

## Article

# Unravelling the Regulation of Asphaltene Deposition by Dispersants Through Macro-Stability in Micro-Mechanism

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## Abstract

The deposition of asphaltenes poses a critical challenge to the petroleum industry, reducing the efficiency of oil wells and, in severe cases, clogging pipelines. Dispersants are widely used to enhance asphaltene stability, but asphaltenes are complex, solubility-defined compounds with variable properties, leading to uncertainties in dispersant microscopic mechanisms, macroscopic effects, and their relationships—requiring further study. This work investigated two anionic dispersants (sodium dodecyl benzene sulfonate (SDBS) and dodecyl benzene sulfonic acid (DBSA)) for dispersing GT asphaltene (GT-ASP, isolated from offshore heavy oil), aiming to improve offshore heavy oil stability. Using an asphaltene–toluene system, it analyzed dispersant effects on GT-ASP stability, particle size, and adsorption and underlying mechanisms. DBSA showed superior performance: at 1000 ppm (*w/v*), it reduced GT-ASP average particle size from ~160 nm to ~29 nm and increased the onset of the flocculation point (OFP) from 33.5 vol% to 63.0 vol%, driven by chemical adsorption, hydrogen bonding, and  $\pi$ – $\pi$  conjugation. In contrast, SDBS promoted aggregation: particle size reached 257 nm (1000 ppm (*w/v*)) and 1271 nm (5000 ppm (*w/v*)), with OFP at 54.6 vol%, likely due to  $\text{Na}^+$ -induced charge neutralization, insufficient steric hindrance, and “micellar bridges” via SDBS self-aggregation. Finally, this study makes a valuable contribution to both the theoretical guidance and the practical application of asphaltene dispersants.

**Keywords:** asphaltene; dispersant; stability; mechanism



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## 1. Introduction

Global energy demand continues to grow steadily, driving the exploration and development of heavier petroleum fractions as conventional light oil reserves are gradually depleted [1]. According to projections by the International Energy Agency (IEA) and China’s National Energy Administration, Asia’s oil demand is expected to reach 52.3 million barrels per day by 2040—a 35.7% increase from current levels. This growth in demand is primarily driven by China’s exploitation of offshore heavy oil and India’s industrial expansion. This places unique pressure on regional energy supply security and the need for efficient oil extraction technologies [2,3]. This rising demand has led major oil-producing and consuming nations worldwide to prioritize the development of heavy oil resources,

given that heavy oil now accounts for an increasing proportion of the world's remaining petroleum reserves. In regions including the Middle East, North America, and South America, heavy oil production has become a key strategy to maintain stable energy supplies, making it an indispensable resource for alleviating global energy supply—demand imbalances [4]. Nevertheless, the aggregation and deposition of asphaltenes, a critical challenge in the heavy oil industry, severely restricts the efficient utilization of heavy oil resources during recovery and transportation [5].

Asphaltenes are the most structurally complex and polar component in crude oil, rich in heteroatoms and polar functional groups—traits that make them prone to association, which in turn leads to aggregate formation and precipitation [6]. This precipitation process increases heavy oil viscosity, leading to high energy consumption and low production rates during recovery, as well as reduced transportation efficiency in pipeline operations. It further causes technical challenges such as reservoir pore plugging, wellbore blockage, and wettability reversal [7]. Additionally, it raises environmental treatment costs and induces economic losses, significantly hindering the development of the heavy oil industry [8]. The deposition process of asphaltenes can generally be divided into three sequential stages: precipitation, aggregation, and deposition. First, studies on crude oil systems indicate that asphaltenes undergo molecular association through intermolecular interactions to form aggregates, which are stabilized as micelles within a resin-rich protective environment [9]. However, current research has shown that variations in crude oil composition, as well as changes in processing temperature and pressure, can all induce the aggregation and deposition of asphaltenes. For instance, an imbalance in the ratio of aromatics or non-polar saturates to resins or asphaltenes, or resin concentrations that are too high or too low, can exacerbate asphaltene aggregation [10]. And temperature and pressure also affect the stability of asphaltene by altering the phase state of crude oil and the energy barrier of asphaltene aggregates, with different solvent systems having different regulation modes [11]. Such perturbations often trigger the further aggregation of micelles into larger clusters, which subsequently coalesce into flocs. This process disrupts wellbore characteristics, alters asphaltene phase behavior, impairs crude oil flow properties, and ultimately leads to asphaltene deposition in wellbores, pipelines, and other production equipment.

Of the solutions developed to mitigate asphaltene deposition, the addition of asphaltenes dispersants is widely recognized as the most economical and safe mainstream technology [12]. These dispersants are primarily classified into surfactant-type, inorganic, and polymer-based categories, with surfactant-type dispersants being widely studied. Their interactions with asphaltenes are dominated by acid-base interactions,  $\pi$ - $\pi$  stacking, and hydrogen bonding, which significantly influenced by structural features such as alkyl chain length and head group type [13,14]. However, existing studies have yielded contradictory findings: some report that dispersants can reduce the size of precipitated asphaltene aggregates or inhibit their subsequent aggregation, while others note that dispersants may actually promote aggregation [15,16]. Further research has also indicated that dispersants can exhibit diverse behaviors, including acting as stabilizers, enhancing agglomeration, or having no effect [17]. Notably, existing performance evaluations often show significant discrepancies between laboratory results and field applications. In addition, while this study focuses on GT-ASP dispersion during oil extraction, it is worth noting that effective dispersants like DBSA could also bring indirect benefits to downstream refineries: by reducing asphaltene aggregation in crude feedstocks, they may lower coking rates in atmospheric/vacuum distillation units (a common bottleneck in heavy oil refining) and improve the efficiency of light oil fractionation—though further research is needed to quantify these refinery-side effects.

Furthermore, the complex molecular structure of asphaltenes significantly affects the polarity, associativity, and stability of the intermolecular forces between asphaltenes and dispersants [18]. Therefore, there is an urgent need to elaborate on the mechanism by which dispersant adsorption influences asphaltene stability from the perspective of asphaltene microstructure. Thus, the aim of this study is to address three core questions: How do dispersants with different functional groups or interactions differ in their regulation of GT-ASP stability? Does dispersant concentration lead to saturated adsorption on GT-ASP surfaces? Is the asphaltene—toluene model suitable for studying offshore asphaltene—dispersant interactions, despite eliminating interference from other crude oil components and overlooking the natural regulatory role of resins? All of this aims to elaborate on the mechanism by which dispersant adsorption influences asphaltene stability from the perspective of asphaltene microstructure.

This study focuses on GT-ASP and establishes an asphaltene—toluene system as the model oil sample, which can simulate the high aromatic hydrocarbon content of offshore heavy oil and eliminate the interference of crude oil impurities. Although it may be limited compared to whole crude oil and overlook the natural asphaltene stabilizing effect of resin, which may overestimate the amount of on-site dispersant, this system focuses on the dispersant asphaltene interaction and better reflects its inherent mechanism. A set of characterization techniques was employed to systematically investigate the effects of two typical anionic dispersants on the stability, particle size, and surface structural properties of GT-ASP. The two typical anionic dispersants in this study are sodium dodecyl benzene sulfonate (SDBS) and dodecyl benzene sulfonic acid (DBSA). Compared to previous research of DBSA and SDBS, this study's novelty lies in three aspects: (1) it targets offshore GT-ASP, filling the gap of dispersant research on high-polarity offshore asphaltenes; (2) it uses a scenario-matched mixed solvent to avoid misleading results from single-solvent systems; (3) it clarifies the molecular-level interaction mechanisms via FT-IR and XPS, which were rarely resolved in prior studies. In this study, the objectives are to clarify the action mechanism of dispersants, thereby revealing the differences in interaction between each dispersant and GT-ASP. This ultimately provides theoretical support for the screening and application of high-performance dispersants.

## 2. Materials and Methods

For materials preparation, GT-ASP was isolated from GT crude oil via SARA (saturates, aromatics, resins, asphaltenes) fractionation following ASTM D6560-12 [19,20], and its basic structural parameters are presented in Table 1. The solvents used in this study (toluene and n-heptane) were of analytical grade (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The two anionic dispersants, sodium dodecyl benzene sulfonate (SDBS, 99% purity) and dodecyl benzene sulfonic acid (DBSA, 99% purity), were supplied by Shanghai Maclin Biochemical Technology Co., Ltd., Shanghai, China.

A conductivity meter (HP4263B, Agilent Technologies, Inc., Santa Clara, CA, USA; electrode constant:  $0.107\text{ cm}^{-1}$ , mode: CP-G, averaging times: 8) was used to measure conductivity using a platinum-plated cylindrical cell, with temperature maintained at  $25 \pm 0.1\text{ }^{\circ}\text{C}$  via a thermostatic water bath. First, a GT-ASP-toluene system was constructed using analytical-grade toluene and n-heptane as solvents, and SDBS and DBSA as dispersants. A 1000 ppm (*w/v*) GT-ASP-toluene solution was prepared and mixed with a 1000 ppm (*w/v*) dispersant. The mixture was stirred at 800 rpm for 20 min at  $25\text{ }^{\circ}\text{C}$ . Then, n-heptane was added incrementally (with 5 min of stirring each time). The conductivity data measured by the meter were used to determine the onset of the flocculation point (OFP) via curve inflection, which is the amount of n-heptane added corresponding to this inflection point. This experiment was repeated three times and the average value

was taken. And, a segmented linear regression algorithm was adopted (identifying the conductivity curve slope changes) to detect the OFP inflection. A Zeta/PALS analyzer (Brookhaven Instruments Corporation, Nashua, NH, USA; input voltage: 220 V, frequency: 2.00 Hz, replicates: 3 parallels per group) and a trinocular projection polarizing microscope (BA310-T, Motic Industrial Group Co., Ltd., Xiamen, China, magnification: 400 $\times$ ) were used for particle analysis. The analyser measured the size distribution and average size of GT-ASP particles using a toluene-n-heptane mixture (60:40 (*v/v*)) as the solvent and a dispersant gradient of 1000–5000 ppm (*w/v*), utilizing the particle size testing function in the Zeta/PALS analyser. Meanwhile, the microscope observed the aggregation morphology. A Bruker Tensor II Fourier transform infrared spectrometer (FT-IR, Bruker Tensor II, Bruker Corporation, Berlin, Germany; wavenumber range: 4000–400  $\text{cm}^{-1}$ , resolution: 4  $\text{cm}^{-1}$ , number of scans: 128) was used. Samples prepared by the KBr pellet method were analyzed by FT-IR to identify functional groups, with a KBr-to-sample mass ratio of 100:1. An X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific Inc., Waltham, MA, USA; excitation source: Al K $\alpha$  radiation,  $h\nu = 1486.6$  eV; survey scan pass energy: 100 eV, high-resolution scan pass energy: 20 eV) was calibrated by C1s at 284.8 eV. During testing, take about 12 mg of asphaltene sample and grind it thoroughly. Then, vacuum dry it at 110–120  $^{\circ}\text{C}$  for 12 h. When preparing the sample, apply it to a 0.5 cm  $\times$  0.5 cm insulation tape with a thickness of about 0.5 mm. Advantage software (v5.9931) was employed for peak fitting and quantitative analysis in structural characterization, provided by Thermo Fisher Scientific (Waltham, MA, USA). XPS spectra of C1s, O1s, N1s, and S2p were analyzed quantitatively with a constrained full width at half maximum (FWHM) ranging from 0.8 to 2.2 eV. The Shirley background subtraction method was applied for baseline correction, achieving an R-squared ( $R^2$ ) value greater than 0.98. In addition, the dipole moments of GT-ASP and dispersants were further calculated, with specific steps referring to the reference [21].

**Table 1.** GT-ASP basic structure property parameters.

| Parameters   | Connotation                                                | Values |
|--------------|------------------------------------------------------------|--------|
| H            | Hydrogen content (wt%)                                     | 8.49   |
| C            | Carbon content (wt%)                                       | 85.63  |
| N            | Nitrogen content (wt%)                                     | 1.86   |
| S            | Sulfur content (wt%)                                       | 0.79   |
| MW           | Average molecular weight (g/mol)                           | 6286   |
| $C_A^*$      | The number of aromatic carbons in a structural unit        | 14.71  |
| $H_{AU}/C_A$ | Condensation degree parameter                              | 0.52   |
| USW          | The average molecular weight of the unit structure (g/mol) | 692    |
| $n$          | The number of structural units                             | 9.08   |
| $f_a$        | Aromatic carbon ratio                                      | 0.47   |

Notes: The \* represents a structural unit.

### 3. Results

#### 3.1. Evaluation of Performance for Asphaltene Dispersants

The conductivity method was used to measure the changes in system conductivity as the volume fraction of n-heptane increased. The OFP of GT-ASP in the toluene-n-heptane system was determined from the inflection point of the conductivity curve. The results are presented in Figure 1. In the absence of dispersant, system conductivity exhibited a stepwise change as n-heptane volume fraction increased: specifically, when n-heptane volume fraction was  $\leq 33.5$  vol%, conductivity showed a linear downward trend. It disrupts the stable dispersion of asphaltene in toluene by inducing the self-association of asphaltene molecules via polar interactions and aromatic conjugation [22]. This leads to the subsequent

formation and gradual sedimentation of aggregates, thus reducing the number of freely mobile charged particles in the system. When the volume fraction of n-heptane exceeded 33.5%, the slope of the conductivity curve increased significantly. This indicated that the GT-ASP aggregates had reached the critical flocculation size, initiating large-scale aggregation and precipitation. This further reduced the concentration of charged particles in the system. From these results, the OFP of GT-ASP without dispersant was identified as 33.5 vol%.

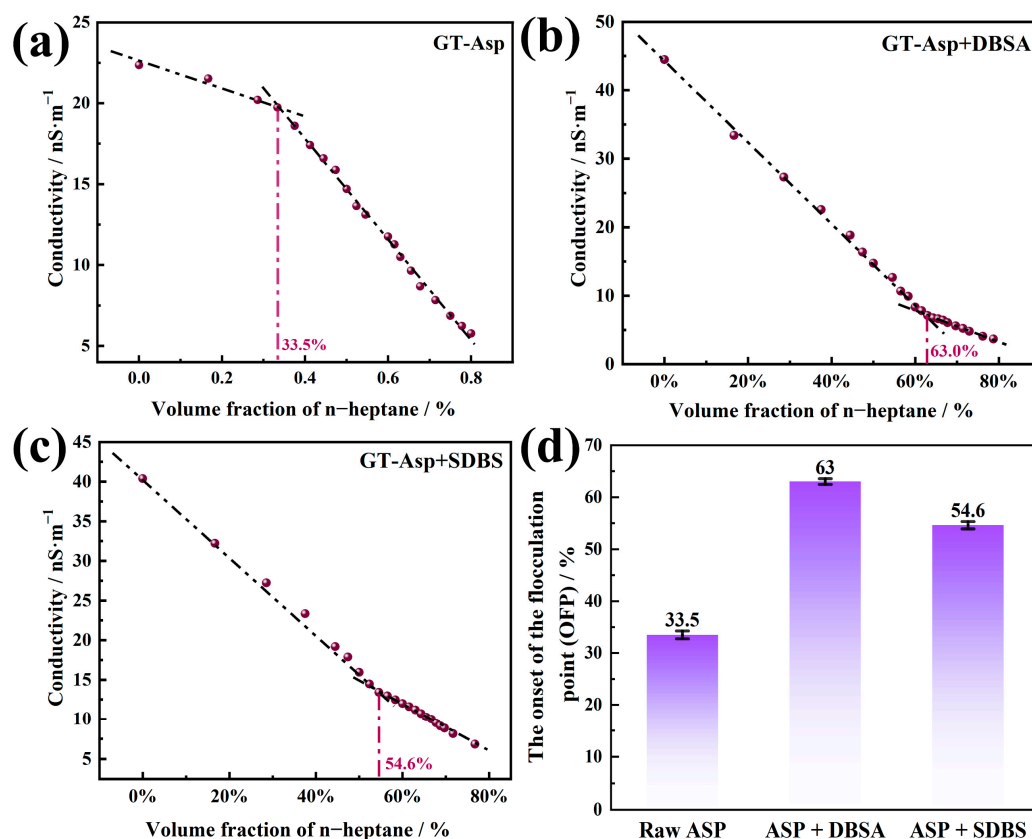


**Figure 1.** Rate of change in conductivity with volume fraction of n-heptane in toluene and n-heptane solution of GT-ASP (a), GT-ASP + DBSA (b), GT-ASP + SDBS (c), and the value of corresponding OFP (d).

Significant differences were observed in the OFP of GT-ASP with the addition of 1000 ppm (*w/v*) of DBSA and SDBS, respectively: the OFP increased to 63.0 vol% and 54.6 vol%, respectively. To increase the reliability of the data, we conducted repeated experiments on OFP and took the average. The results are shown in Figure 1d, with an error range kept within 0.8. In addition, a higher OFP value indicates a stronger ability of the system to resist n-heptane-induced flocculation and enhanced stability of GT-ASP. The results show that these two dispersants can enhance GT-ASP stability through their interactions with GT-ASP. However, DBSA has a more noticeable stabilizing effect, which allows it to more efficiently prevent GT-ASP aggregation and consequently resist n-heptane-induced flocculation.

In addition, we also evaluated the dispersant through polarity testing [21]. The research results show that the dipole moments of GT-ASP, DBSA, and SDBS are 48.6, 7.85, and 1.67, respectively. Among them, the dipole moment of GT-SP is relatively large, indicating that GT-SP has strong polarity, which also makes it easier for asphaltene molecules to self associate. In addition, the stronger the polarity of the dispersant, the easier it is for nearby asphaltene molecules to polarize, leading to dipole interactions and mutual attraction. This

also results in the polarity sequence of the two dispersants being consistent with their effect on increasing the OFP value.

### 3.2. Effect of Dispersants on Asphaltene Aggregation

To elucidate the effect of dispersant dosage on the aggregation behavior of GT-ASP, the influence of different dispersants on the particle size of GT-ASP was investigated. Based on the results of the conductivity experiments, a setup involving a 60:40 (*v/v*) ratio of the toluene-*n*-heptane mixed solvent (OFP near GT-ASP) was chosen. Five dispersant concentration gradients were set: 1000, 2000, 3000 ppm, 4000 ppm and 5000 ppm (*w/v*). A Zeta/PALS analyzer was used to measure GT-ASP particle size under different conditions, with results presented in Figure 2. In the absence of dispersant, the average particle size of GT-ASP was approximately 160 nm. With the addition of DBSA, the average particle size initially decreased to around 29 nm at 1000 ppm (*w/v*) and further reduced to <12 nm at 3000 ppm (*w/v*); beyond this concentration, the particle size remained relatively stable. This trend indicates that DBSA achieves saturated adsorption on the GT-ASP surface, which not only disrupts the aggregate structure of GT-ASP but also increases the intermolecular layer spacing, thereby inhibiting self-association and reducing particle size. In contrast, SDBS addition increased the average particle size of GT-ASP: it rose to 257 nm at 1000 ppm (*w/v*) and further increased to 1271 nm at 5000 ppm (*w/v*). This can be attributed to two key factors. First, the presence of Na<sup>+</sup> ions in SDBS partially neutralizes the negative charge on the GT-ASP surface, thereby reducing the electrostatic repulsion between particles. Second, SDBS exhibits self-aggregation in non-polar solvents, forming micellar bridges that further promote the agglomeration of GT-ASP particles [23,24].

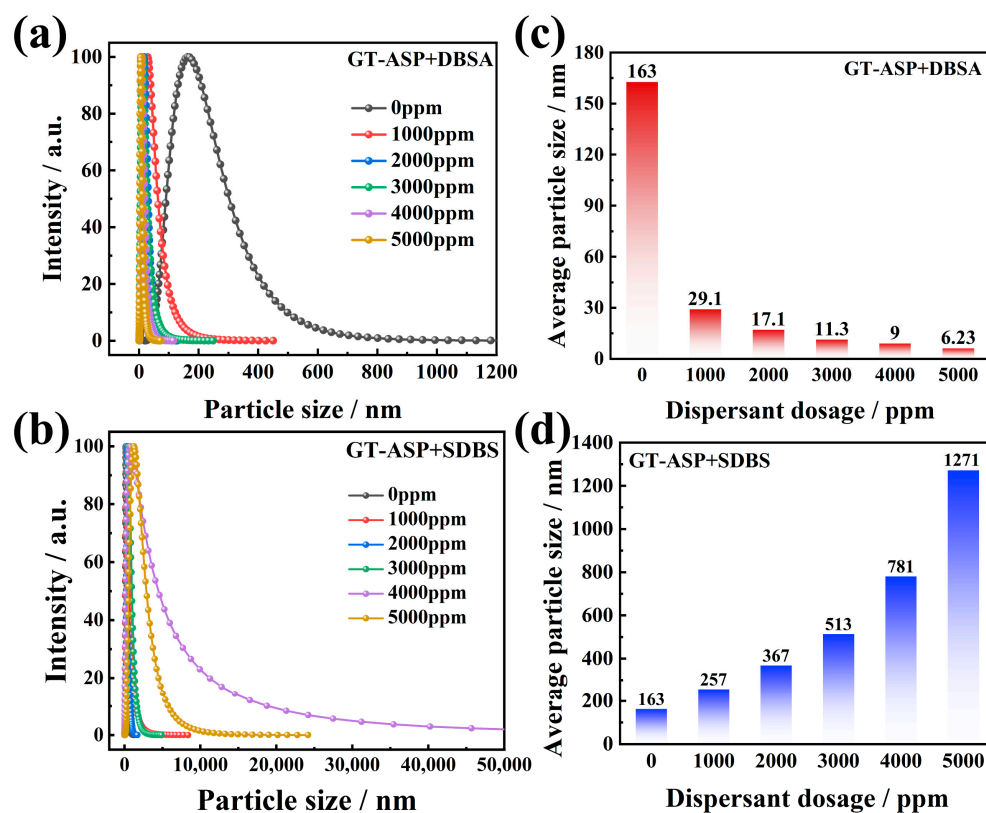


**Figure 2.** The effect of different concentrations of dispersants on the particle size of GT-ASP, particle size distribution of GT-ASP + DBSA (a) and GT-ASP + SDBS (b), and average particle size of GT-ASP + DBSA (c) and GT-ASP + SDBS (d).

To further clarify the differing effects of DBSA and SDBS on GT-ASP, optical microscopy was employed to observe asphaltene aggregation in a toluene-*n*-heptane solution. The volume ratio of the toluene-*n*-heptane solution was 60:40 (*v/v*), which is consistent with previous experimental conditions, and observations were conducted both before and after adding the two dispersants. The concentrations of DBSA and SDBS used in the observations ranged from 1000 to 5000 ppm (*w/v*), and the corresponding results are presented in Figure 3. The results showed that large, obvious asphaltene aggregates formed when no dispersant was added. After adding DBSA at a concentration of 1000 ppm (*w/v*), the number and size of the aggregates decreased significantly. When the concentration of DBSA reached 3000 ppm (*w/v*), the asphaltene particles were dispersed uniformly and no obvious aggregation was observed. This trend was consistent with the particle size data from the Zeta/PALS analyzer, thus confirming the strong dispersion effect of DBSA. In contrast, SDBS promoted asphaltene aggregation: as the concentration of SDBS increased, larger particles and even cluster-like aggregates appeared. This observation was further supported by the conductivity data of SDBS in the toluene-*n*-heptane system, where conductivity decreased as the volume fraction of *n*-heptane increased. This decreasing conductivity provided evidence that SDBS exhibits self-aggregation in the system, which contributes to the effect of SDBS in promoting asphaltene aggregation.

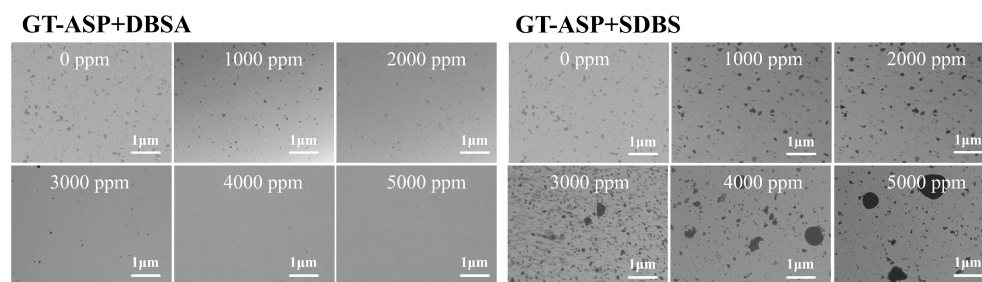


**Figure 3.** Microscopic observation of different amounts of DBSA and SDBS adsorbed by GT-ASP.

Figure 4a,b present the variation in zeta potential as a function of *n*-heptane volume fraction for GT-ASP in the toluene-*n*-heptane system following the addition of dispersants DBSA and SDBS at a concentration of 1000 ppm (*w/v*), respectively. The measurements were conducted under the following conditions: non-polar quartz cell (ZEN0020, Wuhan Gaoshi Ruilian Technology Co., Ltd., Wuhan, China), electric field intensity of 300 V/cm, temperature maintained at  $25 \pm 0.1$  °C, equilibration time of 30 min, and three replicate measurements. As shown in the results, the Zeta potential of GT-ASP without dispersant was +32 mV, which is consistent with the prediction of Coehn's empirical rule (higher dielectric constant of GT-ASP than solvent leads to positive charge). Generally, a larger absolute Zeta potential value indicates better stability of a colloidal system [25]. Notably, the Zeta potential of the GT-ASP system shifted gradually in the positive direction as the *n*-heptane volume fraction increased. This phenomenon can be explained by Coehn's empirical rule, which states that in a dispersion system composed of two non-conductors, the component with a smaller dielectric constant carries a negative charge [26]. As the volume fraction of *n*-heptane increased, the dielectric constant of the mixed solvent decreased. At this point, the difference in dielectric constant between the positively charged GT-ASP and the solvent increased, resulting in a positive shift in the zeta potential of the system. These observations collectively indicate that GT-ASP stability decreases as the *n*-heptane volume fraction increases, and electrostatic repulsion does not act as the dominant force sustaining GT-ASP stability in this system [27,28]. For the DBSA group (Figure 4a), the absolute value of Zeta potential increased linearly with concentration, reaching 52 mV at 5000 ppm—this indicates that DBSA molecules were effectively adsorbed on GT-ASP

surface via electrostatic attraction, expanding the electric double layer and enhancing electrostatic repulsion. In contrast, the SDBS group (Figure 4b) showed a decreasing trend in Zeta potential absolute value (from 25 mV to 12 mV), suggesting insufficient adsorption of SDBS (possibly due to steric hindrance of its sodium salt group), which failed to modify the double layer structure effectively. These results further confirm that DBSA has better dispersion stability than SDBS, which is consistent with the particle size analysis results in Figure 2.

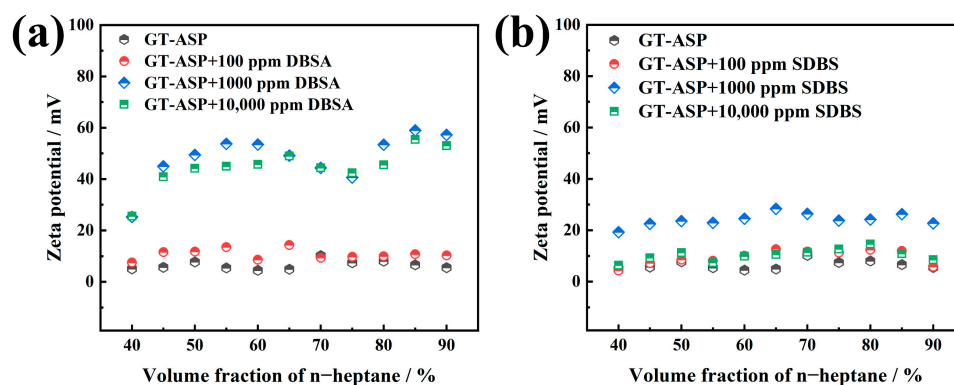


**Figure 4.** Changes in Zeta potential of GT-ASP adsorbed with different concentrations of DBSA (a) and SDBS (b) as a function of n-heptane volume fraction.

Comparison of the effects of different dispersant concentrations reveals that GT-ASP is overall positively charged in the toluene-n-heptane system. Upon adding 100 ppm (*w/v*) DBSA, the Zeta potential of the system increased slightly in magnitude. Specifically, this is because DBSA initially stabilizes GT-ASP, thereby increasing the concentration of positively charged GT-ASP in the solution. When the DBSA concentration rose to 1000 ppm (*w/v*), the zeta potential of the system increased significantly, indicating that a greater quantity of GT-ASP was stably dispersed. Further increasing the concentration to 10,000 ppm (*w/v*) led to a Zeta potential of the system that was slightly lower than that at 1000 ppm (*w/v*). This is attributed to the saturated adsorption of DBSA at this point—excess DBSA existed as negatively charged species, neutralizing part of the positive charges of GT-ASP in the solution. The system exhibited a similar variation trend under the action of SDBS. However, SDBS contains ionizable  $\text{Na}^+$  cations. Additionally, it exhibited lower solubility in the system and a weaker GT-ASP-stabilizing effect than DBSA, resulting in a significantly smaller variation range of the Zeta potential of the system compared to the DBSA group [29].

### 3.3. Analysis of Dispersant Adsorption on Asphaltene

Figure 5 presents the FT-IR spectra of GT-ASP before and after the adsorption of DBSA and SDBS. Changes in the absorption peaks of characteristic functional groups facilitate the identification of interaction types and differences in interaction strength between the dispersants and GT-ASP. In Figure 5a, after GT-ASP adsorbed DBSA, the spectrum retained the inherent peaks of GT-ASP (e.g., aromatic C=C stretching, alkyl C-H stretching) and exhibited new peaks at 1184, 1131, 1041, and 1012  $\text{cm}^{-1}$ . These peaks correspond to the vibrations of the sulfonic acid group ( $-\text{SO}_3\text{H}$ ) [30], with the 1184  $\text{cm}^{-1}$  peak showing a signal-to-noise ratio (SNR) of 28.6 (far above the significant peak threshold of  $\text{SNR} > 3$ ) and a relative intensity (normalized to aromatic C=C at 1600  $\text{cm}^{-1}$ ) of 0.62. Since physical adsorption does not alter functional groups, the emergence of these statistically significant new peaks confirmed the occurrence of chemical adsorption between DBSA and GT-ASP. Additionally, the original N-H stretching peak of pristine GT-ASP (3449  $\text{cm}^{-1}$ ) shifted to 3428  $\text{cm}^{-1}$ , with a total shift of 21  $\text{cm}^{-1}$ —a magnitude exceeding the physical adsorption

range ( $<10\text{ cm}^{-1}$ ) [29]. This shift arises because oxygen in the  $-\text{SO}_3\text{H}$  group of DBSA formed hydrogen bonds with the N–H or O–H groups of GT-ASP, which weakened the bond energy and reduced the vibration frequency [31]. This interaction enhanced the adsorption of DBSA on GT-ASP, disrupted the self-association of GT-ASP particles, and ultimately improved the dispersion of GT-ASP in crude oil.

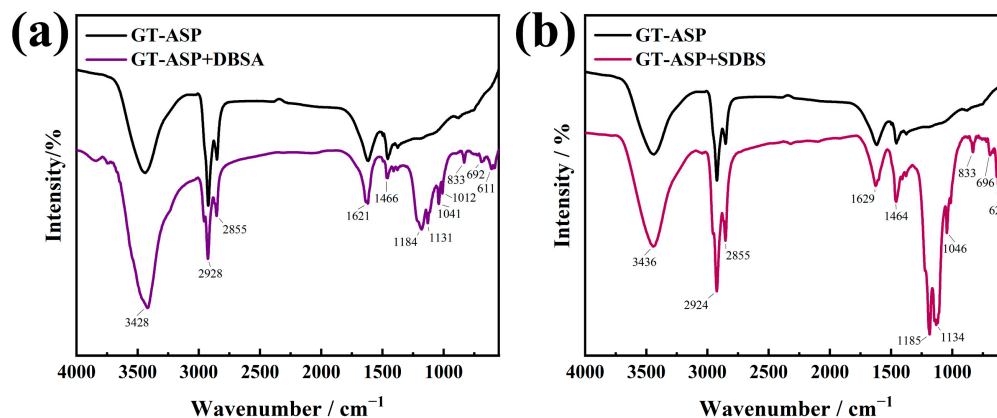


**Figure 5.** Changes in the FT-IR of GT-ASP before and after adsorption with DBSA (a) and SDBS (b).

In Figure 5b, GT-ASP after adsorbing SDBS exhibited an N–H peak shift of  $12\text{ cm}^{-1}$  (magnitude  $< 15\text{ cm}^{-1}$ ) but no  $-\text{SO}_3\text{H}$  peaks—this is because SDBS contains no free  $-\text{SO}_3\text{H}$  groups. The  $\text{Na}^+$  in SDBS formed coordination bonds with the N atoms of GT-ASP [32], which limited N–H vibration; however, this interaction was weaker than that between DBSA and GT-ASP. Near  $3440\text{ cm}^{-1}$ , GT-ASP after adsorbing DBSA had higher absorbance and a broader width for the N–H or O–H peak than GT-ASP after adsorbing SDBS, a trend consistent with the Lambert-Beer law [33]. This observation confirmed that a greater amount of DBSA was adsorbed and that the hydrogen bonds formed were stronger, which supported the superior dispersion effect of DBSA. In summary, FT-IR results revealed that DBSA achieved strong adsorption and efficient dispersion of GT-ASP through chemical adsorption and hydrogen bonding, whereas SDBS only exhibited weak physical adsorption and coordination, failing to achieve a dispersion effect. These findings provide a theoretical basis for the optimization of asphaltene dispersants. Additionally, note that a clearly visible absorption band in the  $610\text{--}620\text{ cm}^{-1}$  region was observed in the FT-IR spectra of GT-ASP after DBSA and SDBS treatment, which is attributed to the out-of-plane bending vibration of aromatic C–H bonds in the condensed aromatic cores of GT-ASP. The enhanced visibility of this  $610\text{--}620\text{ cm}^{-1}$  band is due to the disruption of GT-ASP self-aggregates by DBSA/SDBS (either via chemical adsorption/hydrogen bonding for DBSA or partial loosening of aggregates via  $\text{Na}^+$  coordination for SDBS), which reduces the quenching of aromatic C–H vibration signals and exposes more aromatic ring surfaces.

XPS was employed to characterize the surface elemental composition and chemical states of GT-ASP, providing critical insights into the molecular structure of GT-ASP and its active sites for dispersant interaction [34]. Wide-scan and high-resolution XPS spectra of GT-ASP were acquired, with a focus on the major elements: carbon (C), oxygen (O), nitrogen (N), and sulfur (S) (Figure 6). Distinct XPS peaks corresponding to C1s, O1s, N1s and S2p were observed. Semi-quantitative analysis revealed that the relative content was highest for carbon (C, 95.16%), followed by oxygen (O, 3.09%), nitrogen (N, 1.52%) and sulfur (S, 0.23%). This confirms that C and O are the dominant surface elements of GT-ASP. Subsequently, high-resolution XPS spectra of C1s, O1s, N1s, and S2p were deconvoluted to determine the chemical states of the respective elements [35].

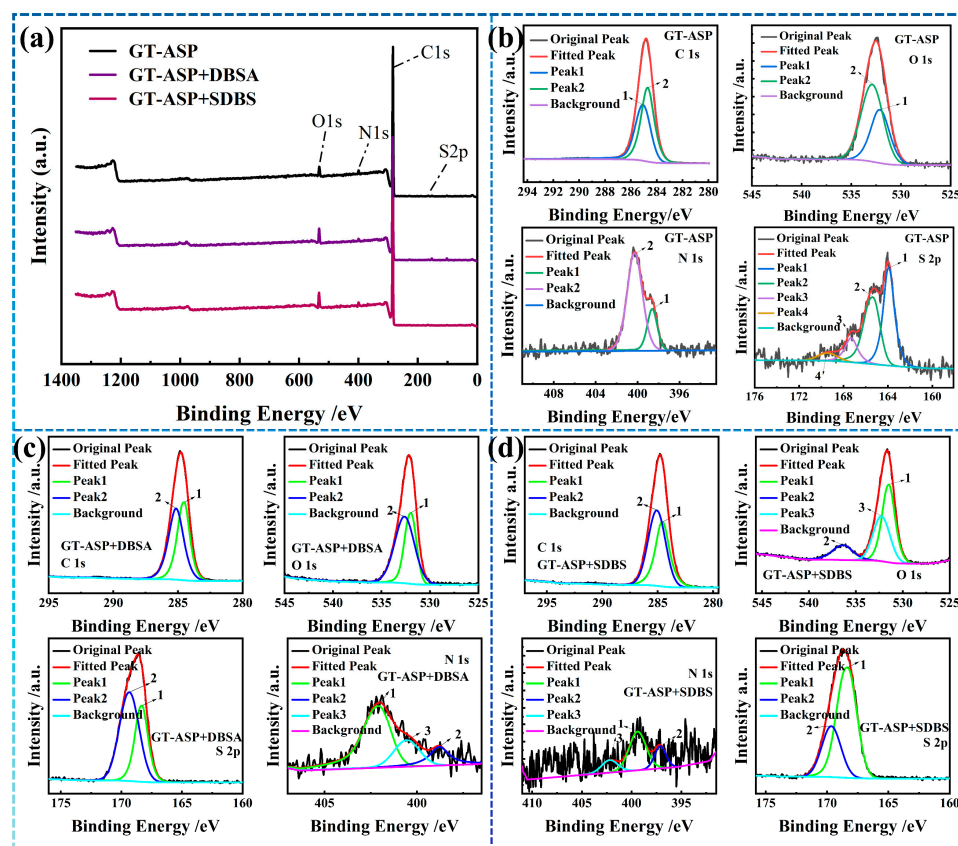


**Figure 6.** Changes in the XPS spectra of GT-ASP before and after adsorption with DBSA and SDBS (a), and corresponding C1s, O1s, N1s, S2p high-resolution spectrum analysis with fitted curves: (b) GT-ASP; (c) GT-ASP+DBSA; (d) GT-ASP+SDBS.

For C1s, two intense peaks at 284.5 eV and 285.1 eV were assigned to  $sp^2$  carbon (aromatic C=C in condensed aromatic cores) and  $sp^3$  carbon (saturated C–C/C–H in alkyl side chains), respectively. This verifies the typical aromatic core-alkyl side chain architecture of GT-ASP and provides a structural basis for subsequent dispersant anchoring via  $\pi$ – $\pi$  stacking or hydrogen bonding [36]. The O1s spectrum exhibited two main peaks at 532.2 eV (corresponding to C–O bonds in ethers or alcohols) and 533.0 eV (corresponding to COO– groups in carboxylates). Deconvolution of the N1s spectrum yielded two peaks at 398.8 eV (pyridinic nitrogen) and 400.2 eV (pyrrolic nitrogen). The S2p spectrum was deconvoluted into four peaks, which correspond to alkyl sulfides, thiophenic sulfur, sulfoxide sulfur, and sulfonic acid sulfate.

For DBSA-modified GT-ASP, XPS analysis showed a significant increase in sulfoxide sulfur and sulfonic acid sulfate in the S2p spectrum—directly confirming the successful grafting of sulfonic acid groups from DBSA onto GT-ASP. This is consistent with the S=O stretching vibration peak at  $1184\text{ cm}^{-1}$  in the FT-IR spectrum. The sulfur content of GT-ASP increased from 0.23% to 0.32%. Additionally, the  $-\text{SO}_3\text{H}$  groups in DBSA (strong hydrogen bond donors) formed directional hydrogen bonds with the pyrrolic nitrogen of GT-ASP (hydrogen bond acceptors), reducing the pyrrolic nitrogen content from 1.13% to 0.21% and confirming dispersant anchoring, thus weakening the self-association of GT-ASP [37]. Protons dissociated from  $-\text{SO}_3\text{H}$  then protonated the pyrrolic nitrogen to form positively charged quaternary nitrogen (evidenced by a new N1s peak at 402.1 eV) [27], which increased the surface potential of GT-ASP particles and enhanced inter-particle electrostatic repulsion. This is supported by the positive shift in Zeta potential and reduced particle size observed via the Zeta/PALS analyzer. For SDBS-modified GT-ASP, the O1s spectrum exhibited a peak at 535.0 eV, corresponding to oxygen atoms in surface-adsorbed

H<sub>2</sub>O, which is consistent with the typical binding energy range of 534.5–535.5 eV associated with adsorbed water [37]. Lacking H<sup>+</sup> donors, SDBS failed to form strong hydrogen bonds with pyrrolic nitrogen or induce quaternary nitrogen formation, and instead relied only on weak coordination between Na<sup>+</sup> and pyridinic nitrogen for physical adsorption [38]. Na<sup>+</sup> neutralized the negative surface charge of GT-ASP, decreasing the system's Zeta potential and inter-particle repulsion, which ultimately promoted aggregation (with the particle size increasing to 257 nm) (Table 2).

**Table 2.** Summary of functional group analysis on GT-ASP surface before and after dispersant treatment.

| Element Type | Peak   | Bonding Energy/ev | Functional Group Type               | Relative Content/% |               |               |
|--------------|--------|-------------------|-------------------------------------|--------------------|---------------|---------------|
|              |        |                   |                                     | GT-ASP             | GT-ASP + DBSA | GT-ASP + SDBS |
| C            | Peak 1 | 284.5 ± 0.3       | Aromatic carbon (sp <sup>2</sup> )  | 44.93%             | 39.02%        | 28.92%        |
|              | Peak 2 | 285.1 ± 0.3       | Aliphatic carbon (sp <sup>3</sup> ) | 50.23%             | 44.03%        | 38.91%        |
| O            | Peak 1 | 532.2 ± 0.3       | C–O–C, C–OH, C–O                    | 1.51%              | 4.96%         | 12.83%        |
|              | Peak 2 | 533.0 ± 0.3       | COO–                                | 1.58%              | 7.86%         | 9.25%         |
|              | Peak 3 | 534.5 ± 0.3       | surface-adsorbed H <sub>2</sub> O   | -                  | -             | 4.06%         |
| N            | Peak 1 | 398.8 ± 0.3       | Pyridinic nitrogen                  | 0.39%              | 0.15%         | 0.09%         |
|              | Peak 2 | 400.2 ± 0.3       | Pyrrolic nitrogen                   | 1.13%              | 0.21%         | 0.23%         |
|              | Peak 3 | 402.1 ± 0.3       | Quaternary nitrogen                 | -                  | 0.56%         | 0.07%         |
| S            | Peak 1 | 163.3 ± 0.3       | Alkyl sulfide                       | 0.1%               | -             | -             |
|              | Peak 2 | 164.1 ± 0.3       | Thiophenes                          | 0.09%              | -             | -             |
|              | Peak 3 | 165.1 ± 0.3       | Sulphoxides                         | 0.03%              | 1.21%         | 3.94%         |
|              | Peak 4 | 169.4 ± 0.3       | Sulfonic acid sulfate               | 0.01%              | 1.99%         | 1.70%         |

Note: - represents not detected.

#### 4. Discussion

DBSA and SDBS exhibit an essential difference in regulating GT-ASP aggregation behavior, which primarily depends on their distinct molecular structures and interaction modes with GT-ASP. Due to the presence of a free sulfonic acid group (–SO<sub>3</sub>H) in the DBSA molecule, DBSA is able to bind to GT-ASP via a synergistic combination of chemical adsorption and hydrogen bonding. This aligns with FT-IR observations, which reveal new –SO<sub>3</sub>H peaks and shifts in the N–H peak, as well as XPS evidence of increased sulfonate content in GT-ASP. Specifically, DBSA not only underwent a chemical reaction with active sites (e.g., pyrrolic nitrogen, hydroxyl oxygen) on the GT-ASP surface to achieve firm anchoring but also disrupted the intermolecular self-association structure of GT-ASP [39]. The Zeta potential of DBSA-modified GT-ASP increased linearly with concentration (1000–5000 ppm) without plateauing, indicating continuous adsorption without self-aggregation. When DBSA concentration reached 3000 ppm (*w/v*), DBSA achieved saturated adsorption on the GT-ASP surface. Specifically, the effect size of dispersion was reflected in an 81.25% reduction in average particle size, and a 100% increase in absolute Zeta potential, clearly quantifying the dispersion efficiency. Furthermore, the alkyl side chains of DBSA formed steric hindrance to prevent re-aggregation, while protonation of pyrrolic nitrogen in GT-ASP (induced by H<sup>+</sup> dissociated from the –SO<sub>3</sub>H group of DBSA) enhanced electrostatic repulsion between particles. Eventually, the average particle size of GT-ASP decreased from approximately 160 nm (in the absence of dispersant) to less than 30 nm. In contrast, the sulfonate group (–SO<sub>3</sub><sup>−</sup>) of SDBS contains Na<sup>+</sup> as a counterion instead of the H<sup>+</sup> in the –SO<sub>3</sub>H group of DBSA; thus, SDBS could only form weak coordination adsorption with GT-ASP via Na<sup>+</sup> [40]. The Zeta potential of SDBS-modified GT-ASP plateaued above 3000 ppm, suggesting self-aggregation in solution that reduces adsorption efficiency. Moreover, Na<sup>+</sup> in SDBS neutralized the negative surface charge of GT-ASP, weakening electrostatic repulsion between GT-ASP particles. Additionally, as observed in particle size

analysis, SDBS tended to self-aggregate in non-polar systems (e.g., the toluene-n-heptane mixture) to form micellar bridges, which further connected GT-ASP particles [41,42]. As a result, the average particle size of GT-ASP increased from approximately 160 nm (in the absence of dispersant) to more than 250 nm, exhibiting a clear aggregation-promoting effect. Furthermore, previous polarity analyses have demonstrated that DBSA exhibits a larger dipole moment than SDBS, indicating stronger polarity and a relatively smaller dipole moment difference with GT-ASP. Therefore, the underlying mechanism can also be elucidated from the perspective of molecular polarity. When the polarity of the dispersant aligns with the polarity characteristics of asphaltene molecules, the dispersant possesses an adaptive polar structure, enabling its dipole moment to engage in strong interactions—such as dipole–dipole interactions and hydrogen bonding—with the localized dipole moments within asphaltenes. This results in maximal adsorption strength, allowing the dispersant to firmly anchor onto and effectively disperse asphaltene aggregates. Conversely, if the dispersant's polarity is too weak—characterized by a limited number of non-polar groups and a dipole moment approaching zero—the intermolecular forces between the dispersant and the polar regions of asphalt become exceedingly weak. This significantly hinders adsorption onto the asphaltene surface, thereby diminishing or even nullifying its dispersing efficacy in the system [21].

## 5. Conclusions

This study focuses on GT-ASP and constructs an asphaltene–toluene model system. It combines multiple characterization techniques to investigate the effects and mechanisms of DBSA and SDBS as asphaltene dispersants. The main conclusions are as follows:

- (1) The anionic dispersants DBSA and SDBS exhibit significant differences in regulating the stability of GT-ASP. DBSA can increase OFP of the system from 33.5 vol% to 63.0 vol%, significantly enhancing resistance to n-heptane-induced flocculation. SDBS only increases OFP to 54.6 vol% and even promotes the aggregation of GT-ASP at high concentrations.
- (2) Dispersant concentration exerts different effects on the particle size of GT-ASP. DBSA exhibits a saturated adsorption effect on GT-ASP. When the concentration of DBSA reaches 3000 ppm (*w/v*), the average particle size of GT-ASP decreases from approximately 160 nm (in the absence of dispersant) to less than 30 nm and then remains stable. In contrast, SDBS continuously promotes GT-ASP aggregation as its concentration increases—at an SDBS concentration of 5000 ppm (*w/v*), the particle size of GT-ASP increases to 1271 nm. For actionable dosage guidance, our data shows that DBSA achieves optimal dispersion at 2000–3000 ppm (*w/v*): below 2000 ppm, adsorption is incomplete (GT-ASP particle size > 50 nm); above 3000 ppm, no additional size reduction is observed (saturated adsorption), leading to unnecessary dispersant waste.
- (3) The key factors leading to the differences in their interaction mechanisms lie in their functional groups and counterions. Mediated by its sulfonic acid group ( $-\text{SO}_3\text{H}$ ), DBSA achieves efficient dispersion of GT-ASP via the synergistic effect of chemical adsorption and hydrogen bonding. In contrast, SDBS induces GT-ASP aggregation due to the charge neutralization effect of  $\text{Na}^+$  (its counterion) and the formation of “micellar bridges” via self-aggregation.

In summary, this study provides theoretical support for addressing asphaltene deposition during heavy oil recovery and transportation, contributing to the efficient utilization of heavy oil resources. Translating to offshore operations, DBSA's validated dispersion efficiency enables more precise flow-assurance scheduling (reducing unplanned shutdowns from ASP blockages) and establishes a clear inhibitor selection protocol (favoring DBSA for

high-salinity, moderate-temperature offshore heavy oil fields), significantly strengthening the study's industrial impact. This study has certain limitations, and the next step will involve actual crude oil validation, pilot-scale shear tests, and high-temperature stability tests to advance the on-site application of dispersants.

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## Abbreviations

The following abbreviations are used in this manuscript:

|        |                                         |
|--------|-----------------------------------------|
| DBSA   | Dodecyl Benzene Sulfonic Acid           |
| SDBS   | Sodium Dodecyl Benzene Sulfonate        |
| GT-ASP | Gt Asphaltene                           |
| FT-IR  | Fourier Transform Infrared Spectroscopy |
| XPS    | X-Ray Photoelectron Spectroscopy        |
| OFP    | Onset Flocculation Point                |

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