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Role of ion-pair interactions on asphaltene stabilization by alkylbenzenesulfonic acids

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ABSTRACT

The dispersion of asphaltenes by dodecylbenzenesulfonic acid (DBSA) has been the subject of several studies in the past. However, it is unclear how these interactions affect the structure of asphaltenes and why asphaltene aggregates are larger in the presence of ionic DBSA. The main goal of this study was to address these points using a combination of high-resolution transmission electron microscopy (HRTEM) and molecular dynamics (MD) simulations. Another objective was to compare ionic DBSA (i.e., dodecylbenzenesulfonate or DBS^-) to nonionic amphiphiles such as alkylphenols. A striking similarity between dodecylbenzenesulfonate and alkylphenols was that both favored the formation of filamentary rather than globular asphaltene flocculates. However the mechanism by which those filaments formed was very different. Two strong electrostatic interactions between DBSA and asphaltenes were found: (i) those between protonated asphaltenes (i.e., AH^+) and DBS^- molecules, which were fifteen times stronger than asphaltene–alkylphenol interactions, and (ii) those between two asphaltene–dispersant pairs (i.e., AH^+–DBS^- ion pairs), which did not exist with alkylphenols. These interactions promoted the formation of large and compact asphaltene flocculates, as compared to small and loose ones formed without DBSA. Flocculates with DBSA could further bind to each other through ion-pair interactions. The binding occurred in series (generating long filaments) or in parallel (generating lateral ramifications). However the series configuration was energetically favored due to less steric effects generated by the side aliphatic chains of asphaltenes and DBSA.

1. Introduction

The dispersion of asphaltene aggregates by amphiphiles is an efficient method for delaying the onset of asphaltene precipitation, thereby controlling their deposition during oilfield processes. Amphiphilic dispersants are usually low molecular weight molecules with a high tendency to interact with asphaltenes and an ability to remain soluble in aliphatic solvents. Therefore, their typical structure consists of a polar head that can associate with asphaltene molecules and an aliphatic chain that can interact with solvent molecules. Among alkylbenzene-derived amphiphiles, p-alkylphenols (nonionic) and p-alkylbenzenesulfonic acids (ionic) proved to be effective asphaltene dispersants and yet behaved differently in apolar media [1]. For both amphiphiles, the mechanism of stabilization consists of two steps: (i) the adsorption of amphiphile onto asphaltene surfaces, and (ii) the formation of a stable steric layer around asphaltenes, limiting their growth.

In a recent study, we showed how nonionic amphiphiles such as alkylphenols interacted with asphaltenes and affected the structure of their flocculates [2]. Alkylphenol molecules saturated the H-bonding sites of asphaltenes and prevented them from interacting laterally between themselves, thus favoring to the formation of flocculates with filamentary rather than globular structures. The effectiveness of alkylphenols was hindered by their self-association and the fact that they interacted at the periphery of asphaltenes, leaving their aromatic cores uncovered [2].

The goal of this study was to extend our previous work to ionic amphiphiles such as dodecylbenzene sulfonic acid (DBSA). Asphaltene interactions with DBSA are significantly stronger than with alkylphenols since acid–base interactions are stronger than hydrogen bonding [1,3,4–8]. The acidic —SO_3H groups of DBSA can protonate the basic groups of asphaltenes containing heteroatoms such as Nitrogen. Recently, Hashmi et al. found that the interaction between asphaltene and DBSA molecules is a reversible chemical acid–base reaction that can lead to formation of ion-pair complexes [9]. Spectroscopic studies by Chang and Fogler revealed that the acid–base interactions are fairly complex and may involve different mechanisms, including hydrogen bonding, electron

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donor–acceptor transfer interaction, and irreversible electrophilic addition reaction [3]. The electrophilic addition reaction of DBSA to the π electrons in the carbon double bond (—C=C—) of asphaltenes promotes the formation of large electronic conjugated complexes. Consequently, asphaltenes tend to form larger aggregates in the presence of DBSA [3].

The formation of large asphaltene–DBSA structures was also observed through adsorption studies and molecular dynamics (MD) simulations [4,10]. DBSA molecules first adsorbed on asphaltene surface then interacted with other DBSA molecules, leading to the formation of hemimicelles around asphaltenes. Unlike other dispersants, DBSA molecules lied perpendicular to asphaltene surface due to their relatively high dipole moment [4,10]. Interestingly, the adsorption propensity of DBSA was highest on the least stable fractions of asphaltenes [11], especially in the absence of metals [12]. These fractions consisted of the largest and most aromatic molecules of oil with low concentrations of acids [11].

Based on these studies, the aggregation of DBSA molecules on asphaltene surface can provide a stable steric layer around asphaltenes and curb their growth in apolar media. As a result, DBSA is able to reduce the size of asphaltene aggregates to sub-micron scale [8,13], or even nanoscale [14], enhance the precipitation onset [6], and decrease the amounts precipitated [5,15]. However, it is unclear how the interactions between DBSA and asphaltenes affect the structure of asphaltenes. Even less clear is why asphaltene aggregates are larger in the presence of DBSA.

The main objective of this study was to address these points and to highlight similarities and differences between alkylbenzenesulfonates and alkylphenols [2]. The effect of the dispersant on the structure of asphaltenes in 4/96 vol/vol toluene/heptane solutions was first investigated by high-resolution transmission electron microscopy (HRTEM). The dispersant self-association was observed at high amphiphile concentrations and confirmed by impedance analysis (IA). Molecular dynamics (MD) simulations using high-performance computing were then performed with a model asphaltene and dispersant molecules in heptane. Umbrella sampling, small-scale, and large-scale MD simulations could explain the asphaltene structures observed by HRTEM.

2. Experimental methods

2.1. Materials

Materials include anhydrous heptane (>99%) from Sigma Aldrich and 4-dodecylbenzene sulfonic acid (>90%) from TCI chemicals.

2.2. Asphaltene precipitation

The precipitation of asphaltenes from crude oil was performed according to ASTM D2007 by mixing crude oil with n-heptane at a volume ratio of 1:40 [16]. The mixture was allowed to equilibrate after stirring and left overnight at room temperature. It was then filtered under vacuum using a 0.2 µm pore size Whatman filter paper. The filter cake was repeatedly washed with n-heptane to remove any resins. The asphaltenes were recovered from the filter cake by dissolution in toluene and then dried after toluene evaporation.

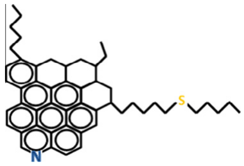
2.3. Impedance analysis

Low-frequency impedance measurements of DBSA-in-heptane solutions were conducted using a 4294A precision impedance analyzer (Agilent, Santa Clara, CA) connected to a 16452A liquid test fixture (Agilent, Santa Clara, CA) through a 16048G 1 m port extension cable with four terminals (Agilent, Santa Clara, CA). Details of the equipment calibration and short compensation are provided in our previous study [2]. Each solution was left to equilibrate inside the liquid fixture and the AC conductivities were recorded after 10 min. A total of 40 point average measurements were taken under a frequency sweep from 40 to 1 MHz at a constant voltage level of 0.5 V and no DC bias. The Z-view software was then used to determine the DC conductivity of DBSA in anhydrous heptane by fitting an equivalent electrical circuit to the experimental data. The circuit and schematic of the experimental set up and procedure can be found elsewhere [17,18].

2.4. High resolution transmission electron microscopy

We used Tecnai TF20 S-Twin High Resolution Transmission Electron Microscope (HRTEM) from FEI. The microscope features a TIETZ F415MP 4k × 4k multiport CCD camera with a 4-port readout and 15 µm pixel size. Asphaltenes (5 mg) were first mixed with toluene (10 ml) containing different amounts of DBSA, and left overnight. Heptane (256 ml) was then added to the mixture so that the toluene/heptane volume ratio is 4/96. The mixtures were allowed to rest at ambient conditions for one day before observation. A 15 nm silicon nitride (Si_3N_4) grid with 9 windows (0.1 × 0.1 mm) was dipped almost horizontally inside each sample for forty seconds, dried for five minutes, and then imaged by the microscope at 200 kV accelerating voltage under bright field

Table 1
Structural parameters of asphaltene model molecule.

Property	Value
Molecular structure	
Dipole moment (Debye)	4.7
Number of aromatic carbons	27
Number of aliphatic carbons	24
Number of hydrogens	55
Heteroatoms	N, S
Aromaticity	0.53
H/C	1.078
MW (g/mol)	713

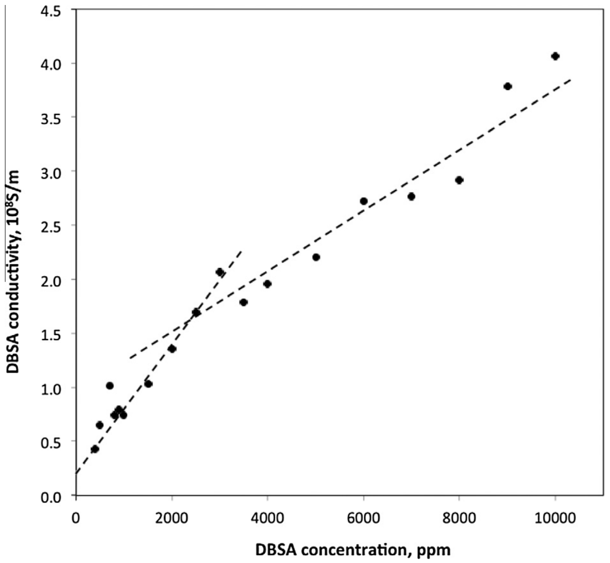


Fig. 1. DBSA conductivity versus concentration in anhydrous heptane.