The synergistic effects of NiO nanoparticles and a chemical inhibitor on the stabilization of asphaltene aggregates

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Abstract
The precipitation and deposition of asphaltene is one of the big challenges during the production of high-API reservoir oils, leading to undesirable financial and technical burdens on the oil industries. Therefore, the inhibition of the asphaltene precipitation/deposition is of prime importance with respect to flow assurance. In this work, NiO nanoparticles were synthesized and dispersed by ultrasonic irradiation into a liquid oil-based commercial asphaltene inhibitor to prepare a nanostructured inhibitor chemical. A dead oil sample from an Iranian oil field, with the asphaltene depostion problem, was blended with aromatics to prepare a model oil. The synergism of the nanoparticles and the chemical inhibitor on the stability of the asphaltene aggregates at harsh de-stabilization conditions was evaluated by two standard tests, i.e. asphaltene dispersant test (ADT) and analytical centrifugal stability analysis of asphaltene (ACSAA). The results indicate that the addition of a tiny dose of the nanoparticles to the chemical inhibitor improves the inhibitor efficiency considerably. It is inferred that the interactions of the nanoparticles with the asphaltene and inhibitor chemical are the underlying stabilization mechanism of the asphaltene.

Keywords: Asphaltene, Inhibitor, NiO nanoparticles, Flow assurance, Precipitation onset pressure

Introduction
Asphaltene is defined as the highest molecular weight and most polar constituents of reservoir oil. It is classically characterized as insoluble in low-molecular weight paraffins and soluble in aromatics such as xylene and toluene [1,2]. During production, due to pressure drop and composition and temperature changes, asphaltene starts to precipitate out of the oil phase, accelerating the asphaltene deposition rate [3]. Well tubing is one of the first places that becomes involved in the asphaltene deposition issues. Changing thermodynamic parameters as well as the shear of flow may intensify the instability of the asphaltene aggregates, leading to enhaced deposition and thus plugging the well tubing. This results in an unfavorable decline in the oil production rate which necessitates the well shut-in and workover operations. During the workover, aromatics are injected by coil-tubing to remove the deposited asphaltene and treat the headache. However, it does not guarantee the flow assurance and the asphaltene is deposited again and impose cyclic workover and shut-in. In order to address the asphaltene deposition challenge, chemical inhibitors are injected continuously through the chemical injection valves (CIV) into the tubing just several ten feet above the perforations [4].

Chemical treatment is considered as one of the most common strategies to prevent asphaltene precipitation. The chemical asphaltene inhibitors are designed in such a way to interact with the asphaltene and inhibit its precipitation, deposition, and thus ensure continual oil flow [5]. These chemicals, with amphiphilic and polymeric molecules, play a role of bridge to stabilize the asphaltene aggregates in the oil phase [6]. A very low dose of the asphaltene inhibitors is capable to guarantee flow assurance and stabilize the asphaltene effectively. These tiny doses make the continuous injection of the inhibitors economical and practical at field conditions.
A great body of research has been devoted worldwide to improve the efficiency of these inhibitor chemicals. It is found that efficiency of these chemicals depends on their polarity, length of the alkyl side chains, and the size of aromatic sheets for firm π-π interactions [7,8].
Recently, the application of nanoparticle-technology in the oil and gas industry due to superior characteristics of the nanoparticles is the subject of investigation [9,10]. nanoparticles show the capability to adsorb the asphaltene aggregates and prevent their precipitation and deposition [11,12]. Several researchers have studied the application of metal oxides nanoparticles for asphaltene adsorption [13–17]. It is reported that nanoparticles, via acid-base and electrostatic interactions with asphaltene aggregates, have the potential to decrease asphaltenes self-association tendencies, inhibiting asphaltenes precipitation.
In this work, the synergetic effects of a commercial asphaltene inhibitor and nickel oxide nanoparticles on the stabilization of the asphaltene aggregates are studied. NiO nanoparticles and the commercial inhibitor with several polar groups in its molecular structure were chosen to shed light on the mechanism of the asphaltene stabilization by the nanostructured inhibitor chemical. Model oils are prepared by blending stock tank oil with xylene. The asphaltene stability is then monitored by two series of standard tests, named asphaltene dispersion test (ADT) and analytical centrifugal stability analysis of asphaltene (ACSAA). It is expected that the nanoparticles improve the efficiency of the chemical inhibitor.

Experimental

Model oil preparation

In order to simulate the behavior of asphaltene aggregates at field conditions, the model oil was prepared by mixing a dead oil sample of an Iranian oil field with xylene. The size and spatial orientation of the asphaltene aggregates were considered as the two properties that need to be mimicked during the preparation of the model oil. The dead oil and xylene were blended at the oil to xylene volume ratio of 80/20. The results of the SARA analysis of the dead oil sample are listed in Table 1. The colloidal instability (CII) of the asphaltene is calculated to be 1.86 which is much higher than 0.9, indicating the high instability of the asphaltene in the field. This may strengthen the necessity for the study to develop a new chemical inhibitor for the asphaltene precipitation.

Table 1. SARA test results.

Fraction	wt.%
Saturate	63
Aromatic	28
Resins	7
Asphaltene	2

Nanoparticles synthesis

NiO nanoparticles were synthesized via a simple participation method. An aqueous solution of 0.1 M $Ni(NO_3)_2.6H_2O$ was titrated by stoichiometric amount of NH_4OH solution for 1 h to fix the pH at 10. After stirring at 60^{o}C for 5h, the mixture was centrifuged and the supernatant was decanted. The solid deposits were then washed with a plenty of deionized water several times to reach the neutral pH. The solid sample was dried in an oven overnight at 80^{o}C and then was calcined at 500^{o}C for 4 h to develop its crystalline structure.

Inhibitors

The oil-based inhibitor used in this work was a product of Zagros chemical & improved oil recovery company. The commercial name of the inhibitor is BZSS. The molecular structure of BZSS contains several functional groups such as ester, hydroxyl, and ether. These groups increase the interactions of the chemical with the asphaltene. Around 1000 ppm of the solid NiO nanoparticles were added the BZSS sample and irradiated by ultrasonic waves to get fully dispersed nanofluid inhibitor. The size distribution of the nanofluid was monitored by dynamic light scattering (DLS).

Methods

To investigate the synergistic effects of the NiO nanoparticles and BZSS inhibitor on the stabilization of the asphaltene, two series of tests including ADT and ACSAA were conducted at harsh destabilization conditions [18,19].

In the ADT tests, a pre-determined volume of the model oil, containing a definite dose of the inhibitor, was added to 10 mL of n-hexane to enforce the precipitation of the asphaltene. It was essential to determine the volume of the model oil that was added to the hexane volume. Therefore, in the absence of the inhibitor chemicals, blank tests with the addition of 100, 200, 300, 400, 500, and 600 µL of the model oil to 10 mL of the hexane were conducted and the mixtures were allowed to rest for 30 min. The sample which shows an acceptable amount of the asphaltene deposit and a measurable turbidity of the supernatant was considered as the optimum volume of the model oil. This optimum volume was then used in all the ADT and ACSAA tests both in the presence and absence of the inhibitors. A dose of 300 ppm of the inhibitors was added to the model oil and stirred. Then, the optimum volume of the oil was added to 10 mL of nC_6 in centrifuge tubes and agitated by hand slowly for 2 min. The mixture was then allowed to rest for 30 min. The amount of the solid deposit was monitored and the turbidity of the supernatant liquid was measured by UV-vis spectroscopy.

In the ACSAA tests, after the addition of the inhibitor to the model oil, the optimum volume of the oil was added to 10 mL of the hexane and the mixture was centrifuged at 1500 rpm for 10 min. Then, the volume of the solid deposits and the turbidity of the supernatant were monitored.

Results and discussion

To determine the optimum volume of the model oil in the ADT and ACSAA tests, a series of blank tests were conducted. Figure 1 exhibits the photograph of the centrifuge tubes after 30 min rest during the blank tests. As observed, the addition of 300 µL of the model oil to 10 mL of nC_6 shows not only a considerable amount of solid deposits but also a measurable turbidity of the supernatant. Therefore, for all the next ADT and ACSAA tests, 300 µL of the model oil were added to the hexane volume.

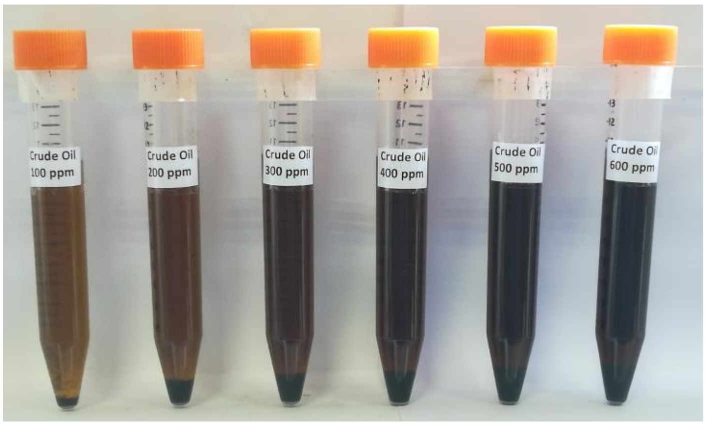
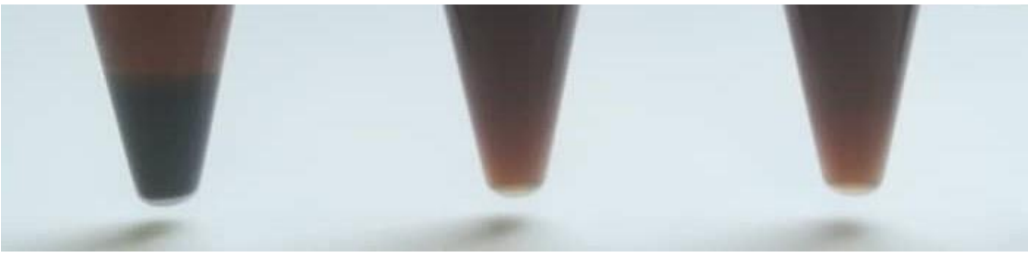


Figure 1. The optical photo of the blank tests done by the addition of 100, 200, 300, 400, 500 and 600 µL of the model oil to 10 mL of nC_6 and the rest time of 30 min.

In the ADT and ACSAA tests, 300 ppm of the inhibitor chemicals, i.e. BZSS and NiO/BZSS, were added to the model oil and their efficiency was measured. Figure 2 illustrates the asphaltene stabilization efficiency of the inhibitors in the ADT test. The results of the ADT tests show that both inhibitors have the capability to disperse the asphaltene aggregates with the efficiency of 100%. This means that the interactions of the inhibitors with the asphaltene aggregates prevent the aggregate growth in the presence of a large volume of normal hexane. Therefore, the gravity force cannot settle down the asphaltene aggregates in the presence of the inhibitors. In the absence of the inhibitors, the asphaltene aggregation leads to the aggregate sizes which are susceptible to deposition by gravity force, as observed in sample A in Fig. 2. The inhibitors through non-covalent interactions keep the asphaltenes suspended in the model oil. Several studies have shown the importance of the polar-polar interactions between the asphaltenes and chemical inhibitors to prevent their aggregate growth [7,8]. The commercial inhibitor contains polar functional groups such as ester, ether, and hydroxyl, which are known as surface-active agents and interact with polar moieties of the asphaltene. These amphiphiles and resin molecules behave similarly to control the asphaltene growth and precipitation.



A B C

Figure 2. The results of ADT tests: (A) blank test (model oil without any inhibitor), (B) model oil with BZSS inhibitor, and (C) model oil with NiO/BZSS inhibitor.

To investigate the effect of shear forces on the asphaltene deposition, the ACSAA tests were conducted. By decreasing the distance between the asphaltene aggregates, the centrifugal force evaluates the stability of aggregates and their interactions with the inhibitor chemicals. The results of ACSAA tests are shown in the Figure 3. As expected, the reference sample has the highest amount of the asphaltene deposits. In addition, compared to the reference sample, the BZSS inhibitor and the NiO/BZSS chemical decrease the deposits by 51 and 58%, respectively. The NiO nanoparticles via acid-base and electrostatic interactions with the asphaltene aggregates, improve the interactions between the asphaltene aggregates and inhibitor molecules. Therefore, asphaltenes self-association tendencies and the amount of the deposit are diminished.

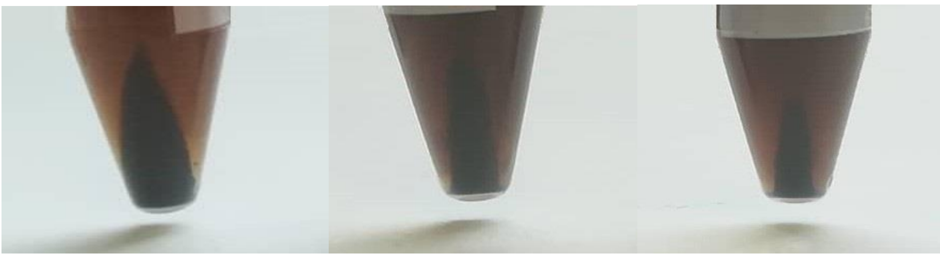


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Figure 3. The results of the ACSAA tests: (A) the model oil without any inhibitor, (B) the model oil with 300 ppm of BZSS inhibitor, and (C) the model oil with 300 ppm of NiO/BZSS

Conclusions

Synergistic effects of a commercial inhibitor and NiO nanoparticles on the inhibition of the asphaltene precipitation and deposition were studied. The following conclusions are made based on the experimental results obtained:

- Based on ADT tests the commercial inhibitor (with and without the nanoparticles) can prevent the deposition of asphaltenes with the efficiency of 100%.
- In the presence of centrifugal forces (in the ACSAA tests), the addition of 300 ppm of the commercial inhibitor decrease the asphaltene deposit by 51% compared to the blank test.
- The addition of 1000 ppm of the NiO nanoparticles into the commercial inhibitor, increase the inhibitor efficiency by 7%.

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