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A Novel Inhibitor for Controlling Iraqi Asphaltene Problems *

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Abstract—Asphaltene precipitation plays a key role in many flow assurance problems like fouling in production facilities, pipelines and refineries. Several attempts have been made to stabilize the asphaltene and prevent its precipitation by using asphaltene inhibitors. This study provides a novel approach to quantifying asphaltene precipitation using a new class of asphaltene inhibitor (Poly (vinyltoluene-co-alpha-methylstyrene)) which selected based on environmentally friendly, functional groups, and polarity to be effective. The experimental data using Turbiscan suggested that the asphaltene inhibitor makes the asphaltene particles more stable due to its unique ability to interact between asphaltene particles and asphaltene inhibitor molecules via π - π interactions and hydrogen bonding. The involvement of using Asphaltene Inhibition Test (AIT) and the results show that the stability of asphaltene increases with increasing the concentration of inhibitor. However, at higher concentrations more than 6wt. % the sedimentation increase and in this case the polymer can cause the formation of precipitation. The present of asphaltene inhibitor is found about (83%) with using optimum concentration of polymer (6wt. %) after 1 week aging. In addition, the analysis by using Infrared spectroscopy revealed that the Iraqi asphaltene consists of functional groups such as aromatic, aliphatic hydrocarbons, sulfoxide, and aliphatic primary amines functions.

Index Terms-- Asphaltene; precipitation; sedimentation; stability.

I. INTRODUCTION

Asphaltene is the heaviest and most polarizable fraction of the crude oil that is insoluble in alkanes, such as n-pentane and n-heptane, but completely soluble in aromatic hydrocarbons, such as benzene and toluene [1]. Asphaltenes fraction is formed of associated systems of various polyaromatics with alkyl side chains; organic molecules containing heteroatoms such as oxygen, nitrogen, and sulfur as well as metals such as vanadium and nickel [2]. Asphaltenes tend to self-aggregate, therefore, several studies reported in order to control asphaltene self-aggregation and hence its stability. Asphaltene is usually responsible for many flow assurance problems such as wettability changes on the reservoir rock, pore clogging in

the reservoir porous media, fouling in wellbore tubing and production surface facilities, and stabilizing emulsions in process facilities [3]. Previous studies have reported that the polymeric inhibitor can play an important role in addressing the issue of controlling the asphaltene aggregations and keep them in suspension stable [4]. 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 [5]. Among these polymers, two classes were particularly investigated in the past, organometallic and organic. Hernández-Altamirano et al. used a class of organometallic polymers that can be considered to be effective as corrosion inhibitors and asphaltene inhibitors [6]. 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. Polymers containing both aromatic portions as well as strongly polar functional groups such as amide or carbonyl have been quite successful for preventing asphaltene precipitation [7]. Ghaffer et al. tested a series of propoxylated dodecyl phenol formaldehyde polymers with three different molecular weights using heavy crude oils in heptol solutions [8]. The results showed that the onset of asphaltene precipitation increased with increasing polymer molecular weight. The study postulated that the presence of the propoxy (C_3H_7O) side and end chains allowed greater interaction with the asphaltenes, resulting in overall higher absorbance and better performance compared to the non-substituted poly(dodecyl phenol formaldehyde).

Due to their wide range of possible functional groups and relative ease of production, a considerable literature has grown up around the theme of polymeric inhibitors. In this paper addresses the strategy to reduce the asphaltene precipitation problem by using a new effective asphaltene inhibitor (oil soluble organic polymer) to stabilize and prevent asphaltene precipitation. To our knowledge, no previous study has analysed and controlled for Iraqi asphaltene precipitation by using (Poly (vinyltoluene-co-alpha-methylstyrene)).

2 Experimental work and procedure

2.1 Materials

Iraqi crude oil was used for asphaltene extraction. N-heptane (extra pure, > 97%), anhydrous toluene (Sigma Aldrich, 99.8%), Poly (vinyltoluene-co-alpha-methylstyrene) was used as a new asphaltene inhibitor and purchased from Sigma Aldrich.

2.2 The extraction of asphaltenes from Iraqi crude oil

The extracted of asphaltenes was carried out by mixing crude oil with n-heptane at a volume ratio of 1:40. The mixture was allowed to equilibrate after stirring and left overnight at room temperature. It was then filtered under vacuum using 0.2 μm pore size Whatman filter paper. The filter cake was repeatedly washed with n-heptane to remove any resins until the effluent from the filter became colorless. Finally, the asphaltene dissolved with toluene and n-heptane (Heptol) (30:70 volume ratio) to form asphaltene solution.

2.3 Infrared spectroscopy and elemental analysis:

Infra-red spectrometry allows to investigate the functional groups present in a sample. The elemental composition (C, H, N, O, S) of the Iraqi asphaltene were determined by Elemental Analyser (CHNS-O).

2.4 Asphaltene stability measurements

The stability of asphaltene was rapidly evaluated using a Turbiscan instrument (Formulation, France). Figure (1) presents the measurement principle diagram from the Turbiscan Lab Expert type stability analyser. The main advantage of Turbiscan is to predict the destabilization phenomena for asphaltene and the effect of adding asphaltene inhibitor on the stability of asphaltene. The asphaltene sample was put in a glass cylindrical cell and analysed by a light which scanned the sample cell from the bottom to the top.

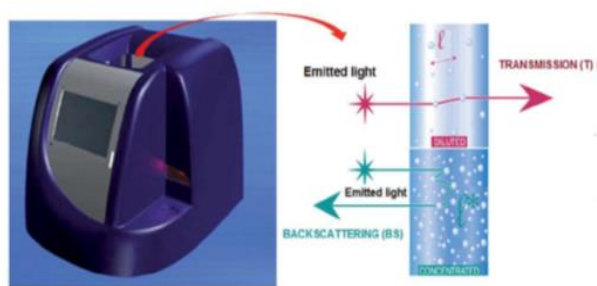


Figure. 1: Measurement principle diagram of the Turbiscan Lab Expert type stability analyzer.

2.5 Asphaltene inhibition test (AIT)

The asphaltene solution was treated with polymer. The asphaltene was allowed to precipitate with gravity, followed by adding of various dosages (1, 2, 4, 6 and 8 wt. %) of inhibitor. The homogenization of the sample was achieved for a period of (1hr) using a magnetic stirrer at 900 rpm. Asphaltene and Heptol (30:70 vol. %) were placed in graduated centrifuge tubes and the total volume of solutions were 8 ml. A sample of asphaltene solution without polymer was used as a control.

Finally, the samples were left undisturbed for a specific period of time (also known as aging time) and the amount of sediment obtained was recorded in mL at the end of the experiment. The aging times were 1 hr., 24 hr. and 1 week. The principle for evaluation of the performance of polymer using (AIT) consists in comparing the amount of sediment obtained in mL for the different dosages with respect to the asphaltene without polymer.

3. Results and discussion

3.1 Asphaltene characterization

Infrared spectroscopy is one of the most-well known tool for assessing the structure and functional groups for asphaltene. The structure of asphaltene molecules in this study consists mainly of linear, branched, and naphthenic hydrocarbons attached to large aromatic clusters. The IR spectrum basically shows characteristic peaks that correspond to modes of the functional groups in the asphaltene spectrum. The results demonstrated in Fig. (2) show that the Iraqi asphaltene consists of aromatic, aliphatic hydrocarbons, sulfoxide, and aliphatic primary amines functions. In the aliphatic, C-H stretch range and CH_3 stretching dominate over CH_2 . These functional groups are responsible for the interactions between asphaltene molecules and inhibitor molecules.

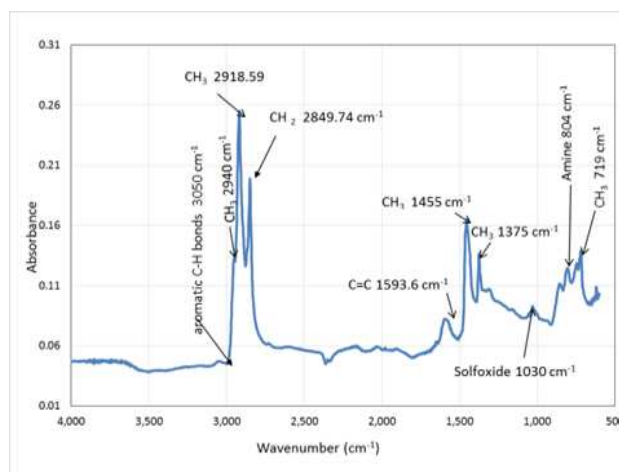


Figure. 2: IFR analysis for Iraqi asphaltene.

3.2 Asphaltene stability

The inhibitor is used to control asphaltene precipitation by adsorption at the surface of asphaltene molecules and to keep asphaltene particles stable against precipitation [10, 9]. Asphaltene solution with Heptol (30:70 vol. ratio) is expected to undergo precipitation of asphaltenes when stressed and will be unstable. The most interesting aspect of stabilization asphaltene is investigated by using Turbiscan. The variation in the transmitted light from the asphaltene solution due to the formation of asphaltene precipitation was measured in a fixed time interval. The mean transmittance (average transmittance along the tube height) was recorded as a function of time as the asphaltene particles settled. If the chemical additive is effective, it will keep the asphaltenes dispersed in the solution and prevent them from settling, and consequently the mean transmission remains unchanged [11, 12]. Data from Fig. (3) show the stability trends for asphaltene and the effect of inhibitor on asphaltene precipitation. It can be observed that the mean transmission for asphaltene solution without inhibitor is more than with inhibitor. The decreasing in the mean transmittance can be inferred that inhibitor effectively renders stability to asphaltene.

Other findings from Turbiscan have also important implication for better understanding the effect of inhibitor on delta transmission (ΔT) and delta backscattering (ΔBS). Figure (4) shows the delta transmission and delta backscattering for asphaltene solution was about 30% at 38 mm of the test tube. Whereas, the delta backscattering at the same level was about 6%. However, Fig. (5) shows that at adding (6wt.%) of asphaltene inhibitor, the delta transmission decreases from 30% to 5 % after 1 hr. of scanning. In addition, the delta backscattering decreases from 7 % to about 3 % as well.

Furthermore, the velocity of destabilization of asphaltene (calculated in the middle zone of profiles from Backscattering) as a function of time is another important parameter for asphaltene stability. The mean value of the precipitation velocity (migration rate of droplets) can be calculated by the average between maximum value and minimum value. It is found that the mean value of velocity is reduced from 11 $\mu\text{m}/\text{min}$ to 3 $\mu\text{m}/\text{min}$ at adding 6 wt. % of inhibitor.

Interestingly, these finding might help us to better understand the mechanism of asphaltene precipitation controlling. The stability of asphaltene after adding the asphaltene inhibitor attributed to a large interaction between both styrene and vinyltoluene rings with asphaltene molecules and hence are effective to control asphaltene precipitation by increasing asphaltene particle-particle separation. These interactions are occurred via π - π interactions between polymer and asphaltene, allowing a change in the aggregate structure that prevents thickening. In addition, the presence of aliphatic chains is critical for providing steric hindrance between the aggregates. As well as hydrogen bonding between the polymer and asphaltene is important for linking the polymer at the asphaltene particles surface.

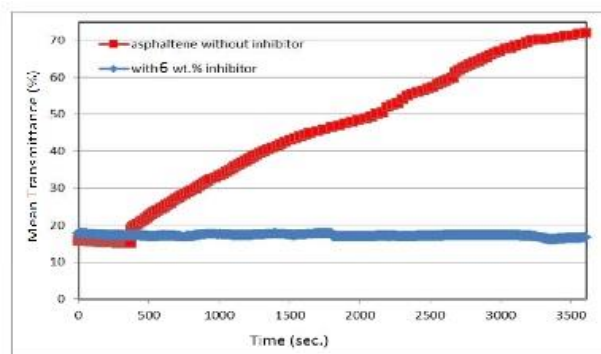


Figure 3: Turbiscan graphs of asphaltene without and with 6 wt. % inhibitor.

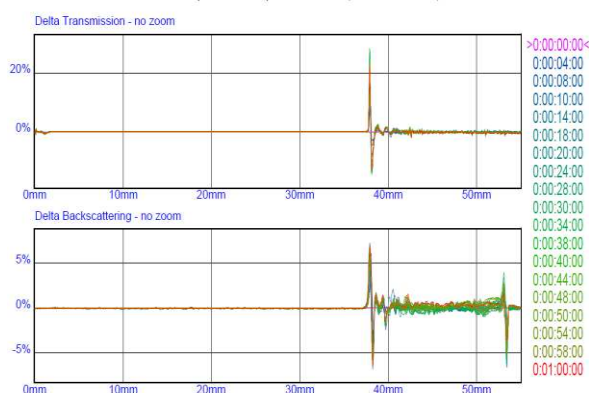


Figure 4 : Delta Transmission and delta Backscattering for 5000 ppm Iraqi asphaltene solution.

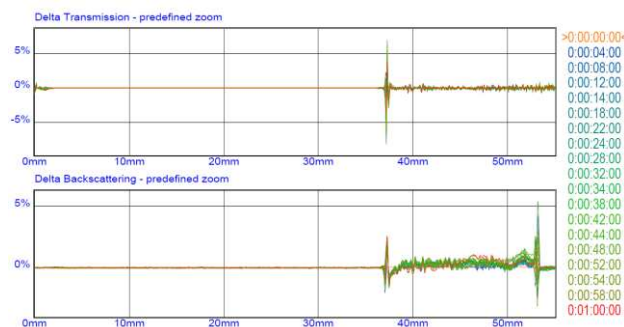


Figure 5: Delta Transmission and delta Backscattering for 5000 ppm Iraqi asphaltene solution with 6 wt. % inhibitor.

3.3. Asphaltene inhibition test (AIT)

To evaluate the performance and effectiveness of polymer for controlling asphaltene precipitation has been carried out by using AIT. The asphaltene solution was treated with polymer at different concentrations 1, 2, 4, 6 and 8 wt.% as described in Section 2.5. The inhibitor was added immediately, and then the samples have been stored for 1hr, overnight and after 1 week in the dark after the asphaltene was mixed with heptol.

A sample of 5000 ppm asphaltene was added to AIT centrifuge tube containing 8 ml of heptol (5:95 vol. ratio of toluene : heptane). The results of sediment amount obtained in the different cases are presented in Table 1. The lower amount of sediment collected means the more efficient the dispersion of asphaltenes. Figure (6) shows the effect of various polymer concentrations on asphaltene precipitation. The results show that the stability of asphaltene increases with increasing the concentration of inhibitor. However, at higher concentrations more than 6wt. % the sedimentation increase and in this case the polymer can cause the formation of precipitation. The main reason for that could be attributed the self- aggregates of polymer at high concentrations.

Table 1: Sedimentation of asphaltene at different concentrations of polymer during aging time.

samples	AIT asphaltene with polymer		
	1 hr (ml)	1day (ml)	1week (ml)
Asphaltene solution	0.4	0.6	0.93
With 1 wt. %	0.3	0.5	0.72
With 2 wt. %	0.2	0.15	0.4
With 4 wt. %	0.11	0.12	0.2
With 6 wt. %	0.05	0.1	0.15
With 8 wt. %	1.01	1.2	1.2

In order to assess the effect of aging time on the amount of asphaltene precipitation, repeated-measures of AIT for 24 hr. and 1 week were obtained. As shown in Fig.(6 B), the amount of asphaltene sedimentation increased after 24 hr. storage for all samples with and without polymer. However, the less amount of sedimentation was at 6 wt. % polymer. Similarly, looking at Fig.(6 C), the sedimentation amount increases for all samples after 1 week aging.

From results in Table 1, we can calculate the percentage of asphaltene inhibition. The % percent inhibition is defined by the following equation:

$$\% \text{ percent inhibition} = \frac{h_0 - h_1}{h_0} \times 100\% \quad (1)$$

where h_0 is the precipitate height without addition of polymer and h_1 is the corresponding height with polymer at the indicated concentration. This criterion provides an estimate of the asphaltenes inhibitor performances at different concentrations. Therefore, the efficiency of polymer for controlling asphaltene at optimum inhibitor concentration (6 wt.%) was about 87.5 % after 1 hr., whereas after 1 week was about 83%. The amount of precipitated asphaltene actually increases with longer aging times.

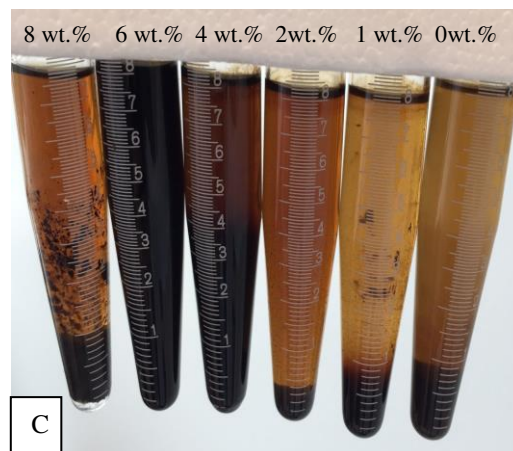
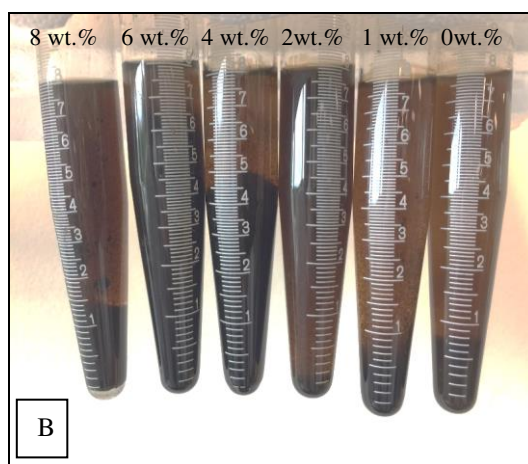
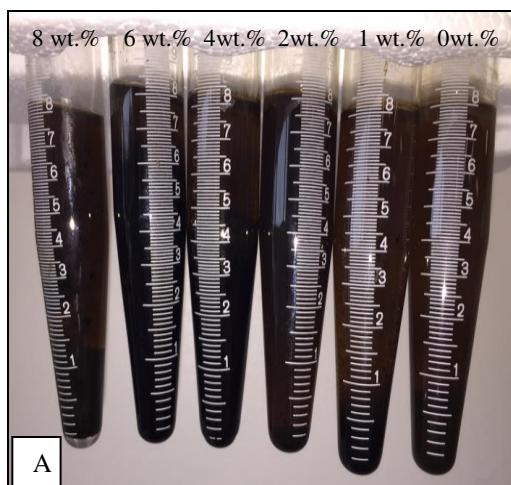


Figure 6. ADT for asphaltene without and with inhibitor after (A) 1hr , (B) 24hr, (C) 1 week.

However, the AIT test requires large amounts of heptane to obtain a clear sample that allows sediment observation through it (95% heptane or more). Therefore, the results

obtained from AIT may be caused confusing because the dispersant cannot be tested at the heptane concentration that causes the highest precipitation of asphaltene and/or the largest asphaltene aggregates. Moreover, this high dilution may not be representative of the conditions at which asphaltene precipitate and aggregate in real systems. However, the most interesting finding in this method is strong relation between the concentration of polymer and the amount of precipitation.

4 Conclusions:

The purpose of the current study was to investigate the effect of using a novel organic polymer inhibitor (Poly (vinyltoluene-co-alpha-methylstyrene)) for controlling asphaltene precipitation. This study has found that Iraqi asphaltene consists of aromatic, aliphatic hydrocarbons, sulfoxide, and aliphatic primary amines functions and these functional groups are very important for interaction between asphaltene and inhibitor molecules. The result from Turbiscan is found that the polymer is effective to keep the asphaltene dispersed in the solution and prevent them from settling. The results from AIT have significant implications to evaluate the performance and effectiveness of polymer for controlling asphaltene precipitation during aging time. These results indicate that the asphaltene inhibitor have a high effectiveness for delaying the asphaltene precipitation in bulk and hence increase the stability of asphaltene at the optimum concentration about 6 wt.%. This attributed to the strong interaction between the polar groups in polymer (vinyltoluene and styrene aromatic rings) and the asphaltene via π - π interactions and hydrogen bonding. However, at higher concentrations more than 6wt. %, the sedimentation increases asphaltene precipitation. The main reason for that could be attributed the self- aggregates of polymer at high concentrations.

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