groups are closer to each other than in PSS, where they may distribute along the polymer chain. In PSS molecules, the distance of the polar groups is related to their content in the polymer composition. Although it is well known that the reaction is random, it is possible to consider that the higher the content of polar groups, the shorter the average distance between them. The flocculant behavior is quite similar for different kind of solvents used to disperse the additives.

More details about the interactions between the polymer and the asphaltene molecules are in progress by FTIR and NMR.

References

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