Journal of Molecular Liquids 230 (2017) 589–599

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Polymers for asphaltene dispersion: Interaction mechanisms and molecular design considerations

Evan Lowry, Mohammad Sedghi, Lamia Goual *

Department of Petroleum Engineering, University of Wyoming, 1000 East University Avenue, Laramie, Wyoming 82071, United States

ARTICLE INFO

Article history:
Received 27 July 2016
Received in revised form 1 December 2016
Accepted 9 January 2017
Available online 14 January 2017

ABSTRACT

The prevention of asphaltene self-assembly is a technical challenge of broad scope since asphaltene aggregates can precipitate and cause fouling in production facilities, pipelines and refineries. Although polymeric dispersants are often used as flow improvers and offer great promise for affordable and effective prevention of deposition, the mechanism by which they affect aggregation is relatively understudied. In order to clarify the nature of interactions between polymers and asphaltenes in aliphatic solvents, systematic molecular dynamics simulations were employed to test several organic polymer structures that were reported to be effective in previous experimental studies. Bulk phase simulations with model asphaltenes with different functional groups revealed that several particular structural attributes are effective for maintaining asphaltene dispersity while preventing full aggregation. A specific polymer was determined to be most effective due to its unique capability to occupy the active stacking sites of asphaltene aggregates (i.e. aromatic cores), thereby preventing further π–π stacking of asphaltenes. In addition, the favored polymer was shown to possess superior solubility in aliphatic solvents and exhibit less chain collapse when compared to the other structures tested. Several suggestions are presented to provide insight to the design of more effective polymeric flow improvers.

1. Introduction

One of the most critical challenges facing the oil industry today is assuring fluid flow through ultra-deep sub-sea wells such as those found in the Gulf of Mexico. Potential impediments include the formation of asphaltene deposits in flow lines due to changes in fluid composition, leading to significantly high intervention costs. Variations in fluid composition usually occur due to mixing with lighter oils or release of light alkanes near the bubble point pressure. Since asphaltenes comprise the heaviest and most polarizable portion of crude oils, they tend to aggregate into nanoscale clusters that constitute the building blocks of flocculates in aliphatic media [1]. Flocculation is a kinetic process that occurs as soon as asphaltene aggregates are destabilized [2]. As a result, effective chemical inhibition strategies should target asphaltenes in their early stages of aggregation in the bulk phase. Several polymeric dispersants have been used in the past to prevent asphaltene precipitation due to their wide array of possible functional groups and relative ease of production. In general, the structure of these polymers consists of two main parts: (i) a polar organic backbone with functional groups that favorably interact with asphaltenes, and (ii) aliphatic chains that provide sufficient solubility in alkane solvents [3]. Among these polymers, two classes were particularly investigated in the past, organometallic and organic.

1.1. Organometallic polymers

Hernández-Altamirano et al. studied a class of organometallic polymers that were shown to be effective as bactericidal corrosion inhibitors and asphaltene dispersants [4]. They synthesized a butyl substituted bis-di-organotin (IV) compound that showed the best efficiency at curbing asphaltene aggregation, resulting in nearly 30% reduction in asphaltene aggregation at 0.1 g/L dispersant concentration in liquid heptane. As in other studies, the *n*-butyl chains were presumed to be responsible for enhancing the steric repulsion between the asphaltene aggregates [4,5]. Li et al. also used an organometallic polymer to enhance upgrading effectiveness in heavy oils. The cupric-grafted polymer combinations enabled the enhanced cleavage of C-C and C-S bonds while reducing the viscosity of the mixture, which was noted as an indication of the enhancement in asphaltene dispersity [5]. A positive correlation was observed between increasing alkyl polymer side chain length and the effectiveness of the polymer in dispersing and cleaving the asphaltenes.

1.2. Organic polymers

Polymers containing both aromatic portions as well as strongly polar functional groups such as amide or carbonyl have been quite successful

---

* Corresponding author.
E-mail address: lgoual@uwyo.edu (L. Goual).

http://dx.doi.org/10.1016/j.molliq.2017.01.028
0167-7322/

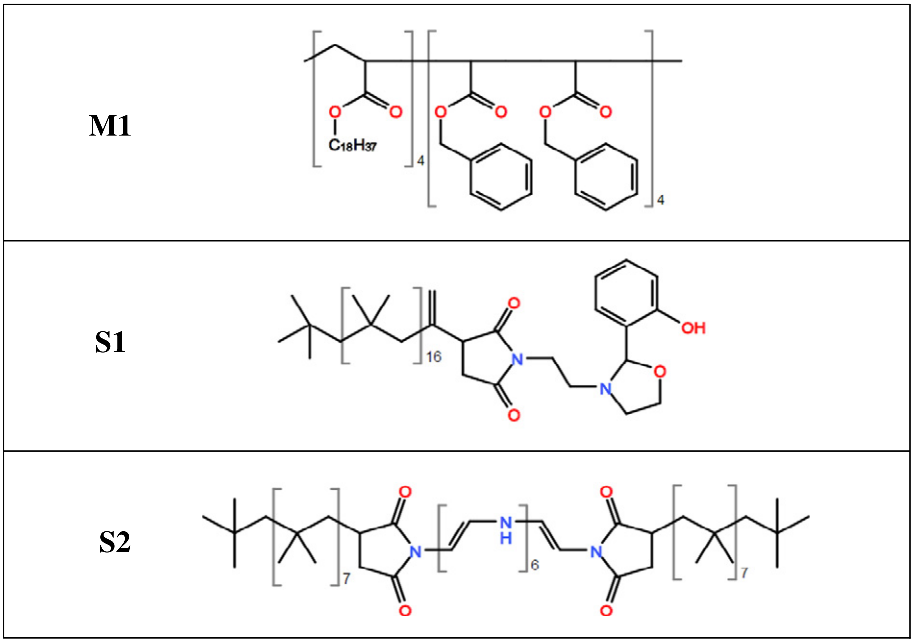

Fig. 1. Polymer structures studied in the MD simulations.

for preventing asphaltene precipitation [6–8]. Ghaffer et al. tested a series of propoxylated dodecyl phenol formaldehyde polymers with three different molecular weights using heavy crude oils in heptol solutions [6]. The oil mixtures in toluene were slowly titrated with heptane to induce precipitation while the light absorbance was measured. The results showed that the onset of asphaltene precipitation increased with

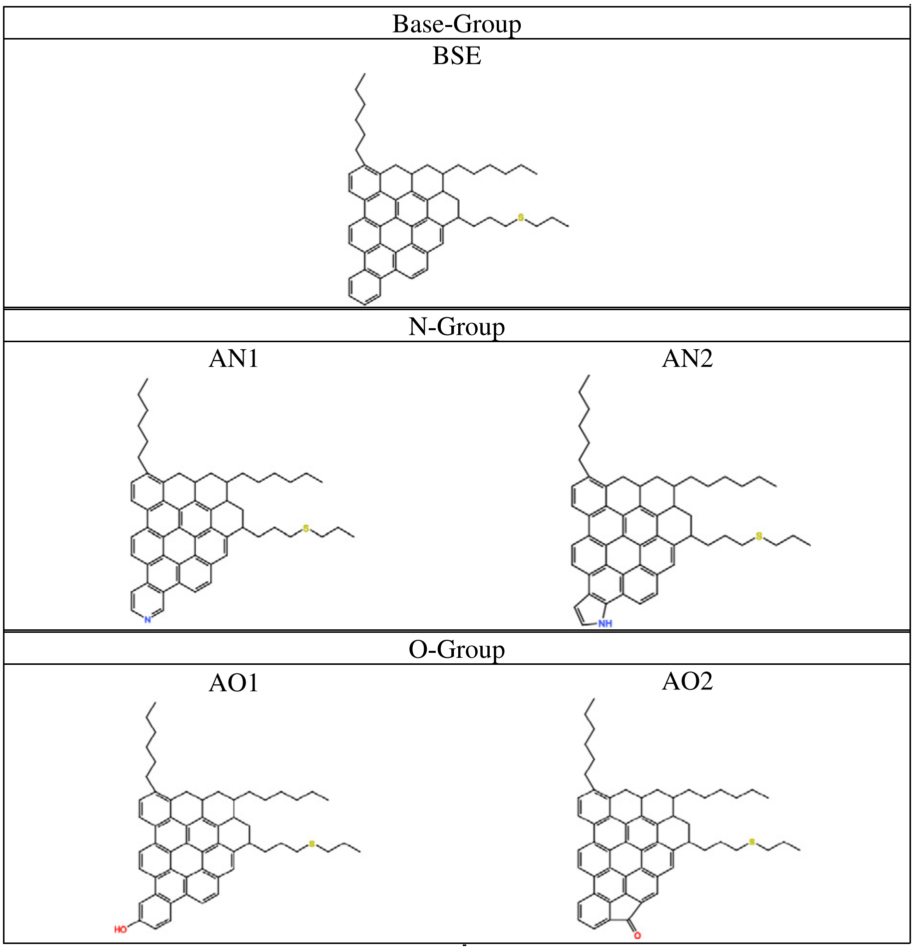

Fig. 2. Asphaltene models used for simulation.