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Synthesis and Evaluation of Poly(dodecyl phenol formaldehyde)-*b*-Poly(oxypropylene) Block Copolymer as Asphaltene Inhibitor/Dispersant

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ABSTRACT

The main objective of the research presented herein was to developed poly(dodecyl phenol formaldehyde)-*b*-poly(oxypropylene) block copolymer for asphaltene precipitation problem and performance of some asphaltene inhibitors\dispersant for a heavy crude oil provided by the Hossia crude oil (Ras Gharib – Egyptian Eastern desert). The dispersants/inhibitors was synthesized in tow steps; 1) synthesis of poly(dodecyl phenol formaldehyde) resin (PDPF) at three different molecular weights (1936, 4047 and 8092) namely PDPF1, PDPF2 and PDPF3 respectively; 2) propoxylation of the prepared compounds to produce PDPF1-*b*-POP, PDPF2-*b*-POP and PDPF3-*b*-POP has molecular weight (3096, 5179 and 9202) respectively. All of the synthesized compounds were evaluated as asphaltene inhibitors/dispersants at 100, 500 and 1000 ppm using UV spectrophotometer. The molecular weights were determined by GPC. The chemical structure of the prepared compounds was confirmed by IR and H^1NMR. The crude oil was analyzed by GC. The results also revealed distinct inhibition of asphaltene precipitation in crude oils.

Introduction

Deposits formation during petroleum production causes several operational troubles such as total or partial blocking of pipelines and reservoirs, such as asphaltenes, resins and paraffin. Due to their aggregative nature [1-3] asphaltene and resins are important deposit forming crude oils heavy fractions. These fractions are constituted by molecules with polycondensated aromatic rings and lateral aliphatic chains, acid–base functional groups and complexed metals, varying in size as well as in their aggregation tendency. [4]

Asphaltenes are a mixture of approximately a million different chemical structures that are characterized by their high aromaticity (~50% aromatic carbons) and high molecular weight. Asphaltenes are usually defined as the most polar fraction of crude oil that are soluble in aromatic solvents such as toluene but insoluble in normal alkanes as *n*-heptane, have molecular-scale sizes in the nanometer range [5,6].

This property is used for the separation of asphaltenes. The above definition is in some sense arbitrary, as the molecular structure of asphaltenes varies significantly depending on their origin, method of oil recovery, and history of extraction.[7]

The nonpolar nature of petroleum systems requires special care in understanding and controlling the factors which can stabilize colloidal asphaltenes. Dispersant type plays an important role in determining how such stabilization occurs in nonpolar suspensions

Chang and Fogler [8], found that the head group of the amphiphile influenced the effectiveness of the amphiphiles, using a series of alkylbenzene-derived amphiphiles as the asphaltenes stabilizers; also, he investigated the influence of the chemical structure on the asphaltenes solubilisation and on the strength of the amphiphile-asphaltenes interactions. Their results showed that the polarity of the amphiphile head group and the length of the alkyl tail controlled the amphiphile effectiveness.

[9]Stephenson and Kaplan and Stephenson and co-workers used an alkyl-substituted phenol-formaldehyde liquid resin with a hydrophilic-lipophilic vinylic polymer as asphaltene dispersants/inhibitors.

Many studies have been conducted on the growth of colloidal asphaltenes particles in hydrocarbon solutions; the flocculation of asphaltenes particles under hydrodynamic shear flow has not been investigated. It bears a significant implication in industrial applications. A mixture of toluene and n-heptane is often used to investigate the stability and the precipitation of asphaltenes. At a certain threshold value of the ratio of n-heptane to toluene, the asphaltenes in solution becomes unstable and asphaltenes particles start to precipitate. It is found that when a concentrated solution of asphaltenes in toluene is added to excess heptane, the precipitated asphaltenes growth from micrometer-sized primary particles increase. [10-12**]**

Flocculations onset points are detecting by several techniques have been proposed in the literatures that are basically directed toward a solution of the product titrated with different ratios of n-heptane: toluene until a solid phase is observed. Such techniques were used like the Oliensis spot test [13] (Taxler, R.N., 1961) using examination of drops applied on filter paper, conductivity measurements, viscosimetry [14] (Jacoby, R.H., 1984;), [15] fluorescence spectroscopy,[16] particle size analysis,[17] heat transfer analysis,[18] microscopic examination of solutions,[19-20] optical transmission and light scattering by particles,[21,22] and by measurement of the interfacial tension. [23, 24].

This work pertains to evaluate the effect of various molecular weights of the prepared polydodecyl phenol formaldehyde resin and its propoxilation derivatives on

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asphaltene inhibition/dispersion of Egyptian asphaltenic heavy crude oil, using UV spectrophotometer technique.

Experimental

Materials

dodecylophenol, formaldehyde, oxypropylene gas, HCl, *p*-toluene sulfonic acid (PTSA), Toluene, *n*-heptane, anhydrous sodium sulfate, benzene. These materials were obtained from Aldrich Chemical Co.

Characterization of crude oil

The crude oil used in this work came from Hossia field (Ras Gharib – Egyptian Eastern desert). The asphaltenes were separated from crude according to procedure described in ASTM D 6560–00(25). The crude oil was analyzed by GC and the physical properties were measured according to ASTM methods, the results were shown in **Table 1**. The photograph of separated asphaltenes is given in **Figure1**.

Figure 1. Photograph of asphaltenes sample

Molecular Weight Determination

Analytical gel- permeation chromatograph water 600 E was used for the determination of molecular weights of the separated asphaltenes by using styragel columns at 408C, flow rate 0.7 ml/minute. The refractive index instrument model Water 4110 was used as a detector, and toluene HPLC grade as a mobile phase.

Synthesis of poly(dodecyl phenol formaldehyde) resin(PAPF)

One mole of dodecyl phenol with 1.2 or 1.4 mole formaldehyde 37% respectively were placed in 4 necks flask fitted with condenser, mechanical stirrer, thermometer and a dropping funnel. 2% of the total weight concentrated HCl was placed in the dropping funnel and added drop wise with continuous stirring for 1 hour. After the addition of HCl had completed the temperature of the reaction raised gradually by heating jacket to 110 ^{o}C. The temperature is maintained at this level for one hour. The temperature was thus raised to 150 ^{o}C. The reactants were allowed to stand at this temperature for another 3, 6, 9 and 12 hour to get different molecular weights. The product was then cooled and dissolved in benzene, washed with 10% NaOH until neutrality has been reached and then dried after phase separation of aqueous phase over anhydrous sodium sulfate. The benzene was then removed by means of a rotary evaporator [26, 27]. The molecular weights of polymer were determined using GPC and listed in **Table 2**.

Synthesis of Poly(dodecyl phenol formaldehyde)-b-Poly(oxypropylene) (PAPF-b-POP)

0.1mole of poly(dodecyl phenol formaldehyde) was charged Into 300mL autoclave. The nitrogen gas was flashed into the system for 5 minutes. The propylene oxide gas introduced to the system under pressure (50 mm Hg). The temperature was raised to 130-160 ^{o}C in the presence of 0.1 % of Na-metal as a catalyst till the desired amount of propylene oxide content was obtained [28,29].

Characterization of the synthesized *poly(dodecyl phenol formaldehyde) resin(PdPF) and Poly(dodecyl phenol formaldehyde)-b-Poly(oxypropylene)*

Infrared spectra of prepared polymer were carried out recorded in polymer /KBr pellets using Mattson- Infinity series FTIR Bench Top961.

The molecular weights of prepared *poly(dodecyl phenol formaldehyde) resin(PAPF) and Poly(dodecyl phenol formaldehyde)-b-Poly(oxypropylene)* Were measured by gel permeation chromatography (GPC) water model 600E. The measurements were recorded at 30°C, under UV-visible spectrophotometer water, mobile phase toluene HPLC grade, column, styragel columns and injection volume.

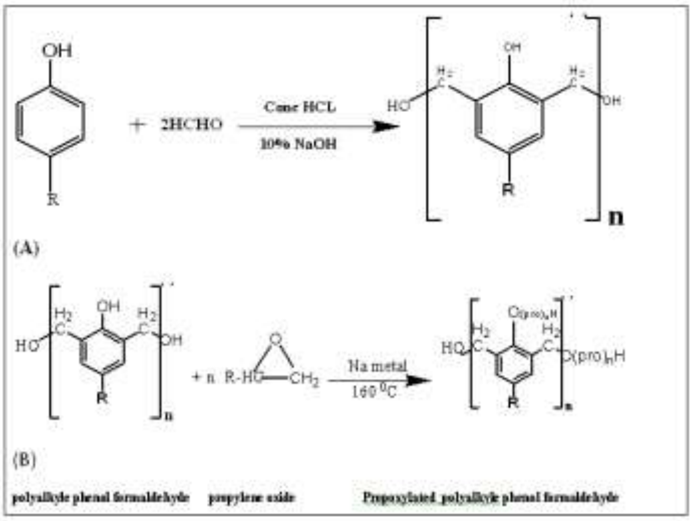

Figure (2): Reaction scheme of A- Synthesized poly(dodecyl phenol formaldehyde) resin(PAPF), B- Synthesized propxylated polydodecylphenol formaldehyde respectively

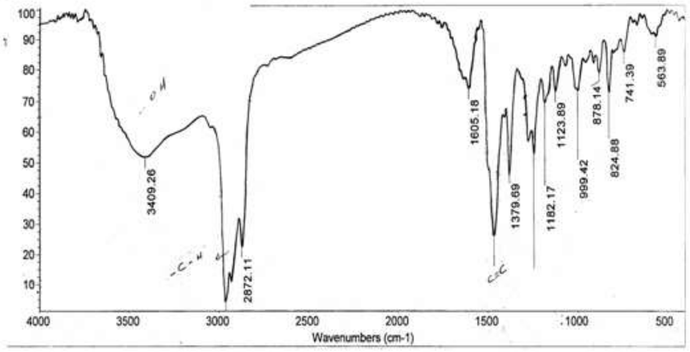

Figure 3: FTIR spectrum of polydodecylphenol formaldehyde

Determination of Onset Point of Asphaltenes Using UV Spectra

Onset points depends on decreasing the optical density of precipitate asphaltenes and are detecting using ultra violet spectrophotometer Shimadzu 120–02 at a wavelength of 190-340 nm.[30,31] In this respect, stock solutions of 0.01 g of Hossia crude oil were dissolved in a mixture of toluene: n-heptane of (20:80, 30:70, 40:60, 50:50, 60:40, 70:30, and 80:20, respectively). Samples of 5 ml of each solution were added to a number of small vials and then vigorously shaken until the mixture appears homogeneous. Then the mixture was allowed to rest at ambient conditions for one day before observation.

After aging for one day, a few drops of each mixture was removed from the vials then centrifuged at 3000 rpm for 30 min in a Beckman TJ-6 centrifuge (relative centrifugal field 1300 g). Measurements of absorbance were carried out for the clear solution at a wavelength from 190 to 340 nm as a function of interval time from 15 minute up to one hour. The experiments were repeated again in presence of different concentration of 100, 500, and 1000 ppm of asphaltenes dispersants as intervals for each vial followed by vigorously shaking until the mixture appears homogeneous. Then the absorbance was measured as before.

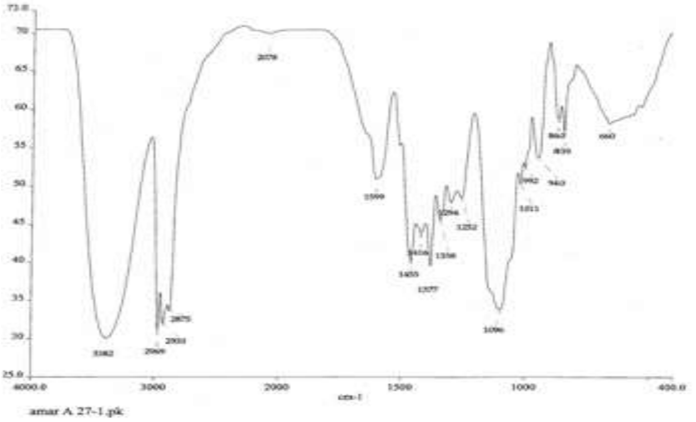

Figure 4: FTIR of prpoxylated polydodecylphenolformaldehyde

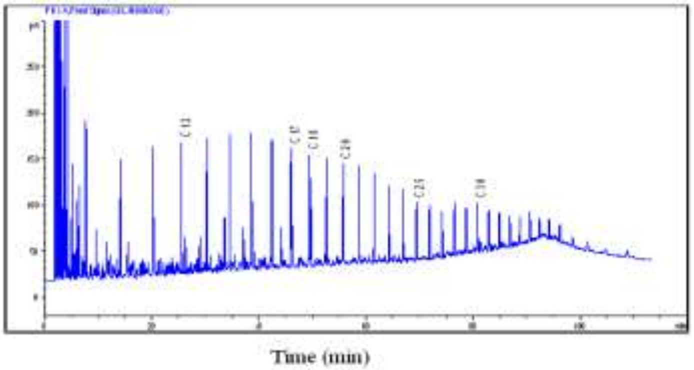

Figure 5: Chromatogram of paraffins extracted from Hossia oil field

Results and discussion

Asphaltenes are the most polar and heaviest component of crude oil, manifests itself in almost all facets of production, transportation, and processing of crude oil. The economic implications of this problem are tremendous considering the fact that a problem work over cost each time could get as high as a million dollars. Asphaltenes precipitation deep inside the reservoir can cause partial or complete blockage of porous media, thus resulting in damage of the reservoir and loss of crude oil recovery [32, 33].

Synthesis of polydodecylphenol formaldehyde

Different molecular weights at different reaction times of poly(dodecyl phenol formaldehyde) resin (PDPF) and poly(dodecyl phenol formaldehyde)-*b*-poly(oxypropylene) block copolymers (PDPF-*b*-POP), were prepared as described in the experimental section. The reaction scheme of the synthesis are listed in **Figure 2.**

Characterization of the prepared polymers and dispersant

The FTIR spectrum of Polydodecylphenol formaldehyde which is represents in **Figure 3** shows the following characteristic peaks :- Absorption bands at 2982 cm-1 (assigned for stretching vibration of the aliphatic CH bond), the appearance of beak at 1605 cm_1 (assigned for stretching vibration of the C=C). The appearance of peak at 1620 cm_1 (assigned for stretching vibration of the (C=C) indicate the presence of unsaturation, 1450 cm_1 (assigned for stretching CH2), 1375 assigned for CH3 peak. The appearance of sharp band at 3409 cm-1 (assigned for OH stretching band). The disappearance of HC=O cm_1 peak (confirm the completion of condensation reaction).

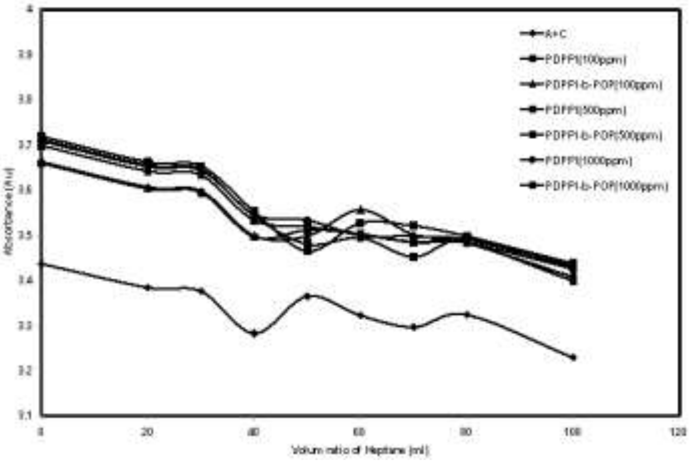

Figure (6): Relation between Absorbance and onset point of aggregated asphaltenes as a function of heptane/ toluene ratio with and without PDPF1 or PDPF1-*b*-POP dispersant

FTIR spectrum of dodecyl phenol formaldehyde)-b-Poly(oxypropylene) (PAPF-b-POP) was represented in **Figure 4**. The data reveals the following characteristic peaks: -Absorption bands at 2926 cm-1 (assigned for stretching vibration of the aliphatic CH bond), the appearance of beak at 1605 cm_1 (assigned for stretching vibration of the C=C). Band at 1450 cm_1 (assigned for stretching CH2), 1375 assigned for CH3 peak. The appearance of sharp band at 3409 cm-1 (assigned for OH stretching band). The chemical structure of the prepared polymers and copolymers was also confirmed by 1HNMR as described the previous research [27].

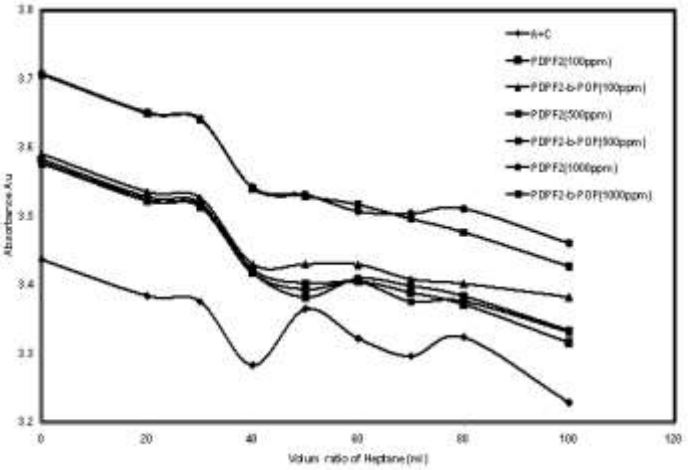

Figure (7): Relation between Absorbance and onset point of aggregated asphaltenes as a function of heptane/ toluene ratio with and without PDPF2 or PDPF2-*b*-POP dispersant

The molecular weights of poly(dodecyl phenol formaldehyde) resin(PDPF) and prpoxylated dodecyl phenol phenol formaldehyde were determined by GPC and summerized in Table 2, Generally, molecular weight of the prepared poly(dodecyl phenol formaldehyde) resin increase with increasing reaction time and the molar ratio of formaldehyde.

Table 1: Hossia Crude Oil Specification

Test required	**Method**	**Units**	**Value**
Kinematics Viscosity 60°C	IP71	cst	100,71
Water Content		*Vol %*	,2
Density at 60° C	IP160	*g/ml*	,9376
Pour Point		° C	+9
Asphaltenes Content,	IP143	Wt. %	11,68
Sulphur Content	D5453	, ppm	39125.7

Table 2: molecular weights of polydodecylphenol formaldehyde and prpoxylated polydodecyl phenol formaldehyde by GPC

Sample		**Molar ratio of formaldehyde**	**Reaction time (Hour)**	**Molecular weight (g)**	
				(PDPF)	**(PDPF3-*b*-POP)**
poly(dodecyl phenol formaldehyde) **(PDPF)**	propxylated polydodecyl phenol formaldehyde **(PDPF3-*b*-POP)**	1.2	3	3091	1936
			6	5197	4037
			9	-	6087
			12	8382	7222
		1.4	3	-	2200
			6	6361	5200
			9	9200	8094
			12	-	12167

Table 4: The absorption spectra data of the asphaltene in absence and presence of different concentrations of PDPF1 dispersant

Volume ratio of Heptane (ml)	**A+C (blank)**	**100ppm**	**500ppm**	**1000ppm**
0	3.436275	3.718773	3.659003	3.711577
20	3.3838	3.661984	3.603126	3.654898
30	3.3754	3.652894	3.594182	3.645825
40	3.282725	3.5526	3.4955	3.545725
50	3.364575	3.464575	3.51135	3.533125
60	3.32185	3.52695	3.50295	3.499125
70	3.296025	3.520325	3.48345	3.497025
80	3.3234	3.4976	3.482775	3.48195
100	3.2285	3.437175	3.425425	3.407475

Table 5: The absorption spectra data of the asphaltene in absence and presence of different concentrations of PDPF1-*b*-POP dispersant

Volume ratio of Heptane (ml)	**A+C (blank)**	**100ppm**	**500ppm**	**1000ppm**
0	3.436275	3.6623	3.6981	3.708332
20	3.3838	3.606373	3.641626	3.651702
30	3.3754	3.597421	3.632586	3.642637
40	3.282725	3.49865	3.53285	3.542625
50	3.364575	3.49825	3.51875	3.4796
60	3.32185	3.50635	3.501025	3.49395
70	3.296025	3.501325	3.48505	3.45215
80	3.3234	3.490225	3.4831	3.49045
100	3.2285	3.4315	3.398325	3.4333

Table 6: The absorption spectra data of the asphaltene in absence and presence of different concentrations of PDPF2 dispersant

Volume ratio of Heptane (ml)	**A+C (blank)**	**100ppm**	**500ppm**	**1000ppm**
0	3.436275	3.582536	3.577878	3.707442
20	3.3838	3.527827	3.52324	3.650826
30	3.3754	3.51907	3.514494	3.641763
40	3.282725	3.42245	3.418	3.541775
50	3.364575	3.402025	3.381625	3.5313
60	3.32185	3.405	3.408825	3.50675
70	3.296025	3.3886	3.39815	3.503325
80	3.3234	3.371325	3.3835	3.5106
100	3.2285	3.315675	3.33365	3.4603

Table 3: the average molecular weight distribution of paraffins of hossia crude oil

Components	Mol. %	Wt. %
Propane	0.715	0.202
i-Butane	0.688	0.256
n-Butane	2.811	1.045
i-pentane	3.125	1.442
n-Pentane	3.817	1.761
Hexanes	10.250	5.648
Heptanes	10.988	7.041
Octane	15.455	11.289
Nonanes	10.278	8.430
Decanes	5.416	4.927
Undecanes	4.325	4.323
Dodecanes	2.901	3.160
Tridecanes	3.603	4.248
Tetradecanes	3.375	4.281
Pentadecanes	2.812	3.820
Hexadecanes	2.718	3.936
Heptadecanes	2.566	3.945
Octadecanes	2.983	4.855
Nonadecanes	1.439	2.471
Eicosanes	1.275	2.304
Eneicosanes	1.005	1.907
Dodeicosanes	0.949	1.885
Tricosanes	0.524	1.088
Tetraicosanes	0.740	1.602
Petaicosanes	0.462	1.043
Hexaicosanes	0.453	1.061
Heptaicosanes	0.937	2.282
Octaicosanes	0.399	1.006
Nonaicosanes	0.423	1.106
Tricontanes	0.575	1.556
Entricontanes	0.342	0.957
Dodetricontanes	0.338	0.975
Tritricontanes	0.377	1.121
Tetratricontanes	0.261	0.798
Pentatricontanes	0.152	0.479
Hexatricontanes	0.151	0.490
Hepatricontanes	0.161	0.535
Octatricontanes	0.110	0.375
Nonatricontanes	0.100	0.351
Total	100.000	100.000
Mol.Wt	156.382	

Table 7: The absorption spectra data of the asphaltene in absence and presence of different concentrations of PDPF2-*b*-POP dispersant

Volume ratio of Heptane (ml)	A+C (blank)	100ppm	500ppm	1000ppm
0	3.436275	3.590229	3.576491	3.706003
20	3.3838	3.535403	3.521874	3.649409
30	3.3754	3.526627	3.513132	3.640349
40	3.282725	3.4298	3.416675	3.5404
50	3.364575	3.43005	3.393475	3.52855
60	3.32185	3.429375	3.403975	3.516525
70	3.296025	3.407975	3.3754	3.495725
80	3.3234	3.40165	3.376125	3.476325
100	3.2285	3.38185	3.33125	3.42665

Table 8: The absorption spectra data of the asphaltene in absence and presence of different concentrations of PDPF3 dispersant

Volume ratio of Heptane (ml)	A+C (blank)	100ppm	500ppm	1000ppm
0	3.436275	3.696477	3.689333	3.685774
20	3.3838	3.640029	3.632993	3.629489
30	3.3754	3.630993	3.623975	3.620479
40	3.282725	3.5313	3.524475	3.521075
50	3.364575	3.538975	3.52915	3.500375
60	3.32185	3.4719	3.52135	3.510375
70	3.296025	3.515475	3.506275	3.499125
80	3.3234	3.501125	3.47695	3.4834
100	3.2285	3.352875	3.397475	3.444

Table 9: The absorption spectra data of the asphaltene in absence and presence of different concentrations of PDPF3-*b*-POP dispersant

Volume ratio of Heptane (ml)	A+C (blank)	100ppm	500ppm	1000ppm
0	3.436275	3.693834	3.680749	3.71265
20	3.3838	3.637426	3.624541	3.655954
30	3.3754	3.628396	3.615543	3.646879
40	3.282725	3.528775	3.516275	3.54675
50	3.364575	3.524725	3.5003	3.5245
60	3.32185	3.5011	3.48535	3.529175
70	3.296025	3.499175	3.505575	3.537775
80	3.3234	3.477625	3.48865	3.517575
100	3.2285	3.4176	3.391675	3.47875

This may be reveals that with increasing reaction time and the molar ratio of formaldehyde moiety facilitates propagation of the polycondensation reaction and hence increase the molecular weights. Three different molecular weights of (PDPF) resin were chosen and propoxylated with polypropelene oxide as described in experimental part. The five molecular weights of prpoxylated dodecyl phenol phenol formaldehyde were also determined by GPC and listed in **Table 2**. The same results were found, molecular weight increase with increasing reaction time and the molar ratio of formaldehyde.

Evaluation of the synthesized **(PDPF) and (PAPF-b-POP)** *as asphaltene inhibitior /dispersant*

A possible way of avoiding asphaltenes precipitation by adding different polymers which disperse the asphaltenes precipitated in solution by delaying the point. Therefore, this study aims to investigate the peptization of asphaltenic crude oil by various oil-soluble polymers [34].

including long-chain hydrocarbon in the form of polyalkylphenol formaldehyde and it s propyxylated one were synthesized and examined as asphaltenes inhibitors [35,36], and their influence on the solubility and reduction of the precipitation were also investigated based on the lag of onset point and increasing of fluidity of viscous crude oils [37]. The experiments were performed by continuously measuring the change in absorbance at 190-340 nm wavelength, upon addition of chemicals, in a solution of asphaltenes in heptane /toluene (100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 respectively by volume).

On the other hand, in this work, the precipitation onset was used just as reference to estimate the additive's effectiveness to hold the asphaltene within the oil phase. Recentworks [38,39] crude oil nature or the structural characteristics of the asphaltene molecules; yet, they also show that the asphaltene stabilization mechanism is equally a function of the additive's nature. In some cases, the effectiveness can be related with a significant decrease in the amount of precipitated asphaltene, not necessarily occurring onset shifting [40]. Yet, it can be verified that the conditions along the processing and production of crude oils are different from those found in the laboratory and, in this case, our results furnish only an indication that supposedly favors the practical use of these substances that, for sure, need further accurate estimation under field conditions.

Hossia crude oil (Ras Gharib – Egyptian Eastern desert) was used for evaluating the performance of the poly(dodecyl phenol formaldehyde) resin(PDPF) and prpoxylated dodecyl phenol formaldehyde copolymers. Their physico-chemical characteristics are given in **Table 1**. In addition, the paraffin content of the tested crude oil was determined using gas-liquid chromatographic analysis for determination the average molecular weight distribution of paraffins **and listed in Table 3.** Histogram of the paraffin content of Hossia crude oil presents in **Figure 5**.

This part of our study is focusing on determining the quantity of light absorption after precipitation. In this respect, each mixture of heptane, toluene and crude oil with and without dispersant have been centrifuged at 3000 rpm for 30 min to precipitate the asphaltenes, dissolved in a fixed amount of toluene and their absorption then measured at a wavelength 190-700 nm using UV spectroscopy. The absorption spectra of the Hossia crude oil in absence and presence of different concentrations (100, 500 and 1000ppm) of prepared polydodecyl phenol formaldehyde (Mwts 1936, 4047 and 8094 namely PDPF1, PDPF2 and PDPF3 respectively), prpoxylated polydodecyl phenol formaldehyde (Mwts 3091, 5197 and 9200 namely PDPF1-*b*-POP, PDPF2-*b*-POP and PDPF3-*b*-POP respectively) of asphaltenes concentrations in heptane/toluene solutions were listed in **Tables (4-9)**. The data reveals that the amount of heptanes used to disperse asphaltene particles (onset point) in asphaltene solution of tested crude oil (A-C blank) is 40ml and 3.282725 Au absorbance. The data show that, precipitation onset point increase compared to blank by increasing the additives concentrations and by increasing the molecular weights. This may be attributed to compatibility between asphalting and the additive particles.

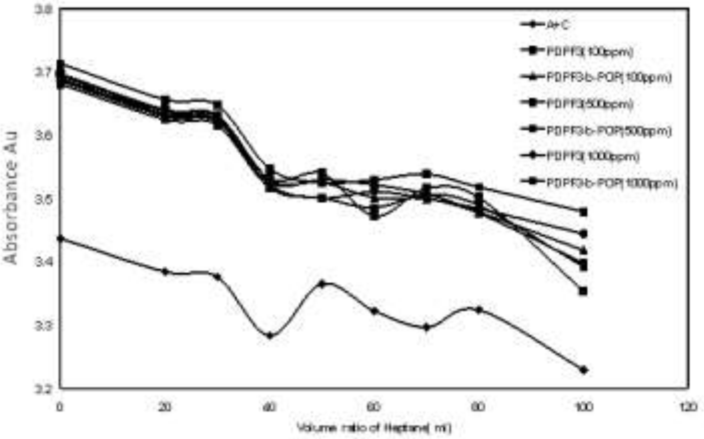

Figure (8): Relation between Absorbance and onset point of aggregated asphaltenes as a function of heptane/ toluene ratio with and without PDPF3 or PDPF3-*b*-POP dispersant

Figures (6-8) show the relation between the absorbance and onset precipitation of aggregates asphaltene in absence and presence of different concentrations of tested dispersants. . The graves illustrate the fact that polydodecyl phenol formaldehyde (Mwts 1936, 4047 and 8094) additives present lower precipitation onset compared with prpoxylated polydodecyl phenol formaldehyde (Mwts 3091, 5197 and 9200). This means that the charge interaction between propoxylated additives and asphalting charge particles more than polydodecyl phenol formaldehyde additives interaction.

This may be explained by the lack of interaction between the alkyl chain moieties of dodecyl phenol formaldehyde monomer in the structure of polydodecyl phenol formaldehyde polymer with the average carbon number of the n-paraffin of the asphaltene component. On the other hand, oxypropylene monomer moiety in dodecyl phenol formaldehyde)-b-Poly(oxypropylene) (PAPF-b-POP) copolymer shows a good match of alkyl chain lengths with the average carbon number of the asphaltene as shown from Figure 4 and Table 3.

Finally the plots show the synthesized additives acted as inhibitors of asphaltenes precipitation in the evaluated concentrations and tested crude oil.

Conclusion

- The molecular weights of poly(dodecyl phenol formaldehyde) resin(PDPF) and prpoxylated dodecyl phenol formaldehyde increase with increasing reaction time and the molar ratio of formaldehyde.
- Precipitation onset point increase compared to blank by increasing the additives concentrations and by increasing the molecular weights.
- The efficiency of propoxylated additives as a *asphaltene dispersants is higher than* polydodecyl phenol formaldehyde additives
- The synthesized additives acted as inhibitors of asphaltenes precipitation in the evaluated concentrations and tested crude oil.

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