

An Investigation of the Effect of Aromatic, Anionic and Nonionic Inhibitors on the Onset of Asphaltene Precipitation

Mohammad Mahdi Shadman¹, Mostafa Dehghanizadeh²,
Amir Hossein Saeedi Dehaghani^{1,*}, Mohsen Vafaie Sefti¹, Nader Mokhtarian³

1. Faculty of Chemical Engineering, Tarbiat Modares University, P.O. Box: 14155-4838, Tehran, Iran

2. Department of Chemical, Petroleum and Gas Engineering, Semnan University, Semnan, Iran

3. Islamic Azad University, Shahreza Branch, Esfahan, Iran

ARTICLE INFO

Article history:

Received: August 31, 2013

Accepted: December 14, 2013

Keywords:

Asphaltene,
Resin,
Inhibitor,
Onset,
Precipitation,
Reservoir

* Corresponding author:

Email: asaeedi@modares.ac.ir

Tel: +98 21 82883314

Fax: +98 21 82883979

ABSTRACT

The organic deposition particularly asphaltenes has many detrimental effects on the oil industries, such as plugging in pipelines, wellbore and facilities which subsequently causes a considerable reduction in well productivity. Adding inhibitor is one of the ways to prevent clustering of asphaltene precipitation in crude oil. In this study, the effect of inhibitors on preventing asphaltene precipitation was investigated by the viscometric method. At first, the different concentrations (1000 ppm, 2000 ppm, 10000 ppm and 20000 ppm) of some aromatic, anionic and nonionic inhibitors were prepared in a dead crude oil sample, and then the inhibition strength of samples was measured. The results showed that the inhibition strength of inhibitors in low to moderate (1000 ppm – 10000 ppm) concentrations has a regular pattern, and it is associated with functional groups in chemical structure of the inhibitors.

1. Introduction

Asphaltenes are the most polar fractions which are dispersed as colloidal clusters in crude oil. The accumulation of these clusters lead to the flocculation of colloids, and accordingly, formation of precipitation. The amphiphile molecules, often used as dispersants and preventive agents, cause the aggregation of asphaltene clusters. Actually, natural resins play the role of inhibitor in crude oil, and their functional groups act as a bridge between polar (asphaltenes) and nonpolar medium (bulk of oil) [1]. Whenever normal alkanes are added to a sample, the balance between micelles and bulk of oil is impaired; consequently, the concentration of monomeric asphaltenes increases in the bulk phase. As soon as the concentration of monomers reaches to the concentration of onset point, the process of deposition starts. The compounds with a nature similar to resins or those with acidic polar head groups that can be attached to micelles, can contribute to stabilization of the micelles. These chemical compounds can include natural resins which are derived from crude oil, or amphiphiles dissolved in oil (surfactants). The amphiphile molecules basically, at least consist of a polar head group and a long hydrocarbonic tail. The amphiphiles dissolved in oil (surfactants), is more effective than aromatics in prevention of asphaltene precipitation [2]. Middea (1991), investigated the amphiphiles dissolved in oil, and found that the head group polarity has a key role in stabilization of asphaltenes. Chang and Fogler (1994) showed that there are two important factors in stabilization of asphaltene: 1) the adsorption of amphiphile on asphaltene surface, 2) the establishment of a stable layer around asphaltene molecules. The researchers also found that an amphiphile should be an acid or similar to acid, because proton of H^+ has an interaction with asphaltenes. If H^+ replaces another group, amphiphile loses its activity. Alsahaf et al. (2002) studied the inhibition effects of resins, toluene, deasphalted Oil (DO) and some of the surfactants [3,4].

Rocha Junior et al. (2006) investigated the inhibition capacity of some new chemical additives on three samples of Brazilian crude oil. The Ethoxylated Nonylphenol (low molecular mass), vegetable oils (Coconut Essential Oil, Sweet Almond, Andiroba and Sandalwood Oil) and organic acids (Linoleic, Caprylic and Palmytic) showed a strong effect in the prevention of asphaltene precipitation [5]. Ghloom et al. (2010), compared inhibition effect of three commercial and three non-commercial inhibitors (light cycle oil (LCO), heavy cycle oil (HCO) and diesel) for Marrat Kuwaiti Reservoirs crude oil. They concluded that commercial basic inhibitors in crude oil contain low saturation and high resins, and acidic inhibitor in crude oil containing high polarity are very effective in prevention of asphaltene precipitation [6]. The capacity of nanoparticles (TiO_2 , ZrO_2 and SiO_2) in organic-based nanofuids for stabilizing asphaltene particles in oil was investigated by Mohammadi et al. (2011). They measured the hydrogen bonds between asphaltene and nano-particles by using Dynamic Light Scattering (DLS) method. The results showed that TiO_2 nanoparticles in the acidic environment can greatly increase the stability of the asphaltenes. On the other, hand ZrO_2 and SiO_2 nanoparticles have less effect on the stability [7].

2. Research Method

The crude oil used in this study included a dead oil sample obtained from Iranian petroleum fields. The resins, saturates and aromatics and asphaltenes of oil sample was specified by SARA test method (Table 1).

Table 1. Characteristics of the used crude oil

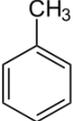
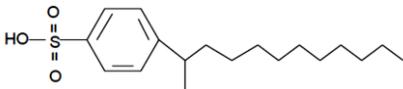
Density ($^{\circ}$ API)	Asphaltene	Resin	Aromatic	Saturation
17.96	13.75	13.36	42.10	30.79

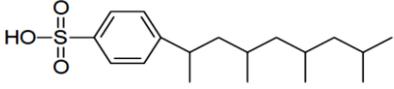
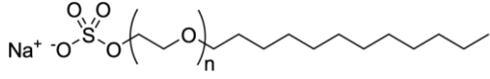
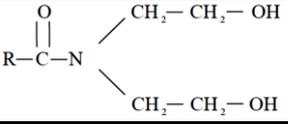
The inhibitors used included aromatic (Toluene), anionic (Linear DBSA, Branched DBSA, Triethanolamine Lauryl Ether Sulfate and Sodium Lauryl Ether Sulfate), nonionic (Coconut Diethanolamide and Ethoxylated Fatty Alcohol 9 Mole). The characteristics of the inhibitors are listed in Table 2 and their chemical structures are shown in Table 3.

Table 2. Characteristics of the used inhibitors

Aromatic Inhibitors	Molecular weight(gr/grmol)	Density at 20 $^{\circ}$ C(gr/cm 3)	---	---	---
Toluene	92.14	0.8667	---	---	---
Anionic Inhibitors	Molecular weight(gr/grmol)	% Free Sulfuric Acid	% Free Oil	Acidity (mgr KOH/gr)	% Anionic Active
Linear DBSA	322	1.35	1.89	183.9	96.4
Branched DBSA	321	1.8	2.2	180	96
Sodium Lauryl ether Sulfate	387	---	1.94	---	70.17
Triethanolamine Lauryl Ether Sulfate	511	---	---	---	39.92
Test Method	-	-	ISIRI3513	ISIRI3178/23	ISO2271
Non-Ionic Inhibitors	% Amid content	% Free fatty matter	%Free amine	% Free fatty acid	Density at 20 $^{\circ}$ C(gr/cm 3)
Coconut Diethanol Amide	82.68	4.3	3.24	0.21	0.9971
Test Method	ISIRI2053	ISIRI2053	ISIRI2053	ISIRI2053	---
---	Acidity (mgr KOH/gr)	Density at 60 $^{\circ}$ C(gr/cm 3)	Molecular weight(gr/grmol)	---	---
Ethoxylated Fatty Alcohol 9 Mole	0.08	0.9998	662.96	---	---
Test Method	AOCS Te 1a-64	---	ISIRI4722	---	---

Table3. Chemical structure of the used inhibitors

Chemical structure	inhibitor
	Toluene
	Linear DBSA

Chemical structure	inhibitor
	Branched DBSA
	Sodium Lauryl Ether Sulfate
$CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_2OSO_3^- N^+(CH_2CH_2OH)_3$	Triethanolamine Lauryl Ether Sulfate
	Coconut Diethanol Amide
$R-(O-CH_2-CH_2)_9-OH$	Ethoxylated Fatty Alcohol 9 Mole

The inhibition strength is studied by measuring onset of asphaltene precipitation in the presence of inhibitors. In this research, the samples were prepared at different concentrations of inhibitor and the effects of inhibitors were measured by viscometric method. Escobedo & Mansoori (1996) studied the viscosity changes during adding a precipitation-solvent in oil sample. They concluded that there is a point at which the viscosity changes increases drastically and this point is considered as the start of asphaltene precipitation (onset)[8].

Figure 1 shows the results of viscometric measurements to determine the onset of studied samples.

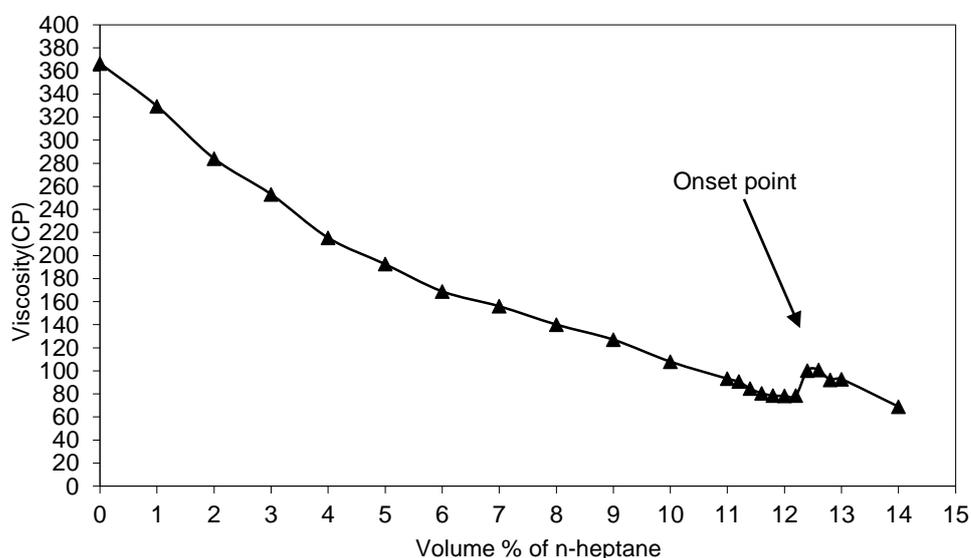


Figure 1. Determination of onset point for original crude oil sample at 20 °

According to Figure 1, the point 12.2 (volume % of n-heptane) $\approx 0.2 \text{ cm}^3$ ($n\text{-C}_7/\text{gr oil}$) is considered as the onset of oil sample. In this work, the Stabinger

Viscometer (Anton par SVM300) was used and the viscosities tests were carried out at 20 °C. The n-heptane (99% purity) has been used as precipitation solvent and its density at 20 °C is 0.683 (gr/cm³). In addition, for measuring the inhibition strength of the used inhibitor, outset, the concentrations included; 1000 ppm (0.1 wt %), 2000 ppm (0.2 wt %), 10000 ppm (1wt %) and 20000 ppm (2 wt %) were prepared. Finally, after reaching equilibrium, the onset points were determined.

3. Results and Analysis

3.1. Effect of aromatic solvent (Toluene)

In this work, toluene was selected to determine the effect of aromatic solvents on the prevention of asphaltene precipitation. The onset of oil sample containing 1000 ppm toluene is shown in Figure 2.

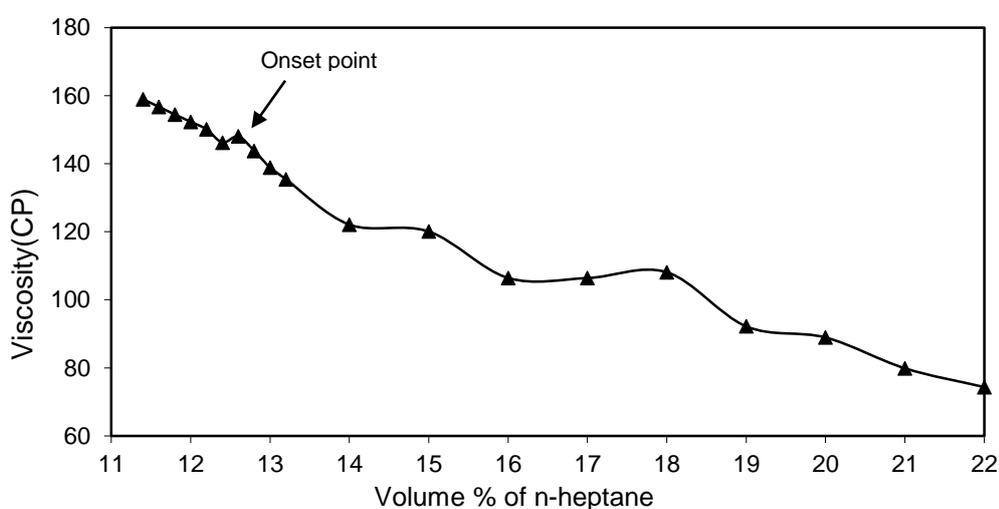


Figure 2. Determination of onset point of asphaltene precipitation of oil sample containing 1000 ppm toluene.

According to this Figure, 1000 ppm of toluene changed the onset from 12.2 (volume % of n-heptane) to 12.4 (volume % of n-heptane). Table 4 shows that high concentrations of toluene in crude oil will lead to an increase in the inhibition strength of toluene; therefore, at high concentrations (20000 ppm) toluene can solve more asphaltene particles.

Table 4. Comparison between the inhibitors used
Onset of Flocculation (Volume % of n-heptane)

Toluene	Linear DBSA	Branched DBSA	Triethanolamine Lauryl Ether Sulfate	Sodium Laurylether Sulfate	Coconut Diethanol Amide	Ethoxylated Fatty Alcohol 9 Mole	concentration
12.4	13.8	13.6	13.4	12.2	14.2	12.4	1000ppm
12.6	14.2	13.8	13.6	12.2	14.8	12.8	2000 ppm
14	18.2	18	16	12.2	20.2	14.6	3000ppm
16	21.2	18.8	16.2	12.2	20.4	14.6	4000ppm

It should be noted that although the toluene solutes asphaltene, it had a poor effect on the inhibition of asphaltene particles. This is because toluene

doesn't have polar groups. In addition, it was demonstrated that the efficiency of each inhibitor was determined by acid-base interactions, and it in turn made the inhibitors molecules be adsorbed on the surface of asphaltenes particles.

3.2. Effects of Anionic Inhibitors

3.2.1. Linear Dodecylbenzenesulfonic (LDBSA)

The onset point of sample (No.1) that contains 1000 ppm linear dodecylbenzenesulfonic is shown in Figure 3.

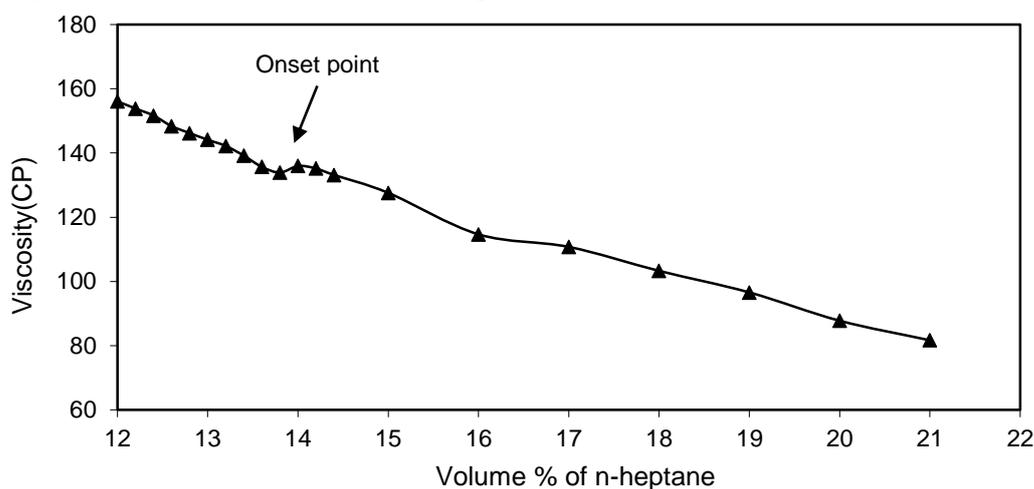


Figure 3. Determination of onset point of asphaltene precipitation of oil sample containing 1000 ppm Linear DBSA.

According to the above Figure, 1000 ppm of LDBSA changed the onset from 12.2 (volume % of n-heptane) to 13.8 (volume % of n-heptane). The inhibition strength is enhanced by increasing the concentration of LDBSA (shown in Table 4), because increasing inhibitor concentration leads to adsorbing more amount of resins on asphaltene micelles, so the stabilizing asphaltene particles is required more n-heptanes, and consequently the onset point is increased. Due to polarity of SO_3H and also having the hydrocarbonic chain (non polar), the LDBSA is more effective than Toluene in prevention of asphaltene precipitation.

3.2.2. Branch Dodecylbenzenesulfonic (BDBSA)

To evaluate the effects of branched chain hydrocarbon inhibitors, the Dodecylbenzenesulfonic was studied. Figure 4 illustrates the onset point of oil sample (no.1) containing 1000 ppm BDBSA.

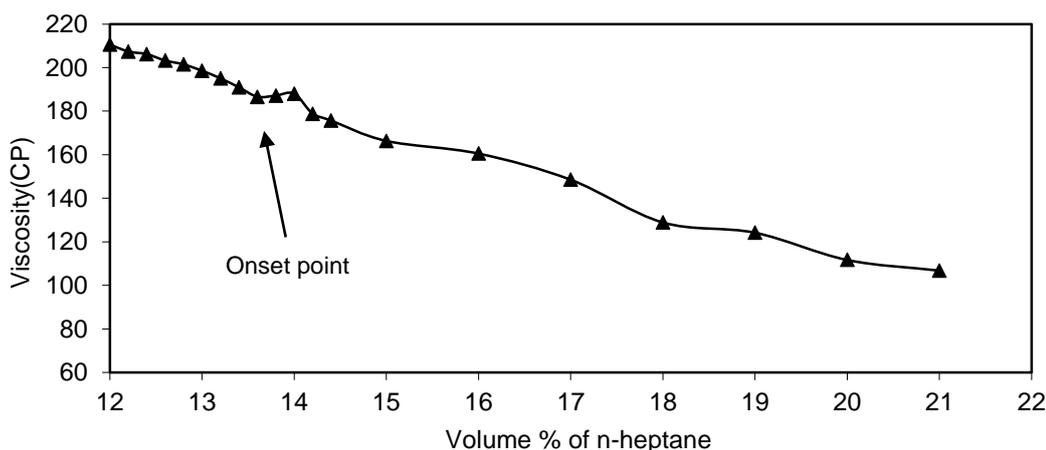


Figure 4. Determination of onset point of asphaltene precipitation of oil sample containing 1000 ppm Branched DBSA.

According to this Figure, 1000 ppm of BDBSA can change the onset of asphaltene precipitation from 12.2 (volume % of n-heptane) to 13.6 (volume % of n-heptane). At first glance, the loss of inhibition strength of branch-DBSA toward its linear type is related to reducing the length of hydrocarbon chain because of branching. The main effect of branching hydrocarbon chain is steric hindrance of methyl groups during the process of adsorbing inhibitors on the asphaltene micelles.

3.2.3. Triethanolamine Lauryl Ether Sulfate (TLES)

Presence of polar groups such as OH and hydrocarbon chains in TLES structure provides an appropriate situation for the adsorption of the inhibitor on asphaltene micelles. As shown in Figure 5, 1000 ppm of TLES changes the onset to 13.4 (volume % of n-heptane).

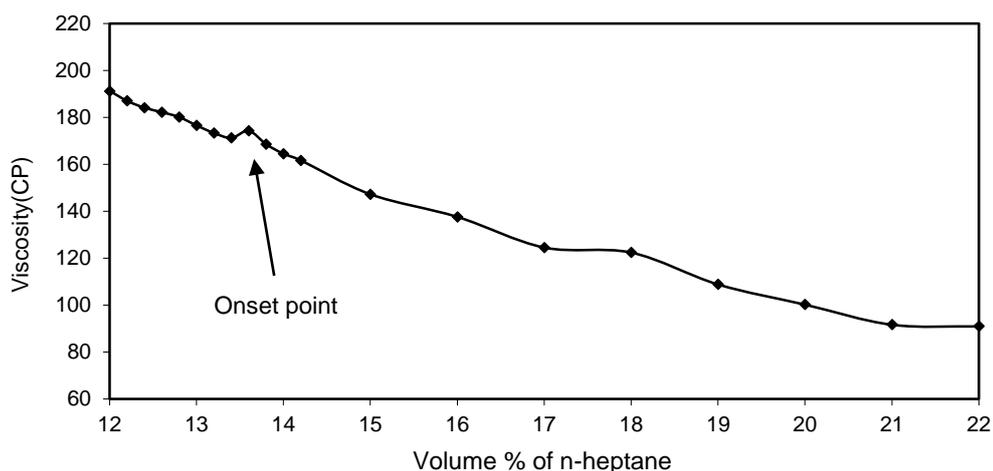


Figure 5. Determination of onset point of asphaltene precipitation of oil sample containing 1000 ppm Triethanolamine Lauryl Ether Sulfate.

Increasing the amount of TLES, at high concentrations has little effect on inhibition strength (Table 4). This behavior indicates that concentrations about

10,000 ppm of this inhibitor is sufficient to cover the surface of asphaltene micelles, and by adding inhibitor at concentrations greater than 10,000 ppm the amount of inhibitor as monomeric increases in the bulk of crude oil, so the amount of n-heptane remains constant to destabilize asphaltene particles and it causes the inhibition strength to change slightly.

3.2.4. Sodium Laurylether Sulfate (SLES)

To compare the inhibitor strength of amino group in TLES structure, the sodium laurylether sulfate (SLES) was selected to evaluate the inhibitor strength. As can be seen in Figure 6 the onset point of sample does not change ($\approx 12.2\%$). Thus, if H^+ is replaced by another group, amphiphile loses its activity, because an amphiphile must be an acid or similar to acids and also the proton of H^+ has an interaction with asphaltenes.

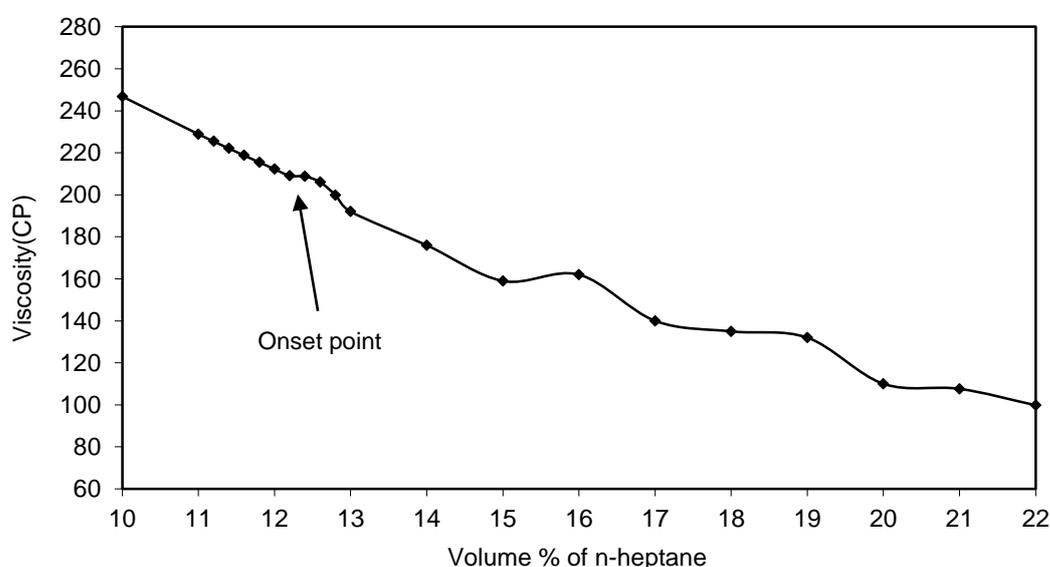


Figure 6. Determination of onset point of asphaltene precipitation of oil sample containing 1000 ppm Sodium Laurylether Sulfate.

3.3. Effects of Nonionic Inhibitors

3.3.1. Coconut Diethanolamide (CDEA)

Coconut diethanolamide (CDEA) has a similar nature to Coconut Essential Oil. The vegetable oils are the mixtures which due to their chemical nature are soluble in crude oils in large amounts and contain compounds similar to amphiphiles which are effective in the prevention of asphaltene precipitation. Table 4 and Figure 7 show the effects of different concentration of CDEA in crude oil sample. An increase in the CDEA concentration in high amounts has little effects on inhibition strength (Table 4).

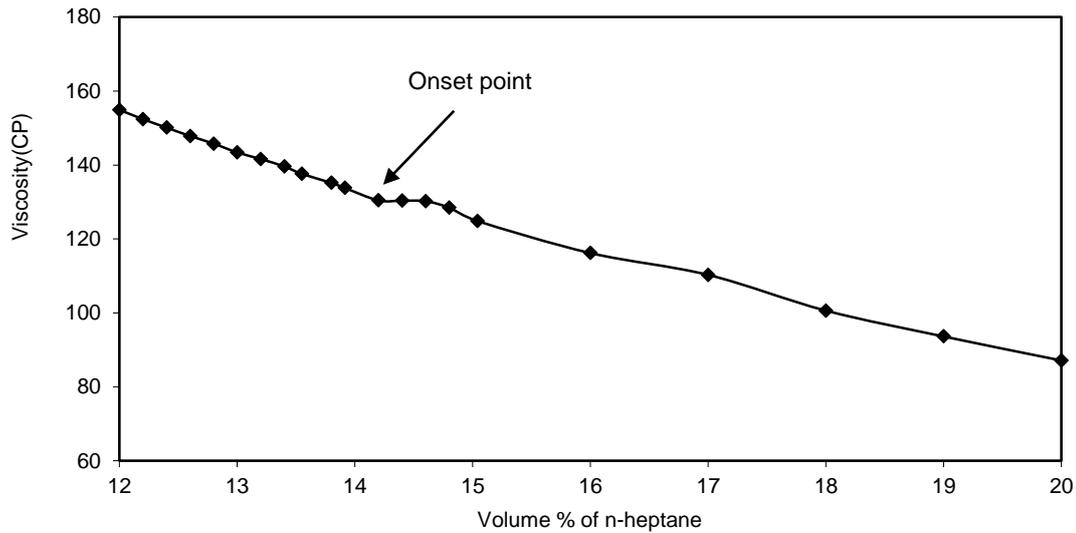


Figure 7. Determination of onset point of asphaltene precipitation of oil sample containing 1000 ppm Coconut Diethanol Amide.

3.3.2. Ethoxylated Fatty Alcohol 9 Mole

The effect of either group in hydrocarbonic chain on inhibition strength was specified by investigating Ethoxylated Fatty Alcohol 9 mole. Table 4 and Figure 8 show the onset of asphaltene precipitation in different amounts of Ethoxylated Fatty Alcohol 9 mole.

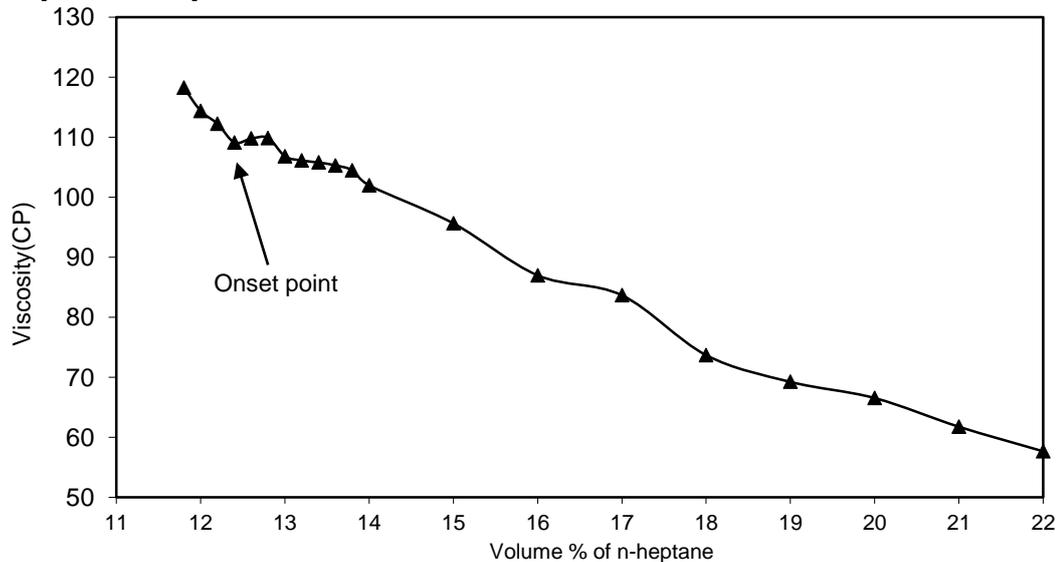


Figure 8. Determination of onset point of asphaltene precipitation of oil sample containing 1000 ppm Ethoxylated Fatty Alcohol 9 Mole.

3.4. The Comparison of Inhibition Strengths

The difference between the onset with and without inhibitor, divided by the onset without inhibitor, was introduced as a criterion to compare the strength of different inhibitors that is called "comparison index of inhibition strength". Figure 9 shows the inhibition strength of the inhibitors used in various concentrations.

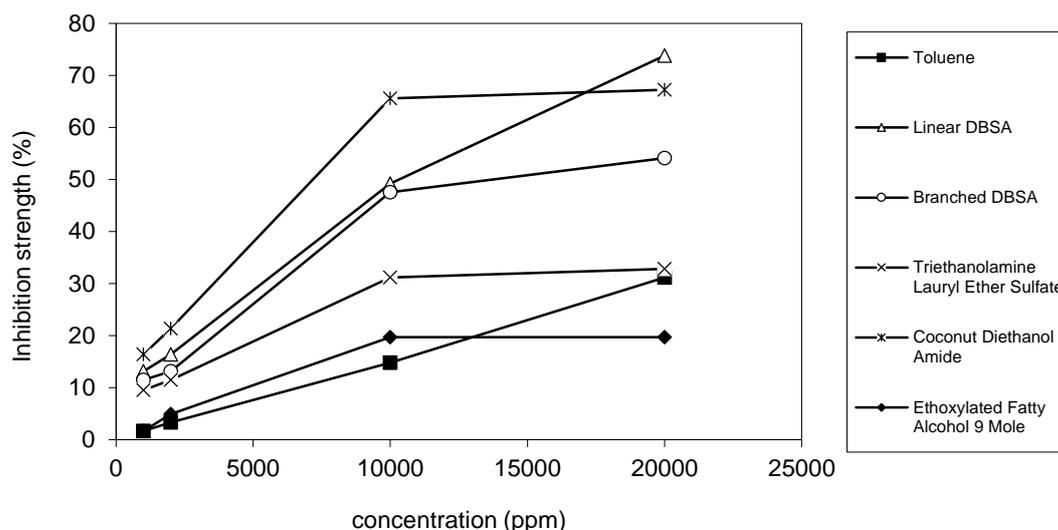


Figure 9. Inhibition strength of inhibitors used in various concentrations.

4. Conclusion

With regard to all inhibitors, the inhibition strength is increased by increasing the concentration of inhibitors up to 10,000 ppm. This behavior indicates that at low to moderate concentrations, by increasing the amounts of inhibitor, the adsorption of inhibitor on the surface of asphaltene micelles will be increased. Some of the inhibitors such as TLES, CDEA and Ethoxylated Fatty Alcohol 9 Mole, have no effect on inhibition strength by increasing their concentrations to more than 10,000 ppm. For these inhibitors, the optimal concentration is about 10,000 ppm.

The Inhibition behaviors of inhibitors at low to moderate concentrations have a regular pattern:

- Toluene has the lowest inhibition strength, because there is no polar groups and hydrocarbonic chain in its structure.
- The polar group of either in the hydrocarbonic chain of Ethoxylated Fatty Alcohol 9 Mole which causes the interaction of these chains with bulk of oil (nonpolar medium) will be less and the inhibition strength will be reduced. This observation revealed that the hydrocarbonic chains have an effective role in inhibition strength.
- Three ethyl amine groups in the chemical structure of TLES cause its inhibition strength to be greater than cocamidopropyl betaine. It should be noted that in the case of inhibitors such as TLES due to having hydroxyl polar groups, the interaction between inhibitor molecules is more than the interaction between inhibitor and asphaltene particles. Thus, the inhibitor is self-accumulated and leads to deposit at high concentrations. Also the self-accumulation of TLES caused a decrease in its inhibition strength toward CDEA which included two hydroxyl groups.
- The acidic power of SO_3H group in LDBSA and BDBSA due to interaction acid-base between H^+ and asphaltene increases the inhibition strength toward other inhibitors. Decreasing length of hydrocarbon chain by branching and steric hindrance between methyl groups reduces the inhibition strength of branched DBSA toward linear DBSA.

- Presence of acidic hydroxyl groups (OH) in CDEA's chemical structure enhances the inhibition strength toward DBSA.
- The amphiphile should be an acid or similar to an acid, because the proton of H⁺ has an interaction with asphaltenes. For this reason, SLES has no effect on the prevention of asphaltene precipitation.

References

- [1] O. C. Mullins, E. Y. Sheu, A. Hammami, and A. G. Marshall, *Asphaltenes, heavy oils, and petroleomics*: Springer, 2007.
- [2] T. A. Al-Sahhaf, M. A. Fahim, and A. S. Elkilani, "Retardation of asphaltene precipitation by addition of toluene, resins, deasphalted oil and surfactants," *Fluid Phase Equilibria*, vol. 194–197, pp. 1045-1057, 2002.
- [3] C. L. Chang and H. S. Fogler, "Stabilization of Asphaltenes in Aliphatic Solvents Using Alkylbenzene-Derived Amphiphiles. 1. Effect of the Chemical Structure of Amphiphiles on Asphaltene Stabilization," *Langmuir*, vol. 10, pp. 1749-1757, 1994.
- [4] C. L. Chang and H. S. Fogler, "Stabilization of Asphaltenes in Aliphatic Solvents Using Alkylbenzene-Derived Amphiphiles. 2. Study of the Asphaltene-Amphiphile Interactions and Structures Using Fourier Transform Infrared Spectroscopy and Small-Angle X-ray Scattering Techniques," *Langmuir*, vol. 10, pp. 1758-1766, 1994.
- [5] L. C. Rocha Junior, M. S. Ferreira, and A. C. da Silva Ramos, "Inhibition of asphaltene precipitation in Brazilian crude oils using new oil soluble amphiphiles," *Journal of Petroleum Science and Engineering*, vol. 51, pp. 26-36, 2006.
- [6] E. F. Ghouloum, M. Al-Qahtani, and A. Al-Rashid, "Effect of inhibitors on asphaltene precipitation for Marrat Kuwaiti reservoirs," *Journal of Petroleum Science and Engineering*, vol. 70, pp. 99-106, 2010.
- [7] M. Mohammadi, M. Akbari, Z. Fakhroueian, A. Bahramian, R. Azin, and S. Arya, "Inhibition of Asphaltene Precipitation by TiO₂, SiO₂, and ZrO₂ Nanofluids," *Energy & Fuels*, vol. 25, pp. 3150-3156, 2011.
- [8] J. Escobedo and G. Mansoori, "Theory of viscosity as a criterion for determination of onset of asphaltene flocculation," *SPE Tech. Pap* 28729, 1996.

بررسی اثرات بازدارنده‌های آروماتیک، آنیونی و غیر یونی بر نقطه شروع رسوب آسفالتین نفت خام

محمد مهدی شادمان^۱، مصطفی دهقانی زاده^۲، امیر حسین سعیدی دهقانی^{۳*}، محسن وفايي سفتي^۴، نادر مختاریان^۵

۱. دانشکده مهندسی شیمی، دانشگاه تربیت مدرس (m.shadman@modares.ac.ir)

۲. دانشگاه سمنان (m.dehghanizadeh@students.semnan.ac.ir)

۳. دانشکده مهندسی شیمی، دانشگاه تربیت مدرس (asaeeedi@modares.ac.ir)

۴. دانشکده مهندسی شیمی، دانشگاه تربیت مدرس (vafaiesm@modares.ac.ir)

۵. دانشگاه آزاد اسلامی واحد شهرضا (nmokhtarian@yahoo.com)

مشخصات مقاله

تاریخچه مقاله:

دریافت: ۹ شهریورماه ۱۳۹۲
پذیرش نهایی: ۲۳ آذرماه ۱۳۹۲

کلمات کلیدی:

آسفالتین،
رزین،
بازدارنده،
نقطه شروع رسوب،
رسوب،
مخزن

* عهده دار مکاتبات:

رایانامه: asaeeedi@modares.ac.ir

تلفن: +۹۸ ۲۱ ۸۲۸۸۳۳۱۴

دورنما: +۹۸ ۲۱ ۸۲۸۸۳۹۷۹

چکیده

رسوبات آلی به ویژه آسفالتین‌ها در مخازن، چاه‌ها و تجهیزات اثرات زیانباری بر اقتصاد تولید نفت دارد، زیرا سبب کاهش میزان نفت تولیدی، بسته شدن تجهیزات تولید نفت می‌شوند. اضافه کردن بازدارنده‌ها به نفت خام، باعث جلوگیری از فرآیند تجمع توده‌های آسفالتین در نفت خام می‌شوند. در این مطالعه، اثر بازدارنده‌ها بر جلوگیری از رسوب آسفالتین با روش اندازه گیری گرانیروی مورد بررسی قرار گرفت. ابتدا غلظت‌های مختلف از بازدارنده‌های آروماتیک، آنیونی و غیر یونی (۱۰۰۰ ppm، ۲۰۰۰ ppm، ۱۰،۰۰۰ ppm و ۲۰،۰۰۰ ppm) در یک نمونه نفت خام مرده تهیه شد و قدرت بازدارندگی نمونه‌ها اندازه گیری شد. نتایج نشان می‌دهد قدرت بازدارندگی بازدارنده‌ها در غلظت‌های کم تا متوسط (۱۰۰۰ ppm تا ۱۰،۰۰۰ ppm) از الگوی منظمی برخوردار است و در ارتباط با گروه‌های عاملی ساختار شیمیایی بازدارنده‌ها می‌باشد.