CHAPTER-3 (I)

EVALUATION OF POLYMERIC FLOW IMPROVERS OR POUR POINT DEPRESSANTS ON KOSAMBA-47 (GUJARAT, INDIA) CRUDE OIL

The purpose of the invention is served when PPDs are introduced into selected Kosamba-47, Kosamba-33 and Bombay High crude oils. Here the PPDs introduced are having straight chain polymeric backbone made up of short chain ester-maleic anhydride-long chain ester terpolymer. The pendant alkyl chain attached to main polymer backbone varies greatly which are formed from fatty and aromatic alcohols. Composition of crude oil varies based on its source and hence PPDs are made to suite that particular crude oil. Hence the search for universal effective pour point depressant continues. Very often it has been observed that additives showing high efficacy in pour point depression are not effective in decreasing viscosity and yield stress and vice versa. However, the crude oils containing asphaltenes show different activities compared to not having asphaltenes or low content towards pour point depression. The type of crude oil and its asphaltenes proportion impacts additives pour point depression activity.

According to the objective of this work, the synthesized additives are tested on highly waxy crude oil from Kosamba field and light crude oil from Bombay High.

3.1.1 Physico-Chemical Properties of Kosamba-47 crude oil

Kosamba-47 crude oil is medium to high density oil. The sample taken is from a particular well from Kosamba field. Kosamba-47 crude oil is highly waxy as it has almost 20 % of wax and shows pour point of 39 ^{o}C which is a problem in summer season also. This amplifies in winter season when temperature goes below 20^{o}C and makes it difficult to handle. The physico-chemical properties of Kosamba-47 crude oil is as shown in table 3.1.

Table 3.1: Physico-Chemical Properties of Kosamba-47 crude oil

S. No.	Parameter	Method	Unit	Result
1	Free water	-	%	Nil
2	Water content	IP-358	%	1.0
3	Density at 15^{o}C	IP-160	Kg/l	0.8743
4	Specific Gravity	IP-200	-	0.8748
5	API Gravity	-	-	30.25
6	Pour Point	IP-15	^{o}C	39
7	Wax content	UOP-46-64	%	19.65
8	Asphaltenes Content	IP-143	%	0.51
9	Saturate	-	%	68.74
10	Aromatic	-	%	23.40
11	Resin Content	-	%	7.35

3.1.2 Pour Point Determination

Standard method ASTM D-97/IP-15 was employed for pour point determination of crude oil under study. During pumping and transportation of crude oil, it is subjected to thermal treatment and also it experiences the shear. It is very important to remove the crude oil sample memory for establishing a repeatable starting point. To ensure this, heating of oil was done above Non-Newtonian temperature limit. Above wax crystallization temperature, thorough mixing is done for complete dissolution of wax crystals and of asphaltene micelles.

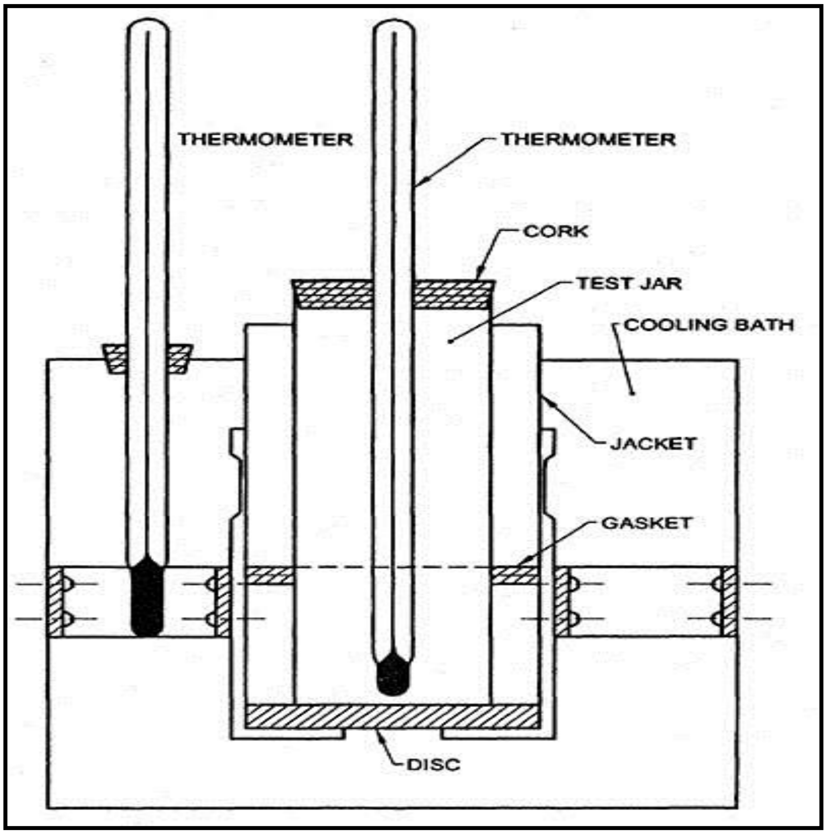

Fig. 3.1 Apparatus for Pour Point Determination

For pour point determination of neat crude oil, 50 ml of neat oil sample was taken and transferred into 250 ml reagent bottle. At this stage, crude oil has totally non-Newtonian behavior. The measured crude oil samples were heated at 60±1 ^{o}C in water bath for 30 minutes. At this temperature, the crude oil shows Newtonian behavior by dissolving wax crystals completely. The neat crude oil sample was transferred to pour point tube. The pour point tube was kept in pour point apparatus surrounded by ice bath. After each 3^{o}C interval, the pour point tube was taken out from the apparatus and tilted to see the flow of oil. When oil stops flow the pour point of the neat crude oil is noted. After that, the required concentration of the additive was added to the neat crude oil and the contents were shaken vigorously for 5 minutes to make uniform mixture. Again the sample is maintained at 60±1 °C for 30 minutes and transferred to pour point tube and cooled to 48 °C, kept in pour point apparatus surrounded by ice bath. After each 3°C drop interval, the pour point tube is taken out from the apparatus and tilted to see flow of oil. The pour point of additive treated crude oil was noted. The pour point data of neat Kosamba-47 crude oil and additive treated crude oil is tabulated in table 3.2.

3.1.3 Rheological Studies

For Newtonian Fluids, shear stress is proportional shear rate. There exists non-linear relationship between shear stress and shear rate for pseudo plastic and dilatant fluid. Pseudo plastic fluid with yield stress follows Herschel-Bulkley model while that without yield stress follows power law model.

$$\tau_{xy} = \tau_0 + K\left[\frac{dvx}{dy}\right]^n$$

Where n=shear rate, τ_o = Yield Stress.

Bingham plastic and Casson type fluid are non-Newtonian fluid with yield stress and are called Viscoplastic materials. At low temperature viscoplastic behavior is observed by waxy crude oils. Non-linear relation in shear rate and shear stress with yield stress is observed in case of Casson fluid. But in case of Bingham fluid, linear relationship exists while viscosity decreases with increase in shear rate (shear thinning) requiring finite shear stress called yield stress to initiate flow. Mathematically,

$$\sigma = \sigma_y + \eta_p\left(\frac{du}{dr}\right)$$

σ = Shear stress (Pa), σ_y = Bingham yield stress, η_p = plastic viscosity (Pa.s) du/dr = shear rate (S^{-1}). This model has been applied to many waxy crude oil. Experimental data has been fitted to Bingham plastic flow model so viscosity and yield stress of virgin and additive treated Kosamba crude oil was measured by zero friction advanced rheometer AR-1500 ex of TA instrument configured with smooth stainless steel truncated cone plate geometry (4 cm in diameter, cone angle of 2° and truncation of 55 μm) and equipped with a Peltier plate temperature control device using this model.

To remove the crude oil sample memory, the crude oil sample was subjected to 60±1 °C for 30 minutes. Then PPD was added at 60±1 °C. The required experimental temperature was regulated under controlled conditions of shear rate and cooling rate due to the sensitivity of measured flow properties to shear and thermal history.

Rheology study of treated and virgin Kosamba-47 crude oil was carried out by AR 1500 ex rheometer at various shear rate and temperature. The respective oil samples were placed on sample platform and geometry was attached. Temperature regulation was done with peltier element inside the plate without any error.

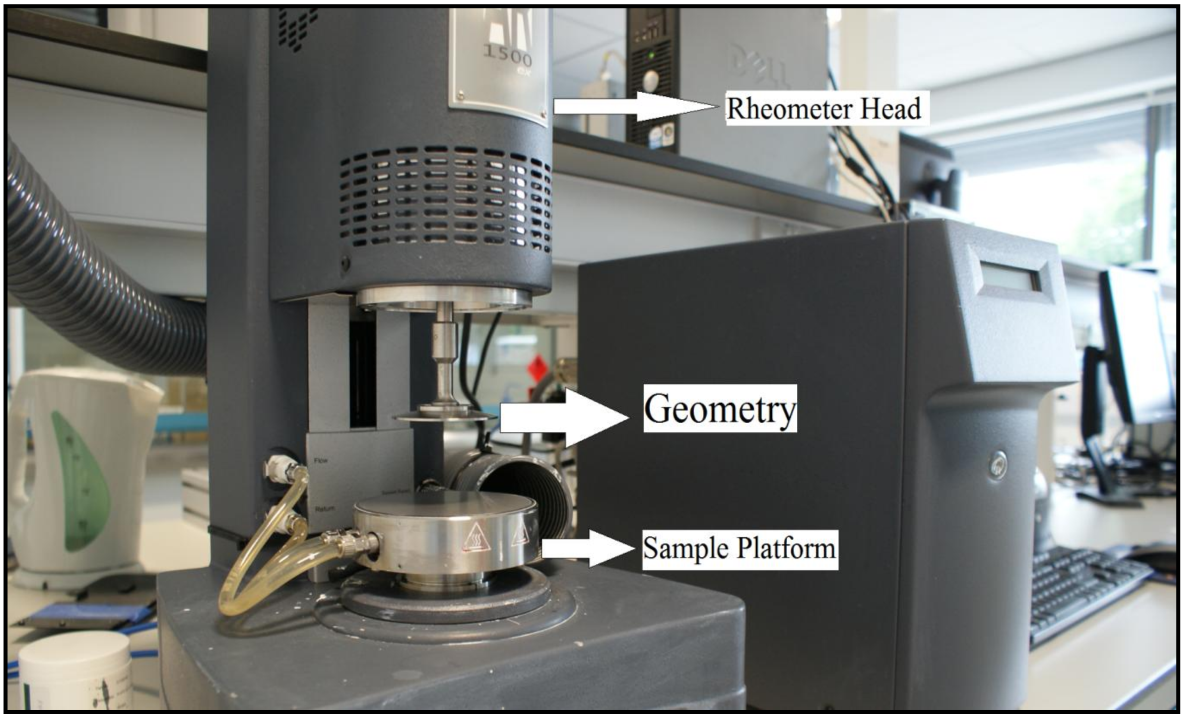

Fig. 3.2 TA AR 1500ex Rheometer Courtesy-http://www.uk-cpi.com

Initially for virgin Kosamba-47 crude oil, shear stress and viscosity were measured at various shear rates. The range for shear rate started from 25 S^{-1} up to 250 S^{-1} with rise of 25 S^{-1} intervals. Once the plot for Shear Rate v/s Shear stress and Viscosity was obtained, Bingham flow model was applied to the obtained curve and values of viscosities and yield stress were calculated.

The above mentioned process was repeated for Kosamba-47 crude oil treated with chemical additives with different concentrations.

The values of viscosities and yield stress for selected additives obtained at various temperatures are as shown in Table 3.3.

3.1.4 Results and Discussion

3.1.4.1 Evaluation of Polymeric Additives as Pour Point Depressants

Table 3.2 Pour point data of Neat and treated Kosamba-47 crude oil

Kosamba-47	Temperature (^{o}C)							
Sample Code	**Virgin Crude**	**100 ppm**	**200 ppm**	**400 ppm**	**500 ppm**	**1000 ppm**	**Maximum depression in pour point**	**Extent of pour point depression**
8-6UA18N	39	36	36	36	36	36	36	3
8-10UA18N	39	36	36	36	36	36	36	3
8-12UA18N	39	36	36	33	33	33	33	6
8-14UA18N	39	33	33	33	33	30	30	9
8-16UA18N	39	33	33	33	33	33	33	6
8-18UA18N	39	36	33	33	33	33	33	6
8-22UA18N	39	36	36	36	36	33	33	6
8-6CA18N	39	27	27	27	27	30	27	12
8-10CA18N	39	30	30	30	30	30	30	9
8-12CA18N	39	30	30	30	30	30	30	9
8-14CA18N	39	30	30	30	30	30	30	9
8-16CA18N	39	30	30	30	30	30	30	9
8-18CA18N	39	27	27	30	30	30	27	12
8-22CA18N	39	30	30	30	30	30	30	9
8-6RA18N	39	36	36	36	36	36	36	3
8-10RA18N	39	36	36	36	33	33	33	6
8-12RA18N	39	36	36	36	36	33	33	6
8-14RA18N	39	33	33	33	30	30	30	9
8-16RA18N	39	36	33	33	30	30	30	9
8-18RA18N	39	36	36	33	33	33	33	6
8-22RA18N	39	36	36	36	33	33	33	6
8-6OA18N	39	36	36	36	36	36	36	3
8-10OA18N	39	36	33	33	33	33	33	6
8-12OA18N	39	33	33	33	33	33	33	6
8-14OA18N	39	39	33	30	30	30	30	9
8-16OA18N	39	33	33	30	30	30	30	9
8-18OA18N	39	36	36	33	33	33	33	6
8-22OA18N	39	36	36	36	33	33	33	6

On lowering temperature, waxy crude oil loses fluidity. This is due to precipitation of wax crystals as thin plates and needles, which overlaps and interlocks to form three dimensional networks. These PPDs block lateral crystal growth as a result of their adsorption on the wax precipitated. [35]

The results of pour point are shown in table 3.2 having pour point of virgin crude oil along with PPD doped crude oil with concentration ranging from 100 ppm to 1000 ppm.

The data shown in the table clearly indicates that all PPD's employed are more or less effective in decreasing pour point of neat Kosamba-47 crude oil.

First series consist of Undecylinic acid based poly (Octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate) terpolymers. Additive 8-14UA18N is most successful in reducing pour point from 39 °C to 30 °C (drop by 9°C) at 1000 ppm dose. It also reduces pour point to 33°C (drop by 6°C) at 100 ppm dose only. With increase in concentration of 8-14UA18N up to 500 ppm there is no further drop in pour point observed. In this series there are four additives which showed drop in pour point by 6 °C. Among these four the most efficient is 8-16UA18N as it showed a decrease of 6°C at 100 ppm dose only. With increase in concentration of 8-16UA18N no change in pour point depression was observed.

The interaction between paraffin and additive plays crucial role in pour point depression as additives tends to work best when its pendent chain matched well with that of paraffin distribution in crude oil. If the pendent chains are too long they may crystallize the polymer from the oil solution at temperature above pour point making it ineffective.

Second series represents Cinnamic acid based poly (Octyl cinnamate-co-maleic anhydride-co-alkyl cinnamate) Terpolymer which has aromatic ring in its polymeric structure. All the additives of this series were found to be effective in reducing pour point by minimum of 9°C and maximum by 12°C. 8-6CA18N reduced pour point by 12°C at 100 ppm. With rise in concentration up to 500 ppm no change was observed. But at 1000 ppm concentration drop observed was only by 9 °C. The other good performing additive from series was 8-18CA18N which decreased pour point from 39 °C to 27 °C (i.e. drop by 12°C) at 100 ppm and 200 ppm concentration. When concentration of 8-18CA18N was increased to 400 ppm and above up to 1000 ppm drop observed was only by 9°C for the mentioned concentration. Rest all additives of this series showed a decrease of 9°C for all concentration of PPD's doped. With increase in concentration, no effect is observed for these additives.

Third series is Ricinoleic acid based poly (Octyl Ricinolate-co-octadecyl maleimide-co-alkyl ricinolate). 8-14RA18N reduced the pour point from 39°C to 30°C (i.e. drop of 9°C) at 500 and 1000 ppm. 8-16RA18N also showed a drop of 9°C at 500 and 1000 ppm concentration. Other additives could reduce pour point by 3°C to 6°C only.

Fourth series represents oleic acid based poly (octyl oleate-co-octadecyl maleimide-co-alkyl oleate). Here 8-14OA18N and 8-16OA18N both were found to decrease pour point by 9°C at concentration 400 ppm to 1000 ppm. Increase in concentration has no impact on pour point. The other additives from the series could change the pour point only by 3 to 6^{o}C only.

3.1.4.2 Evaluation of Polymeric Additives on Rheological Parameters

The origin of viscosity lies in interaction of hydrogen bonds and mutual overlapping of condensed aromatic ring planes of resins and asphaltenes moiety in the crude oil. To achieve viscosity reduction, breaking of hydrogen bonds and inhibition of mutual overlapping of condensed aromatic ring planes of resins and asphaltenes moiety is needed in crude oil. on addition of polymeric additives the hydrogen bond between additives and resins/asphaltenes are much stronger than between resins and asphaltenes in crude oil. Also due to hydrogen bonding between additives and asphaltenes/resins, these get stretched in space and possibility of mutual overlapping of condensed aromatic ring planes is greatly reduced. Hence polymeric additives having polar groups show higher tendency to form hydrogen bonds with resins/asphaltenes eventually behaving as good viscosity index improvers. [25]

Table 3.3 Effect of Additive Concentration on Rheological Parameters of Kosamba-47 Crude Oil

Code	Additive Concentration (ppm)	Temperature (^{o}C)	Viscosity (Pa-s)	Yield Stress (Pa)
Blank	0	39	0.0600	2.341
		36	0.2297	11.38
		33	0.5539	23.55
		30	1.1901	58.21
8-14UA18N	500	39	0.0921	4.641
		36	0.2818	17.92
		33	0.6465	27.35
		30	1.1696	55.96
8-14UA18N	1000	39	0.0925	4.278
		36	0.2655	16.32
		33	0.6741	28.59
		30	1.2256	58.63
8-16UA18N	500	39	0.0390	1.955
		36	0.0939	4.941
		33	0.1190	6.302
		30	0.1991	10.05
8-16UA18N	1000	39	0.0465	2.231
		36	0.1169	6.34
		33	0.1861	8.463
		30	0.3722	12.88
8-6CA18N	500	39	0.0804	2.777
		36	0.2503	14.49
		33	0.5664	28.10
		30	0.8494	40.06

Code	**Additive Concentration (ppm)**	**Temperature (°C)**	**Viscosity (Pa-s)**	**Yield Stress (Pa)**
8-6CA18N	1000	39	0.0752	2.354
		36	0.2647	16.78
		33	0.6736	31.89
		30	1.3309	64.42
8-18CA18N	500	39	0.0802	3.381
		36	0.2359	15.17
		33	0.5439	25.21
		30	0.7972	44.37
8-18CA18N	1000	39	0.0618	2.414
		36	0.2212	14.44
		33	0.4442	23.81
		30	0.7446	32.25
8-14RA18N	500	39	0.0552	1.939
		36	0.2110	11.65
		33	0.4739	20.15
		30	0.8173	39.98
8-14RA18N	1000	39	0.0618	2.506
		36	0.2407	14.48
		33	0.6083	25.17
		30	1.0566	49.96
8-16RA18N	500	39	0.0682	2.673
		36	0.2431	15.21
		33	0.5916	24.79
		30	1.0353	55.23
8-16RA18N	1000	39	0.0671	2.549
		36	0.2630	16.03
		33	0.5969	25.66
		30	0.9945	52.32
8-14OA18N	500	39	0.0424	2.102
		36	0.1254	7.215
		33	0.2387	8.524
		30	0.6686	11.58
8-14OA18N	1000	39	0.0372	1.586
		36	0.1247	5.689
		33	0.2509	13.88
		30	0.3190	16.38
8-16OA18N	500	39	0.0746	3.054
		36	0.2687	15.98
		33	0.6323	26.97
		30	1.0866	54.92
8-16OA18N	1000	39	0.0735	3.492
		36	0.2415	14.98
		33	0.5473	23.00
		30	1.0022	45.44

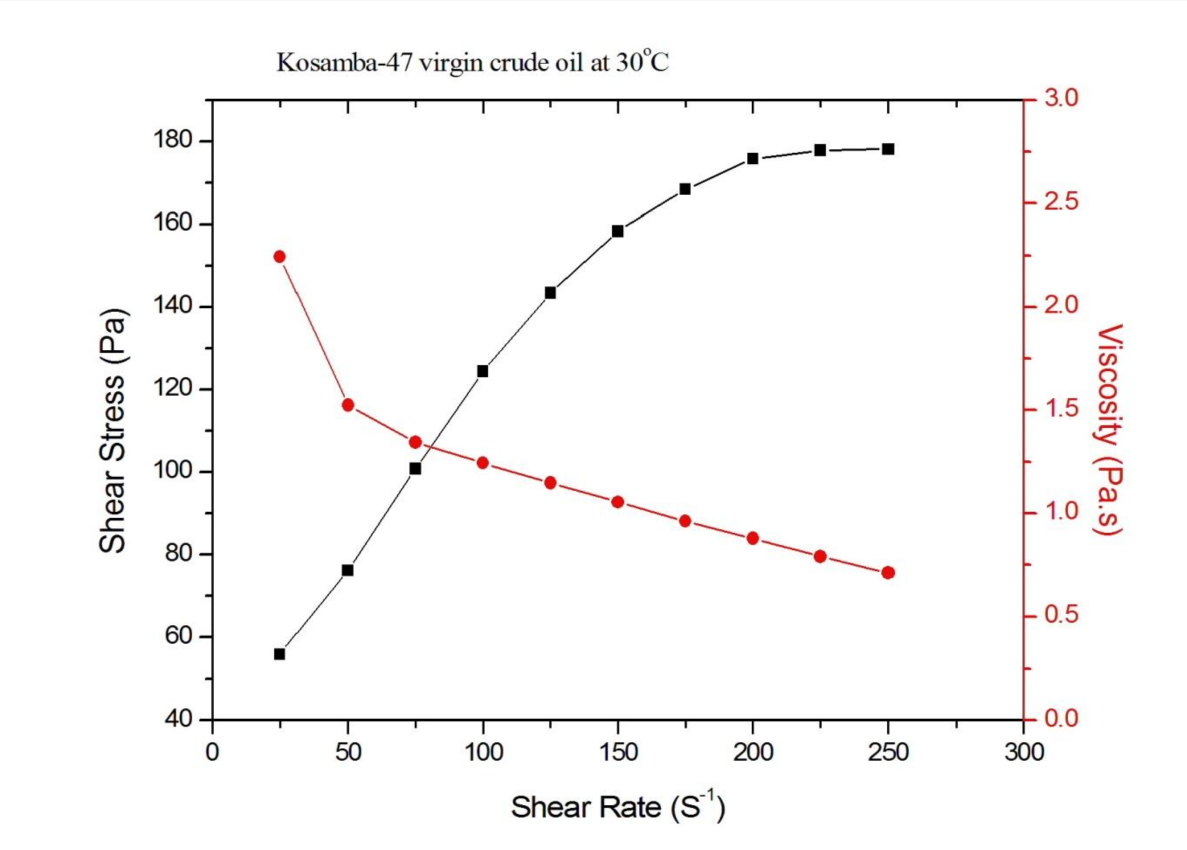

Fig 3.3 Rheogram of Virgin Kosamba-47 crude oil at 30°C

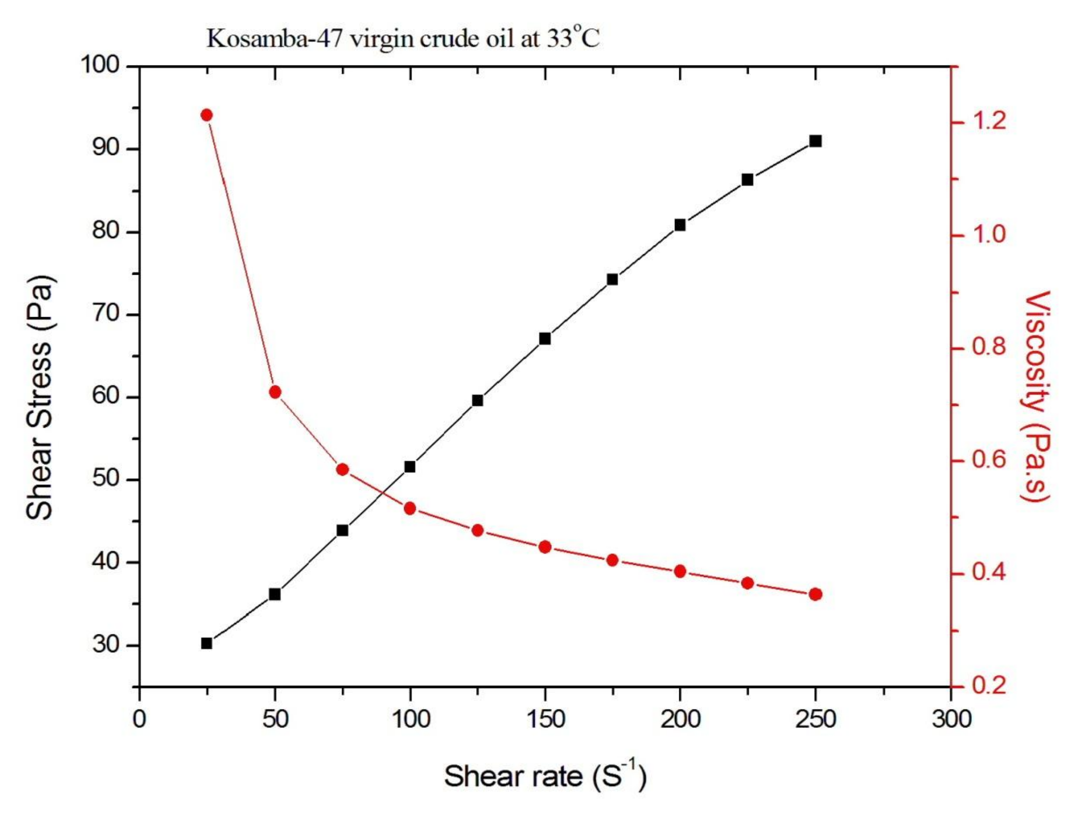

Fig 3.4 Rheogram of Virgin Kosamba-47 crude oil at 33°C

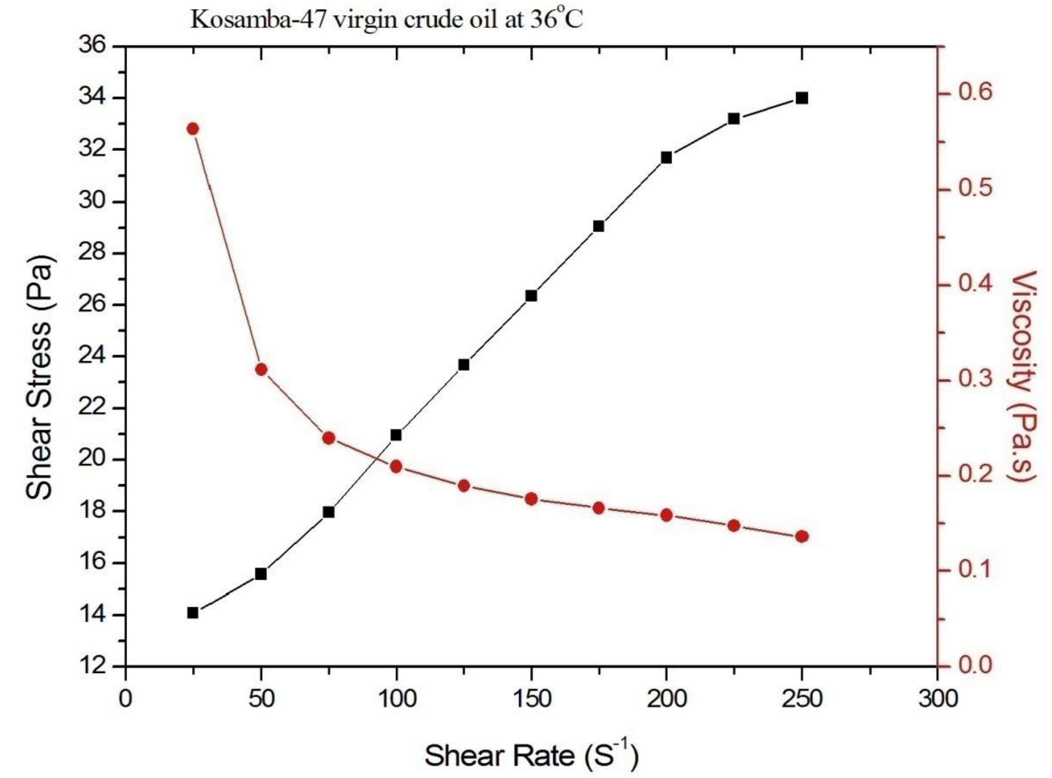

Fig 3.5 Rheogram of Virgin Kosamba-47 crude oil at 36°C

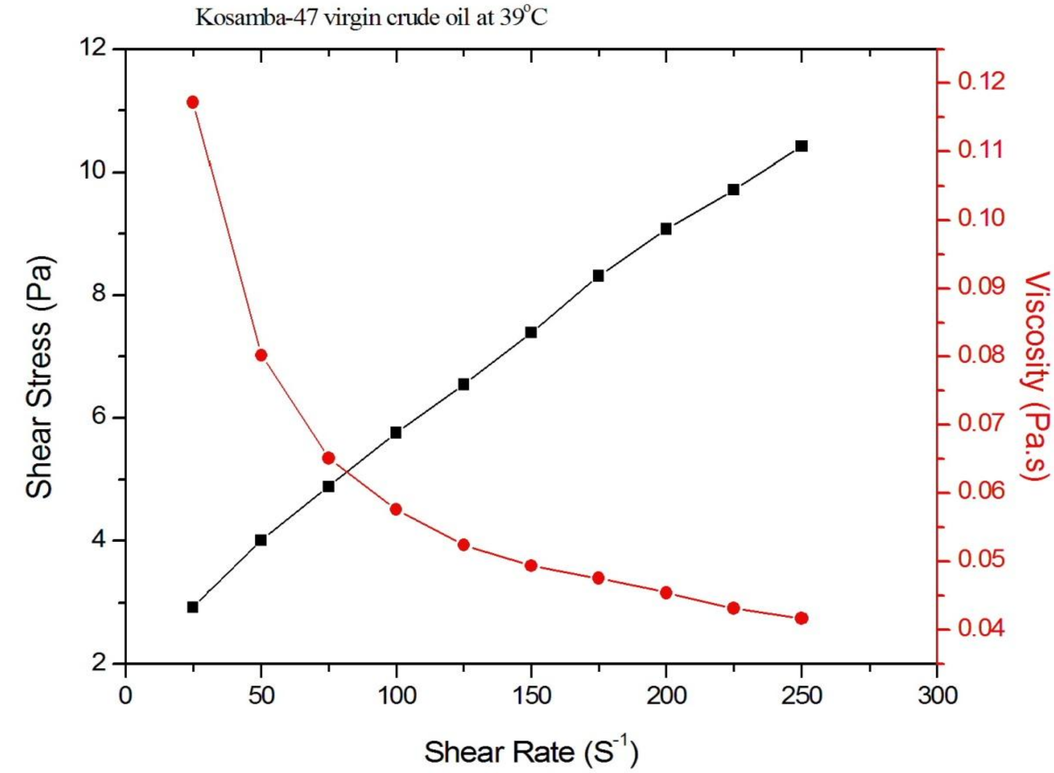

Fig 3.6 Rheogram of Virgin Kosamba-47 crude oil at 39°C

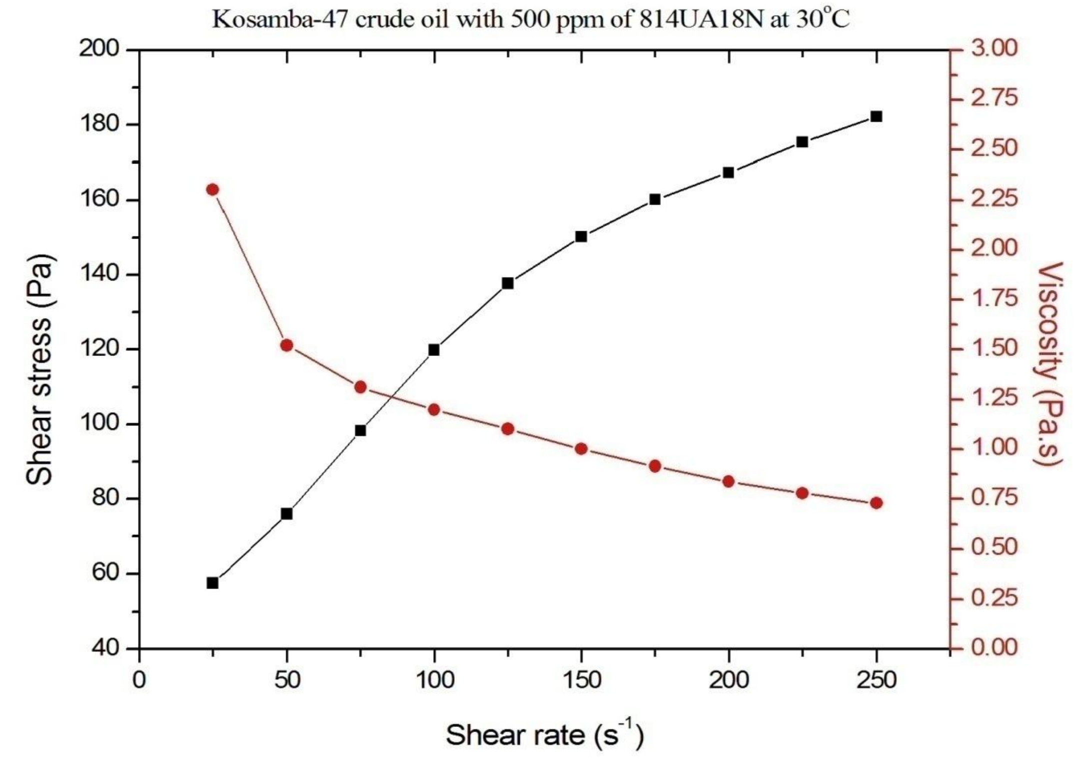

Fig 3.7 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14UA18N at 30°C

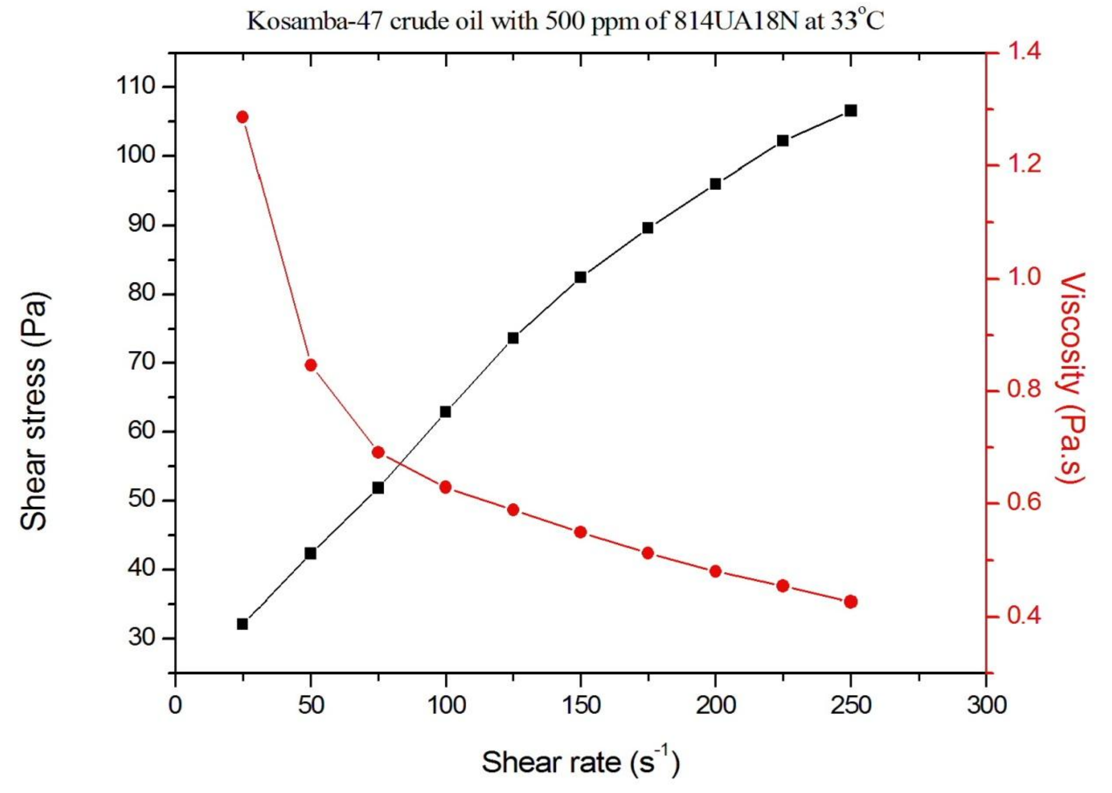

Fig 3.8 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14UA18N at 33°C

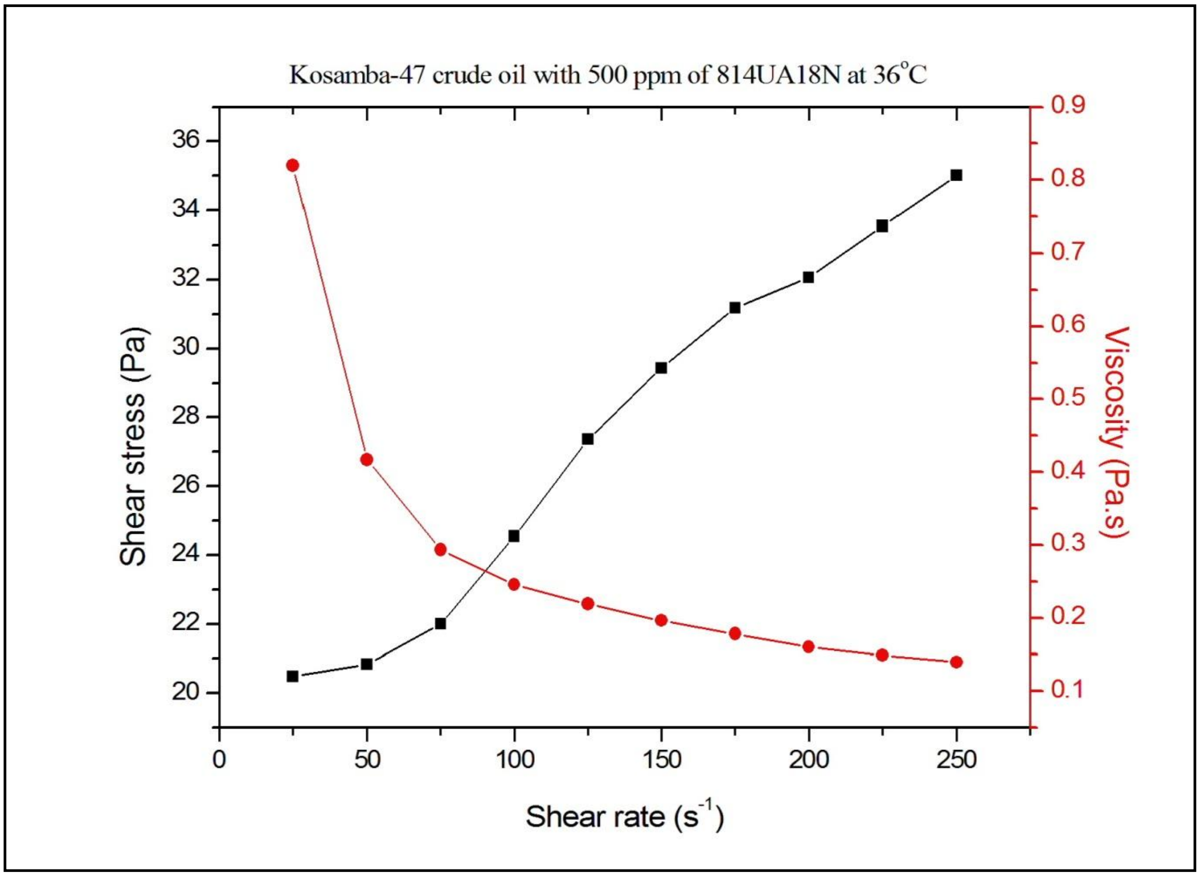

Fig 3.9 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14UA18N at 36°C

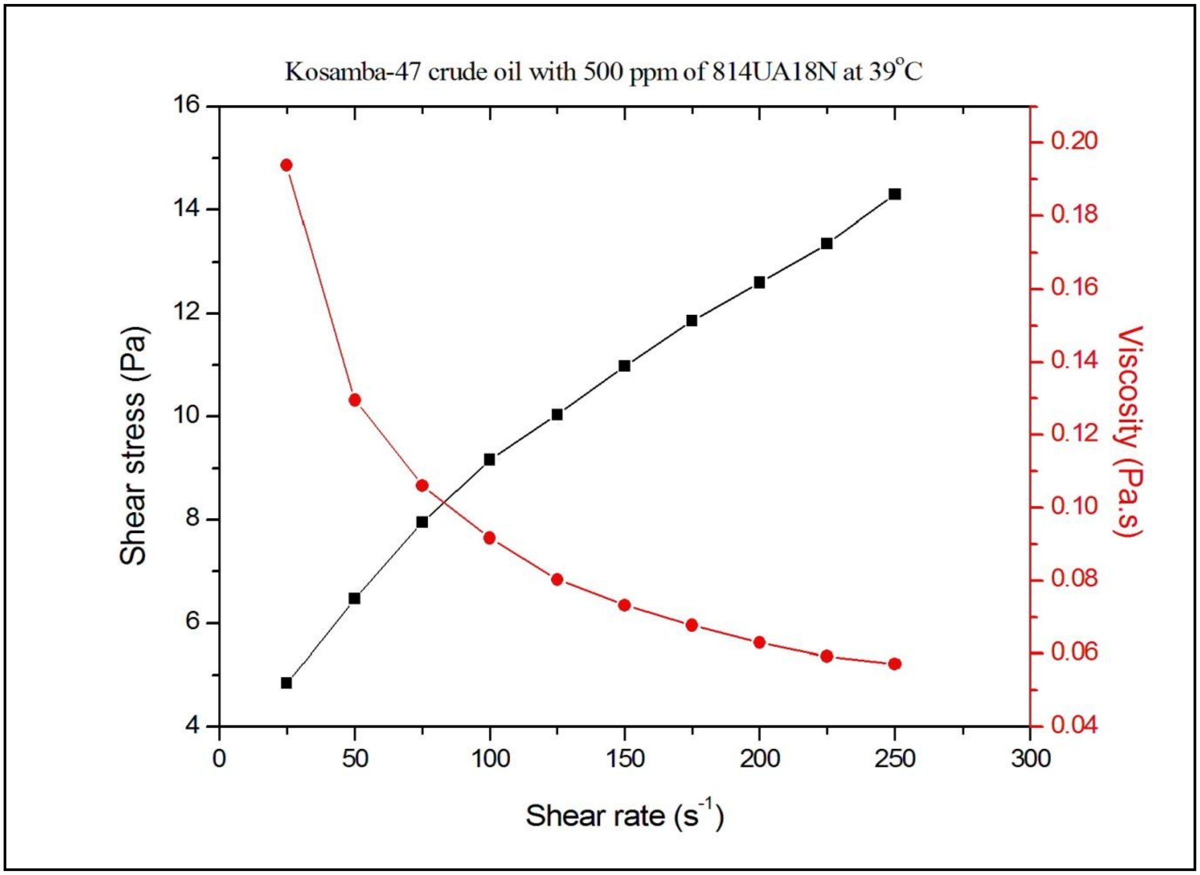

Fig 3.10 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14UA18N at 39°C

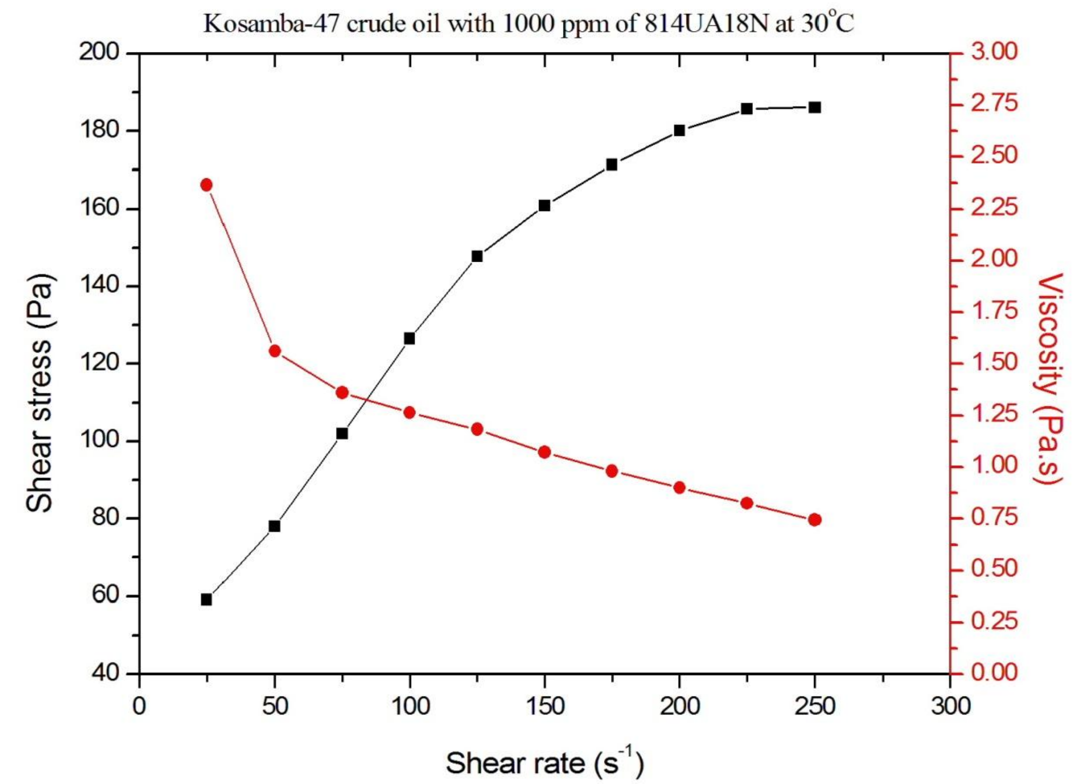

Fig 3.11 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14UA18N at 30°C

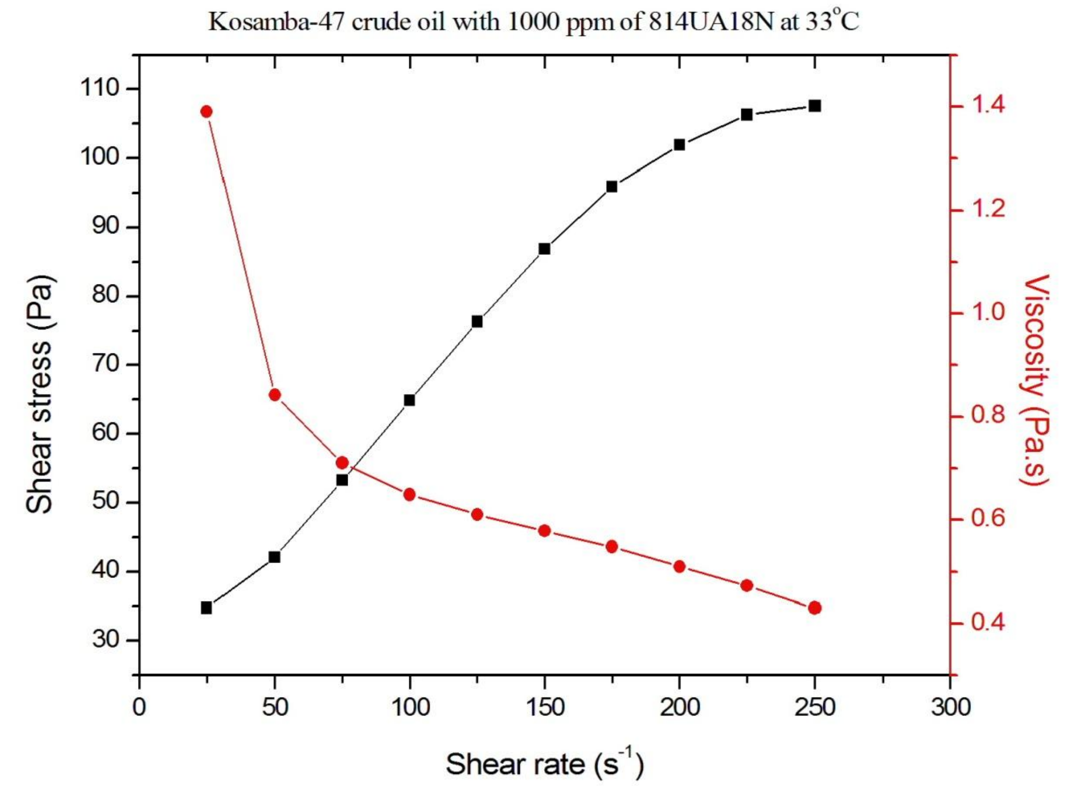

Fig 3.12 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14UA18N at 33°C

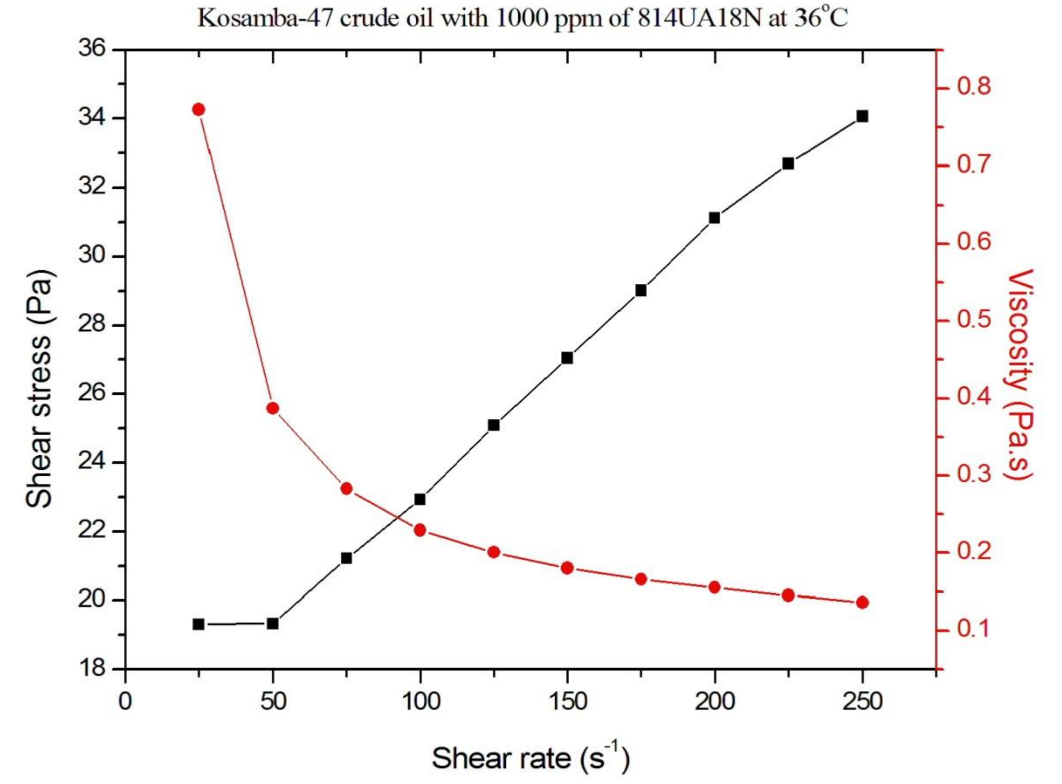

Fig 3.13 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14UA18N at 36°C

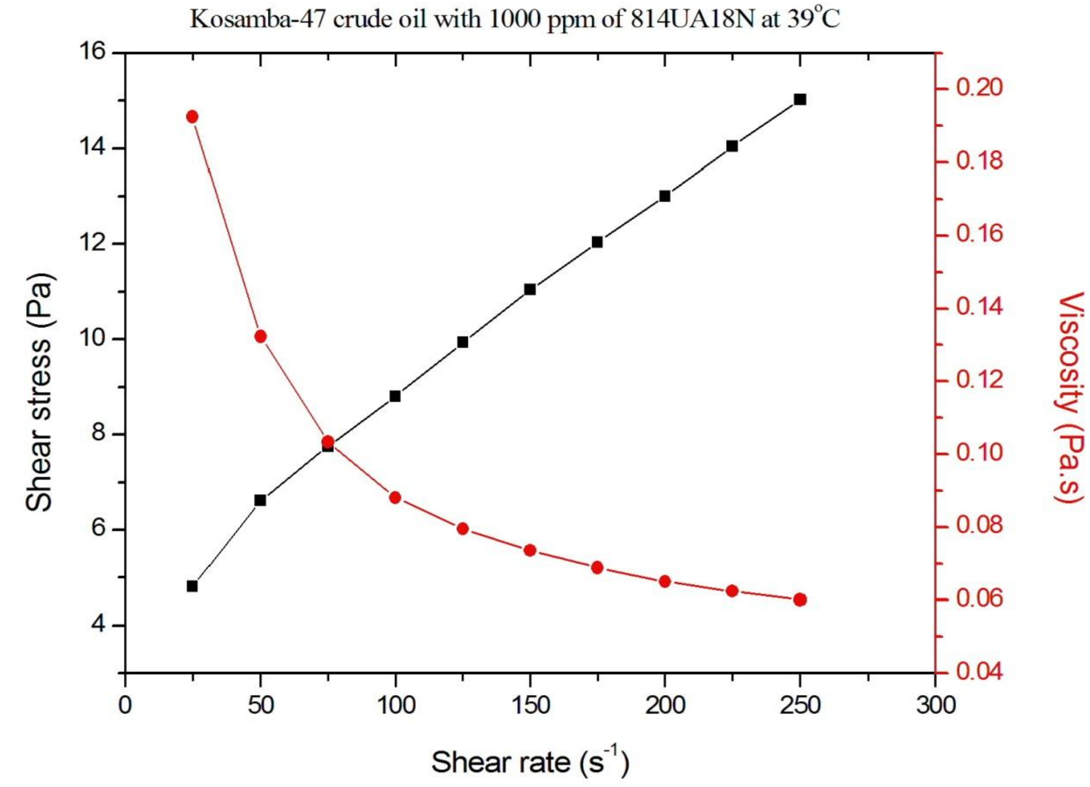

Fig 3.14 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14UA18N at 39°C

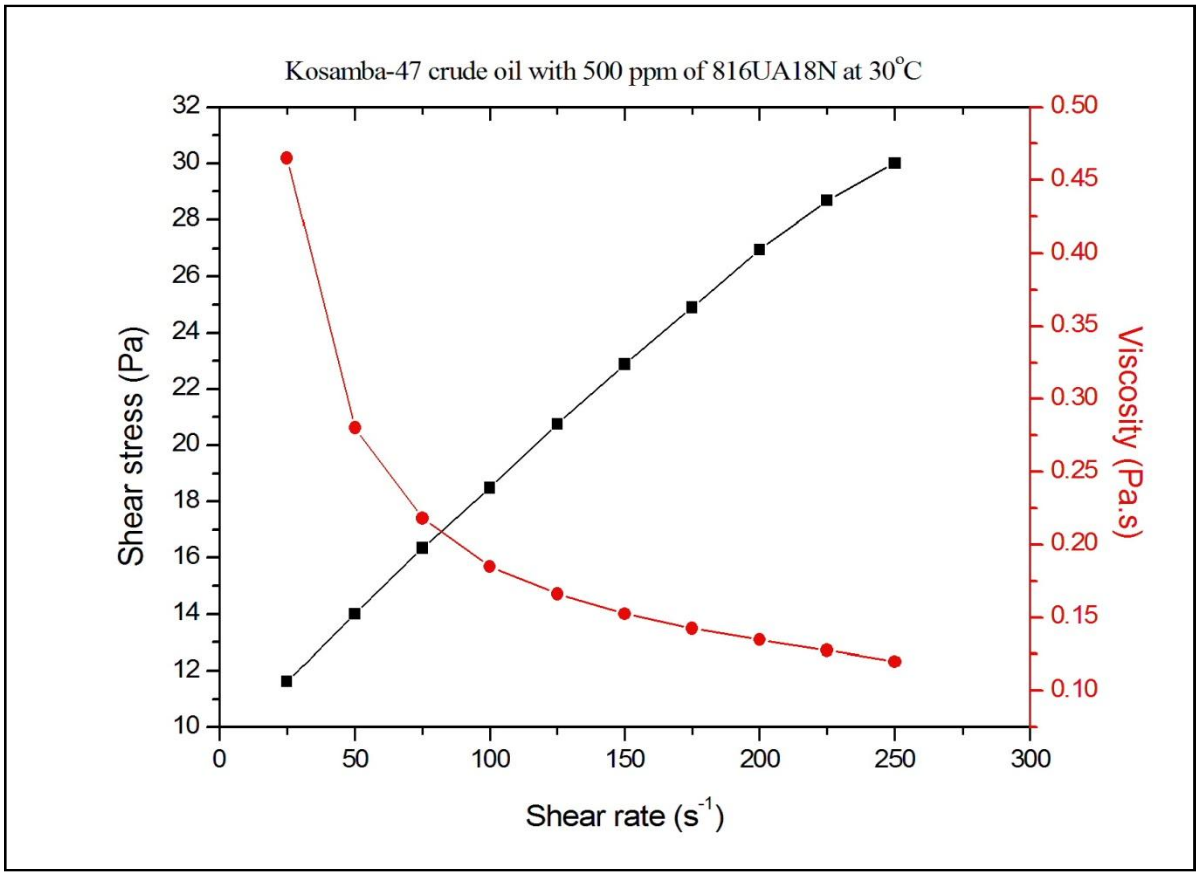

Fig 3.15 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16UA18N at 30°C

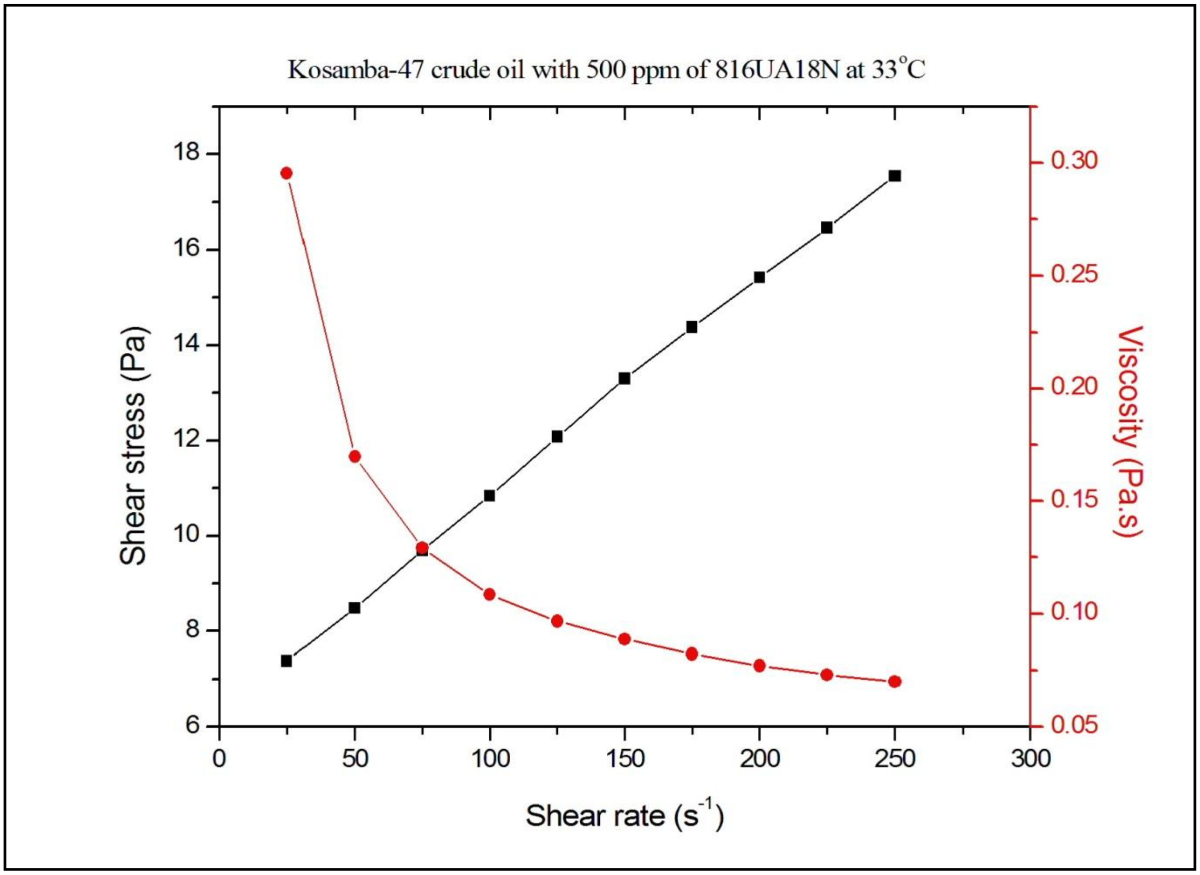

Fig 3.16 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16UA18N at 33°C

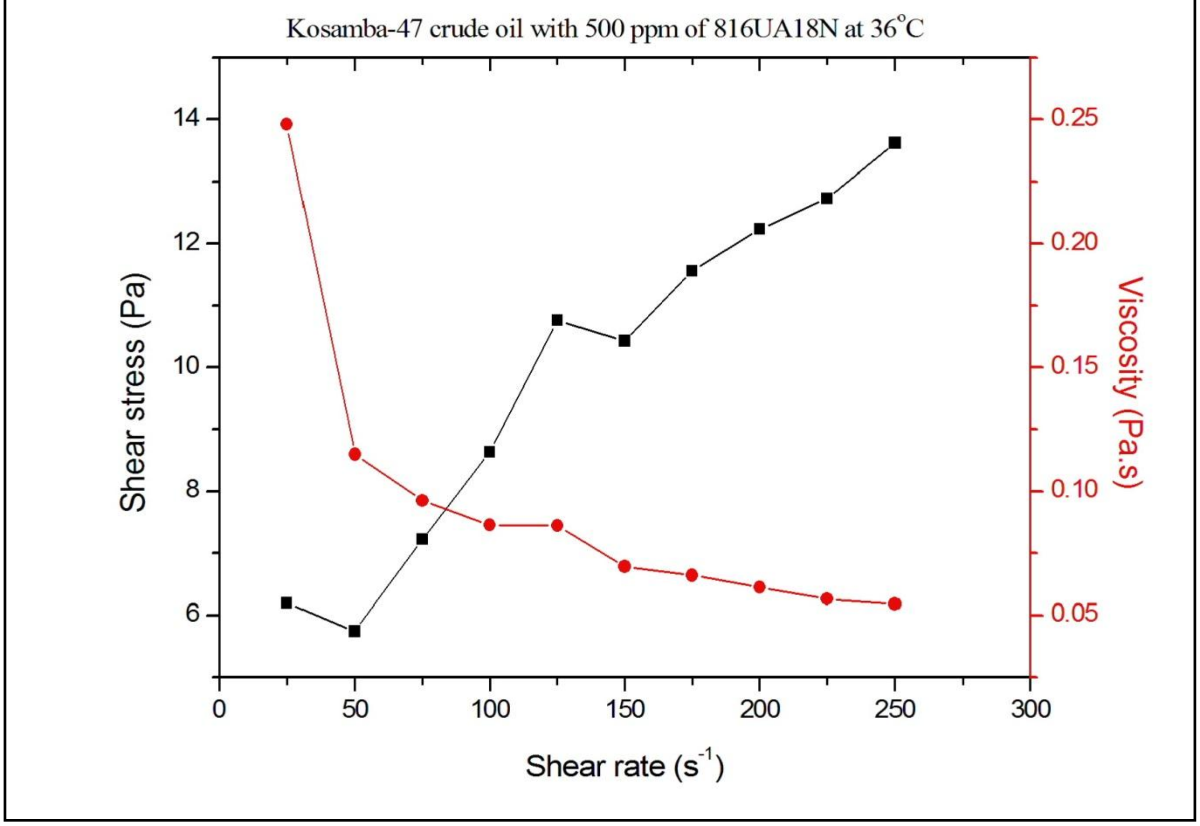

Fig 3.17 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16UA18N at 36°C

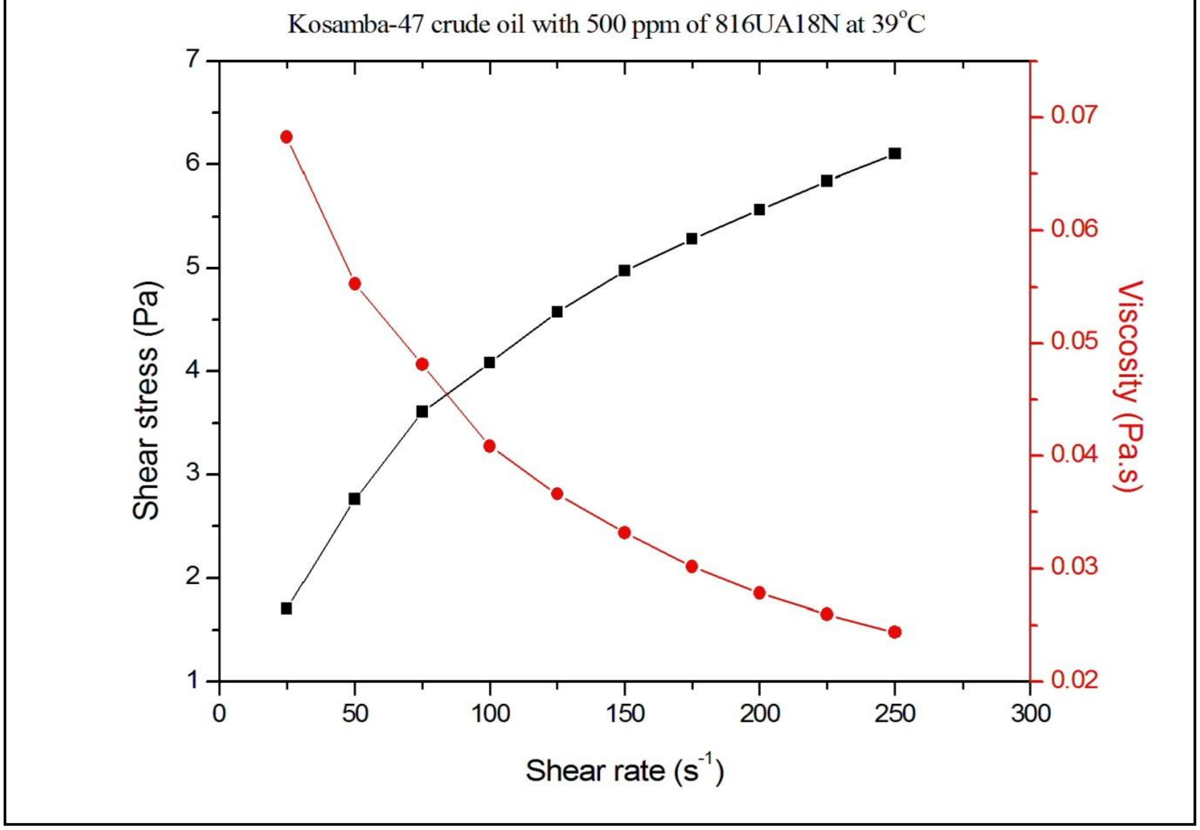

Fig 3.18 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16UA18N at 39°C

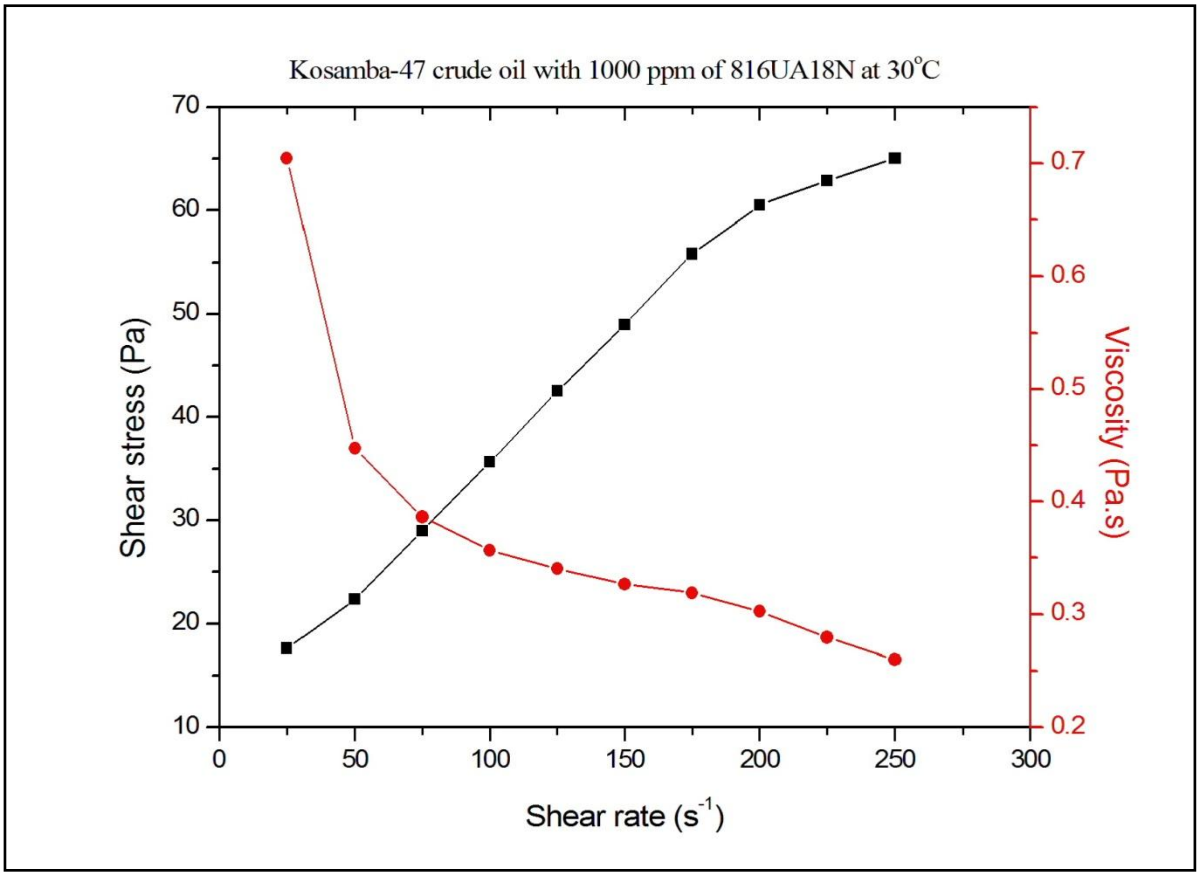

Fig 3.19 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16UA18N at 30°C

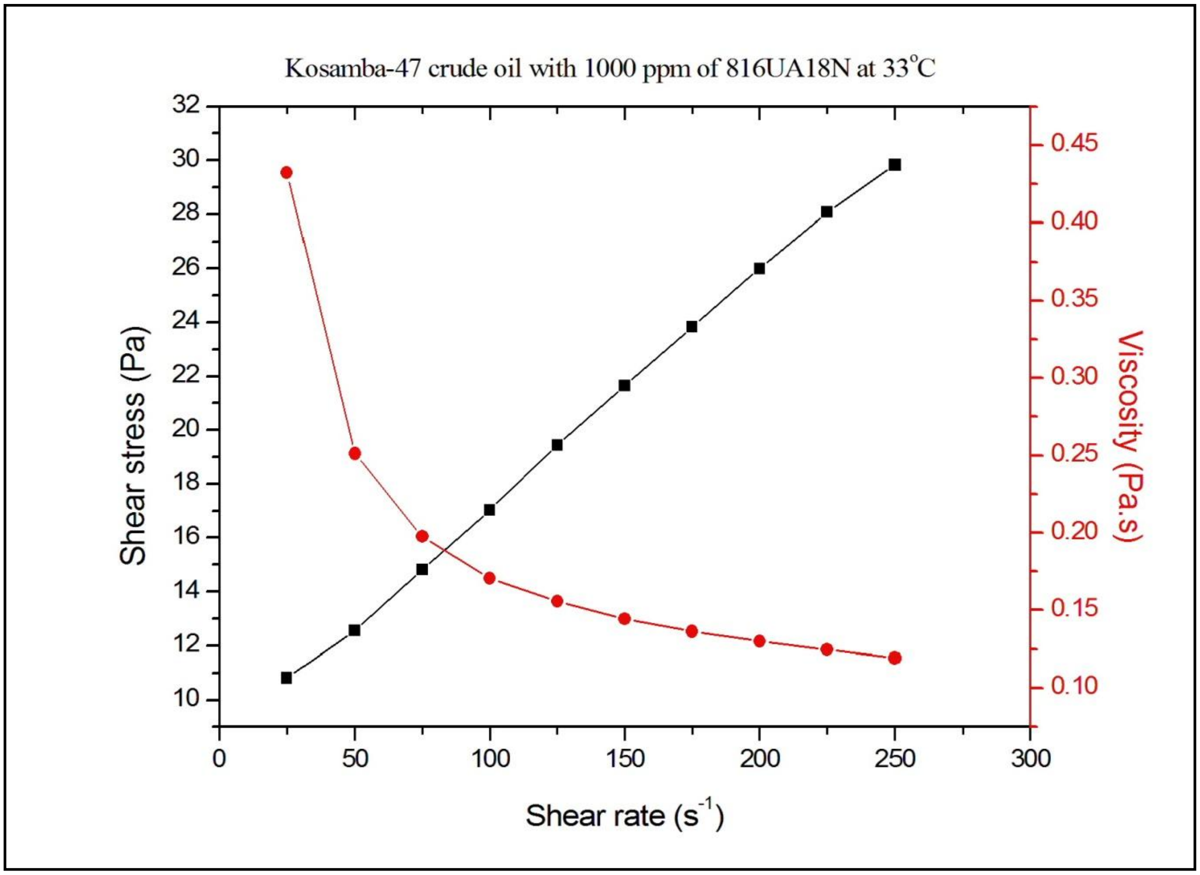

Fig 3.20 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16UA18N at 33°C

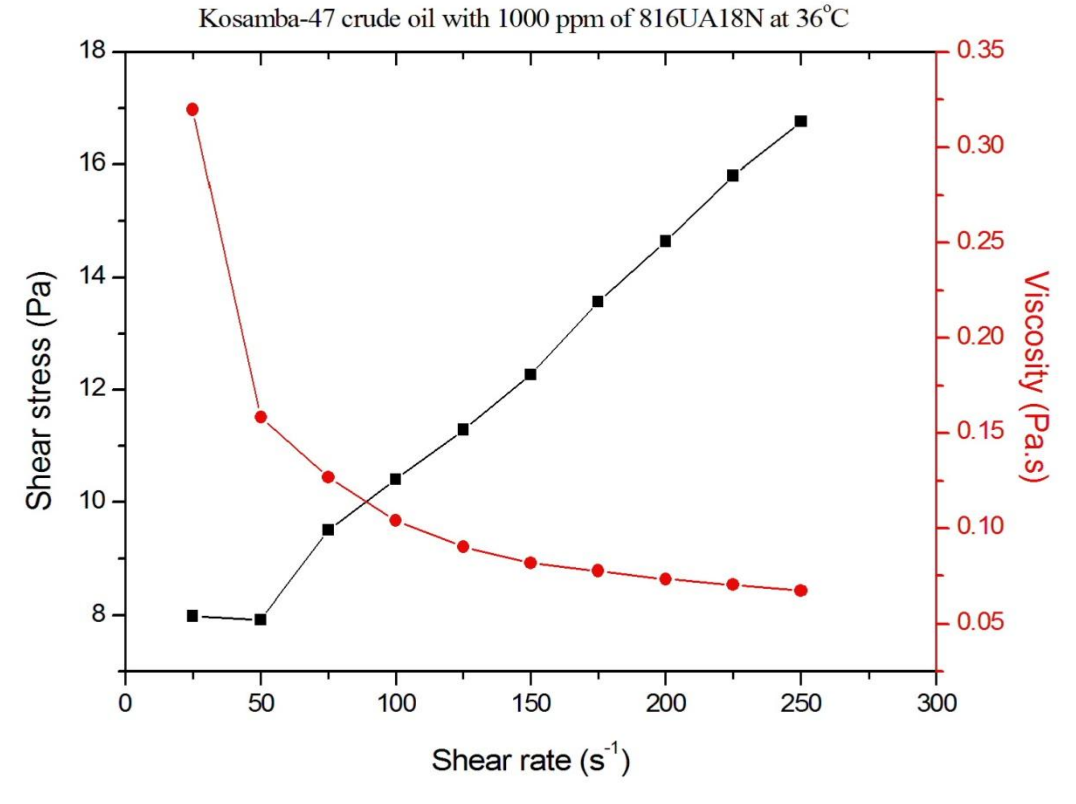

Fig 3.21 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16UA18N at 36°C

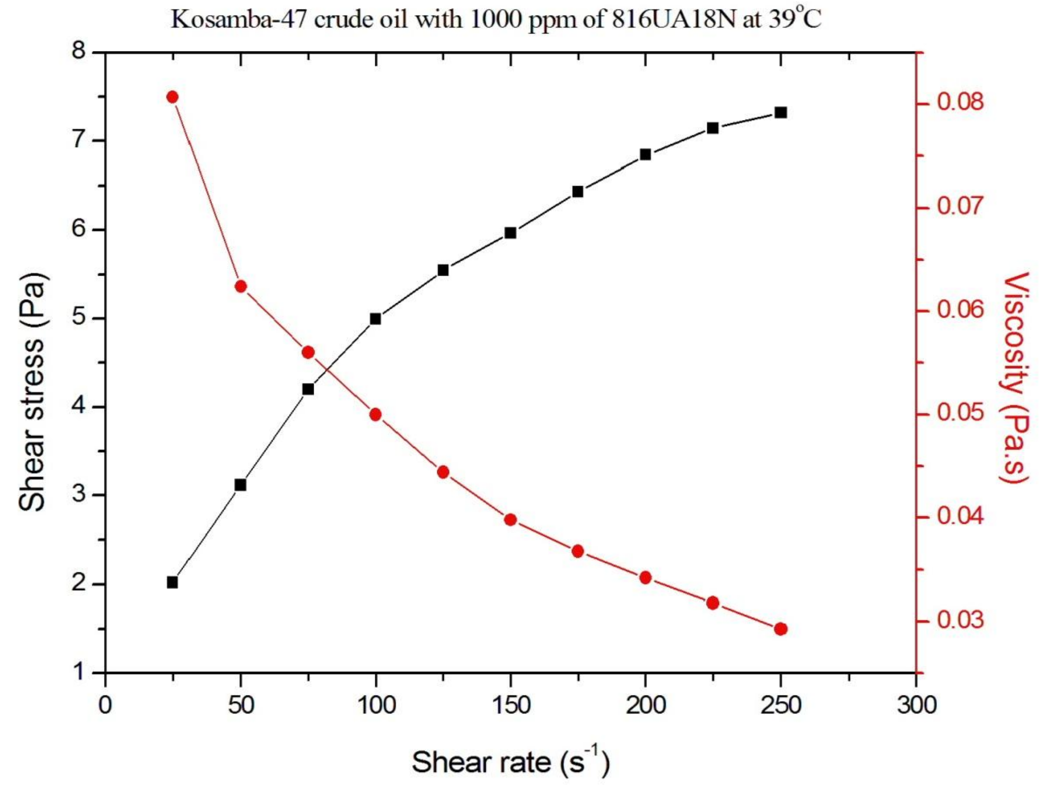

Fig 3.22 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16UA18N at 39°C

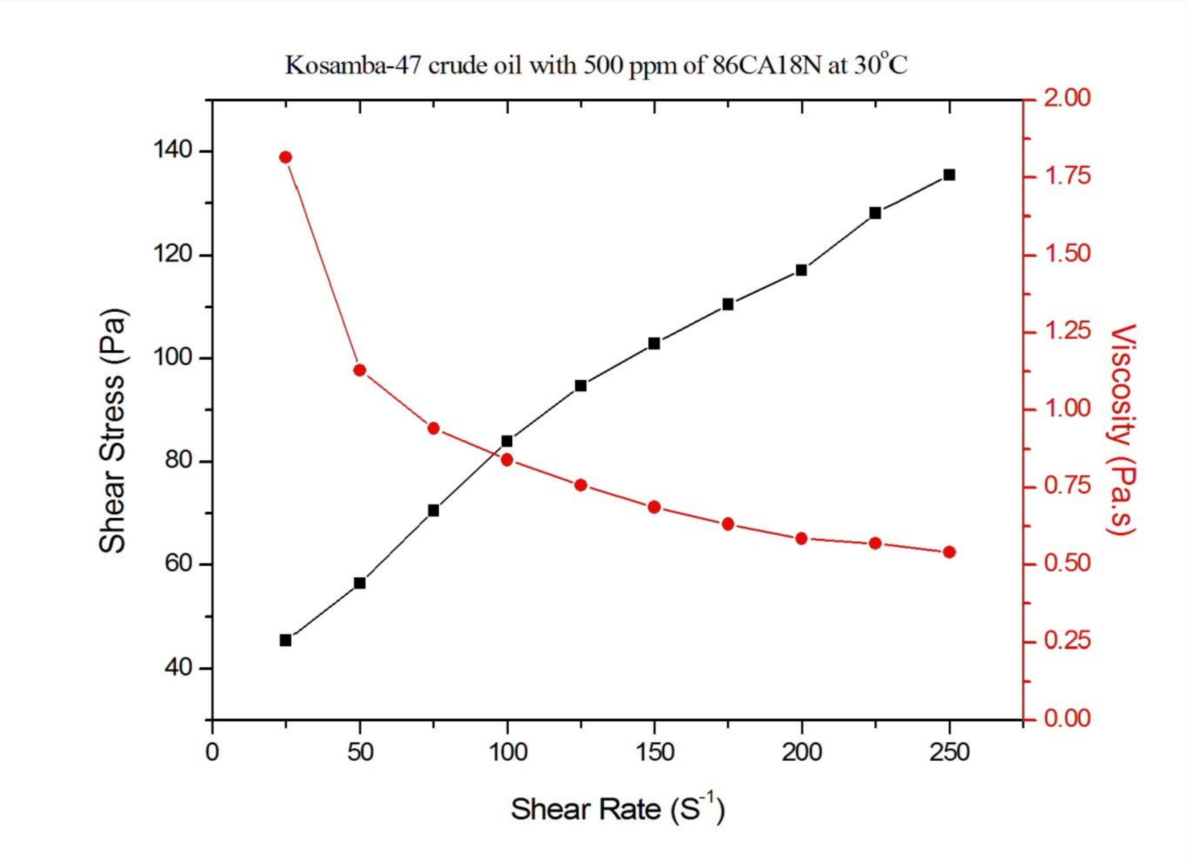

Fig 3.23 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-6CA18N at 30°C

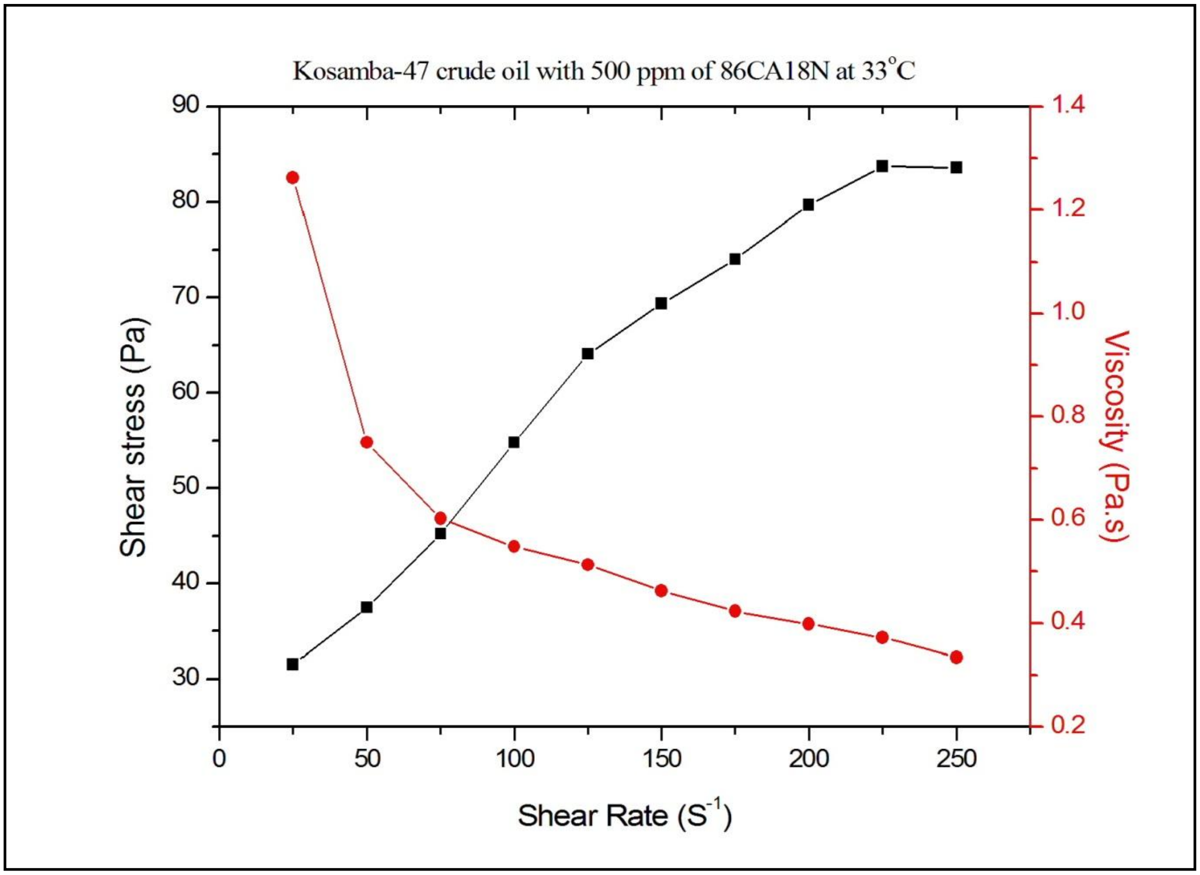

Fig 3.24 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-6CA18N at 33°C

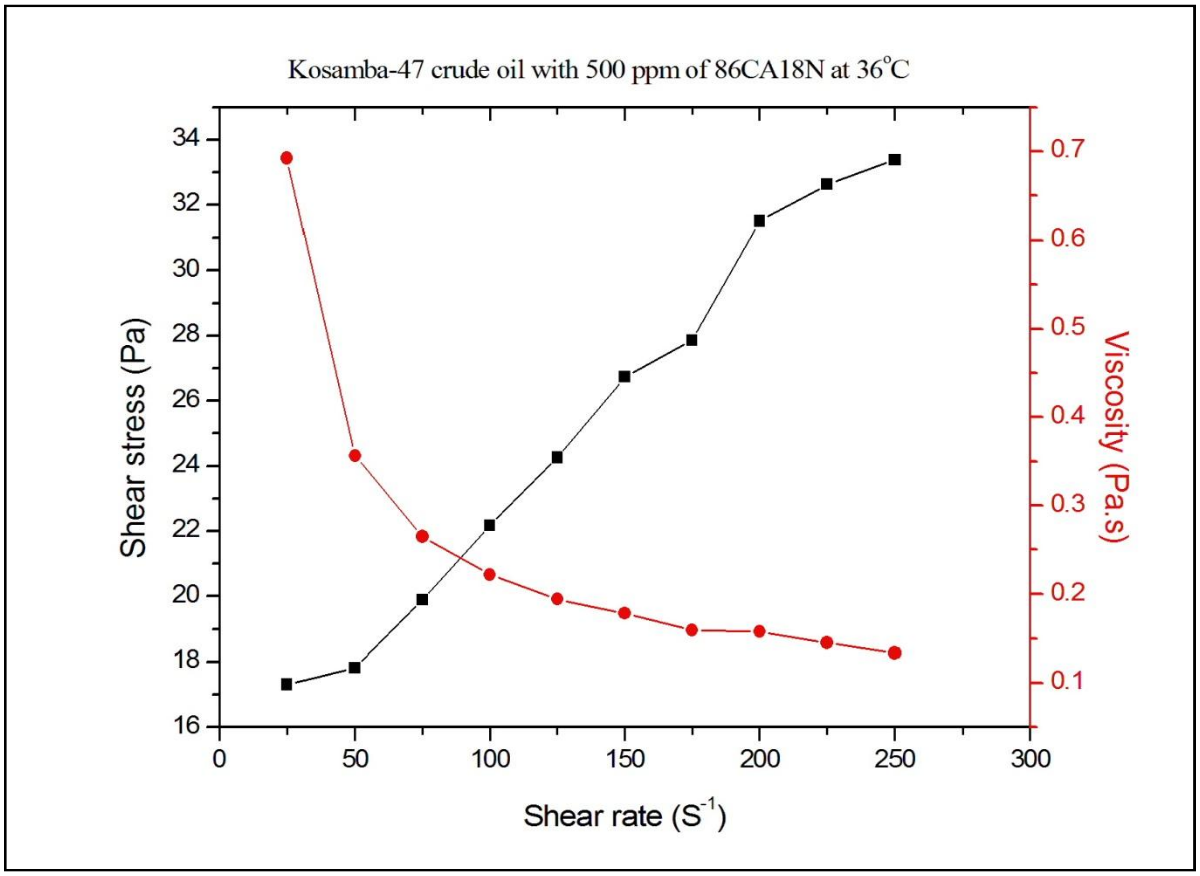

Fig 3.25 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-6CA18N at 36°C

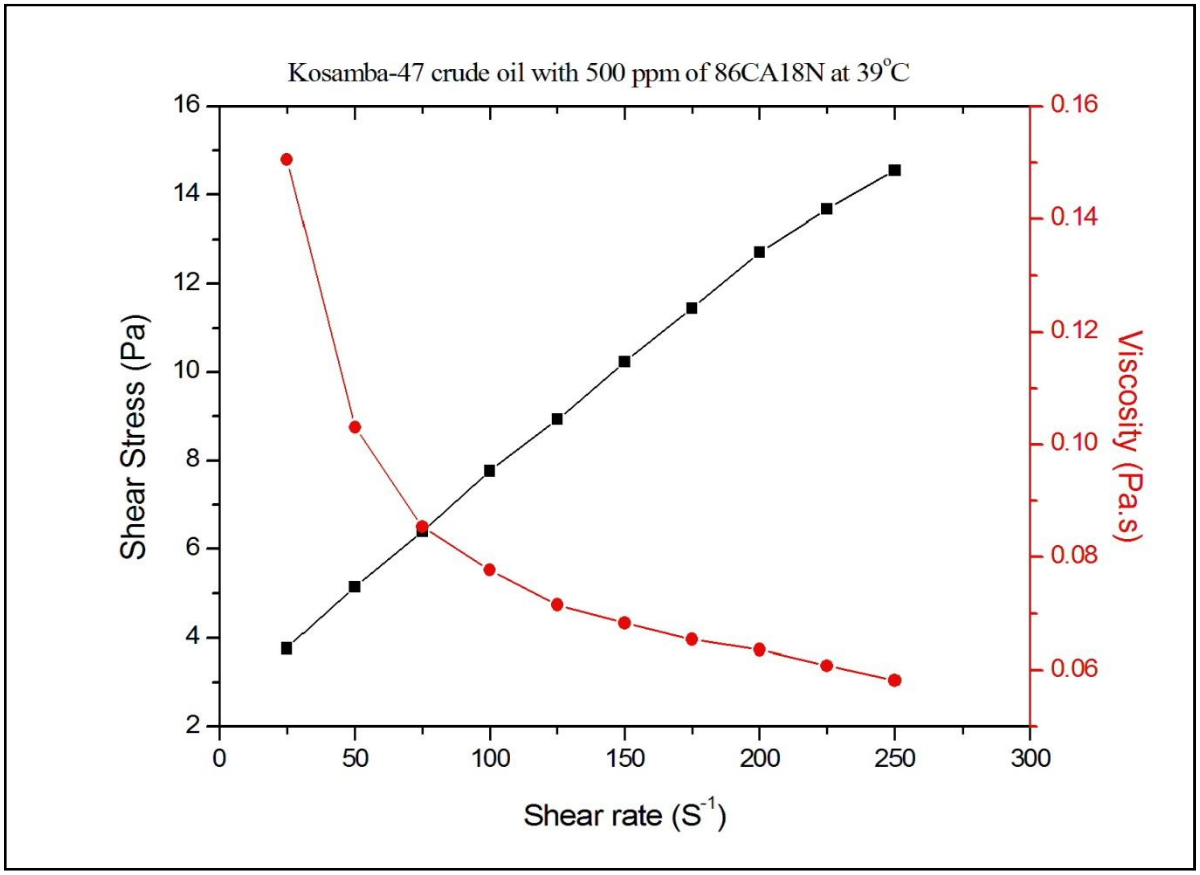

Fig 3.26 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-6CA18N at 39°C

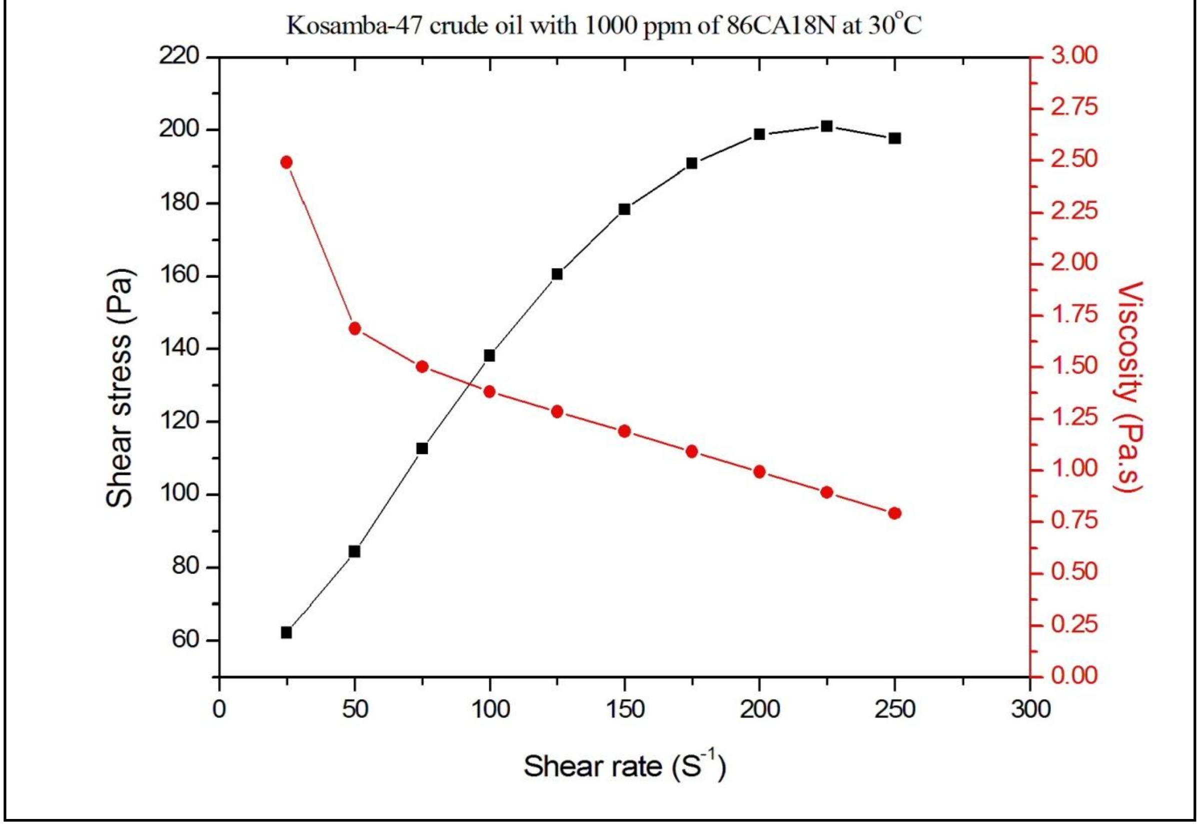

Fig 3.27 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-6CA18N at 30°C

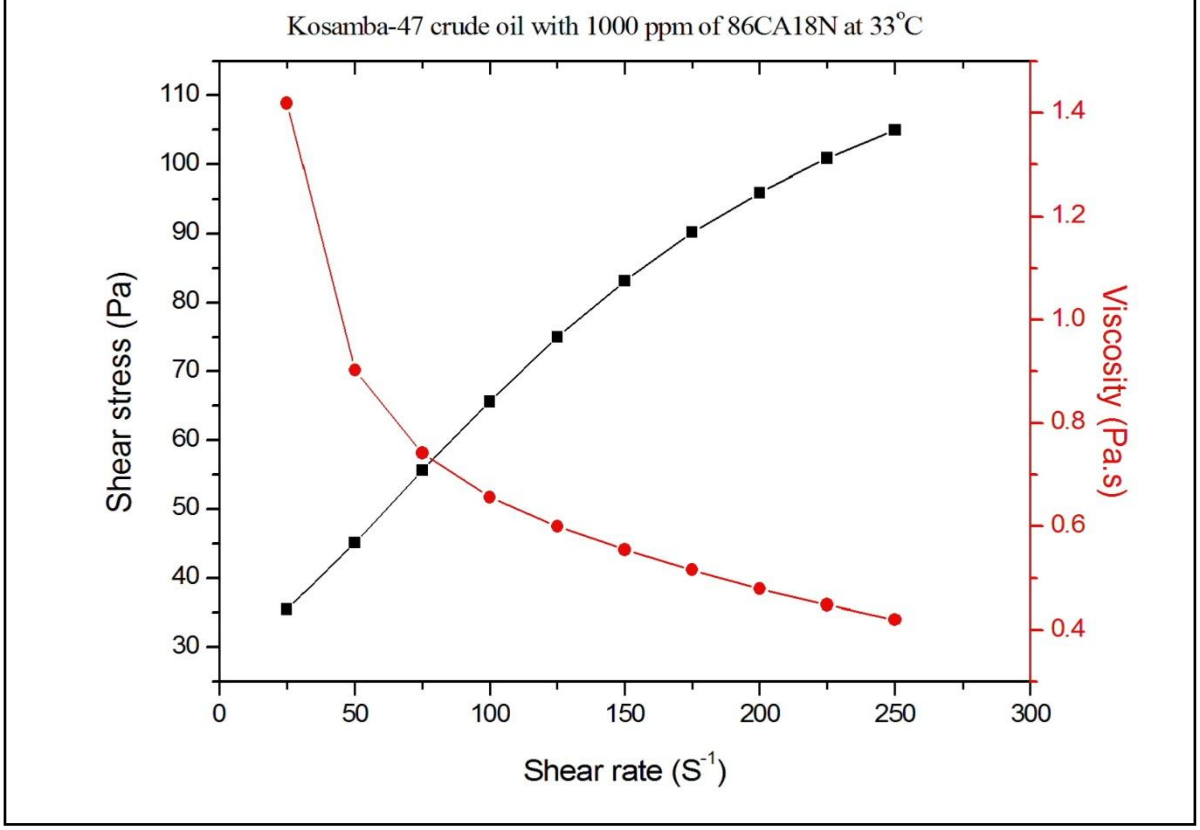

Fig 3.28 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-6CA18N at 33°C

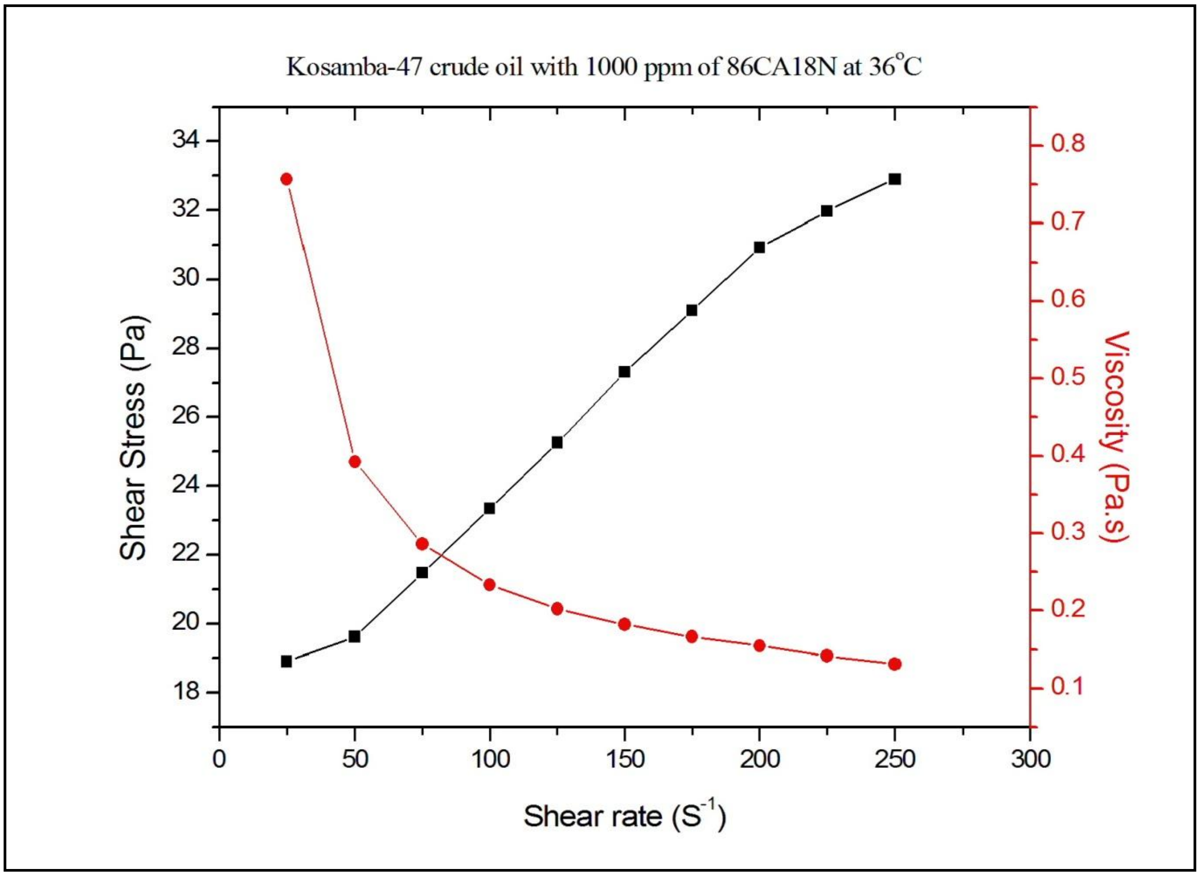

Fig 3.29 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-6CA18N at 36°C

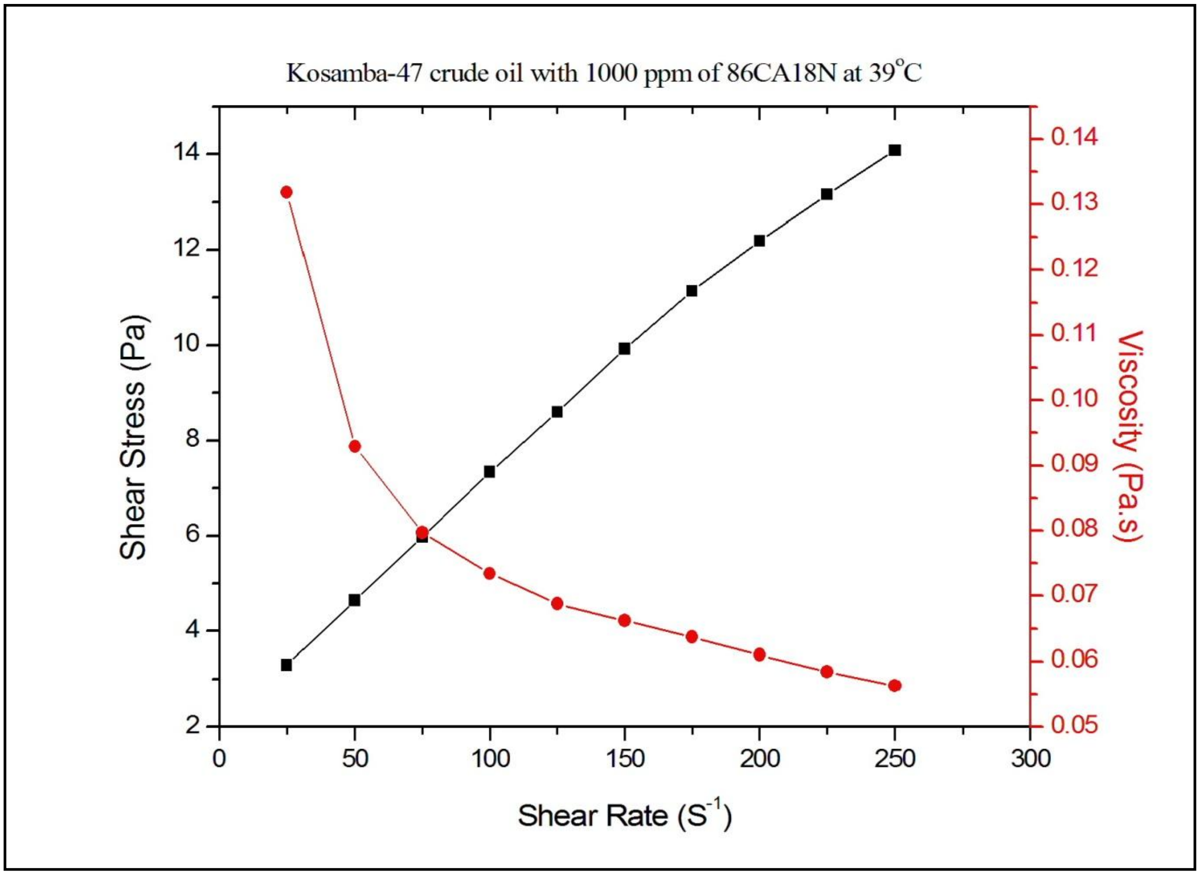

Fig 3.30 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-6CA18N at 39°C

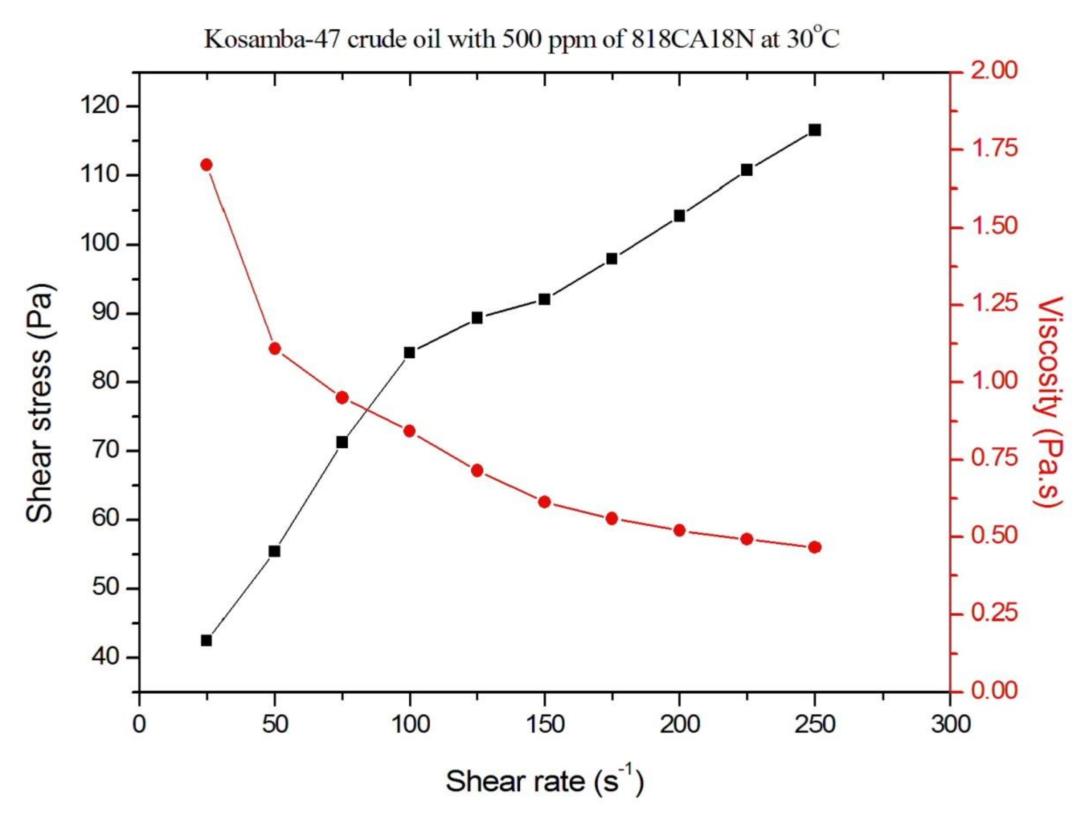

Fig 3.31 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-18CA18N at 30°C

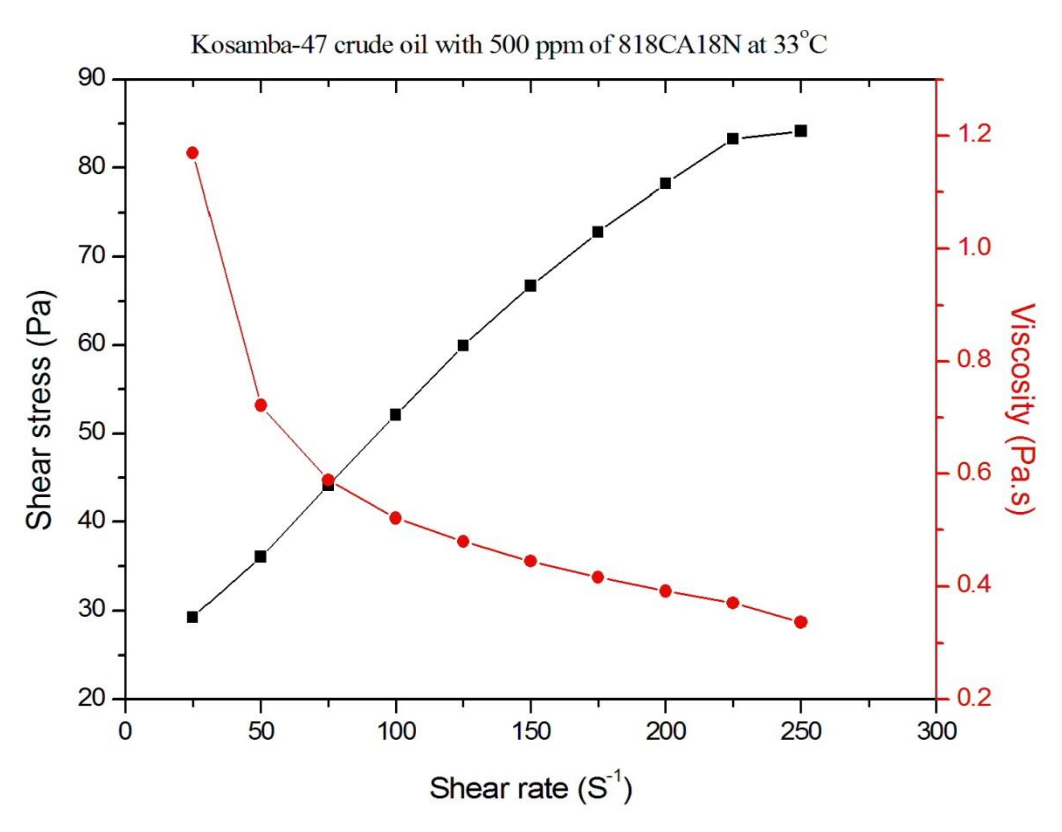

Fig 3.32 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-18CA18N at 33°C

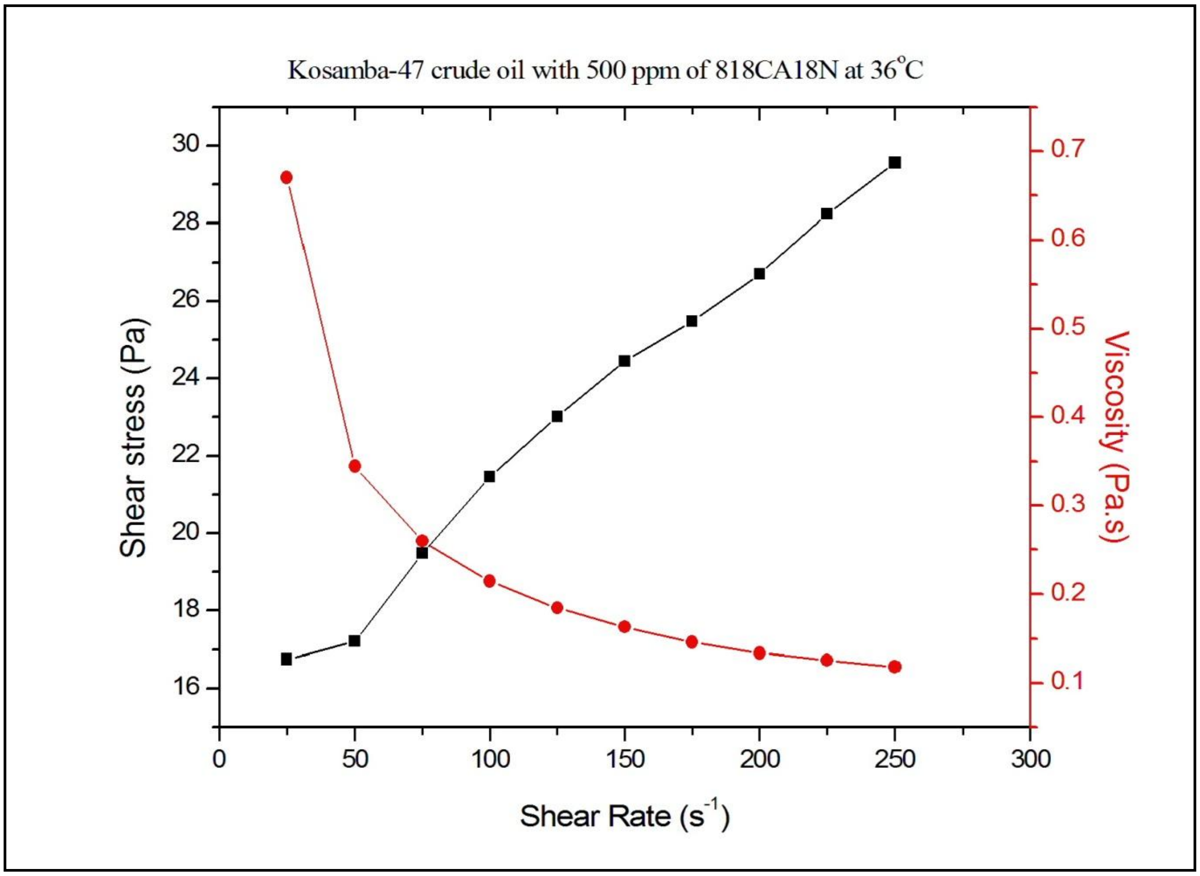

Fig 3.33 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-18CA18N at 36°C

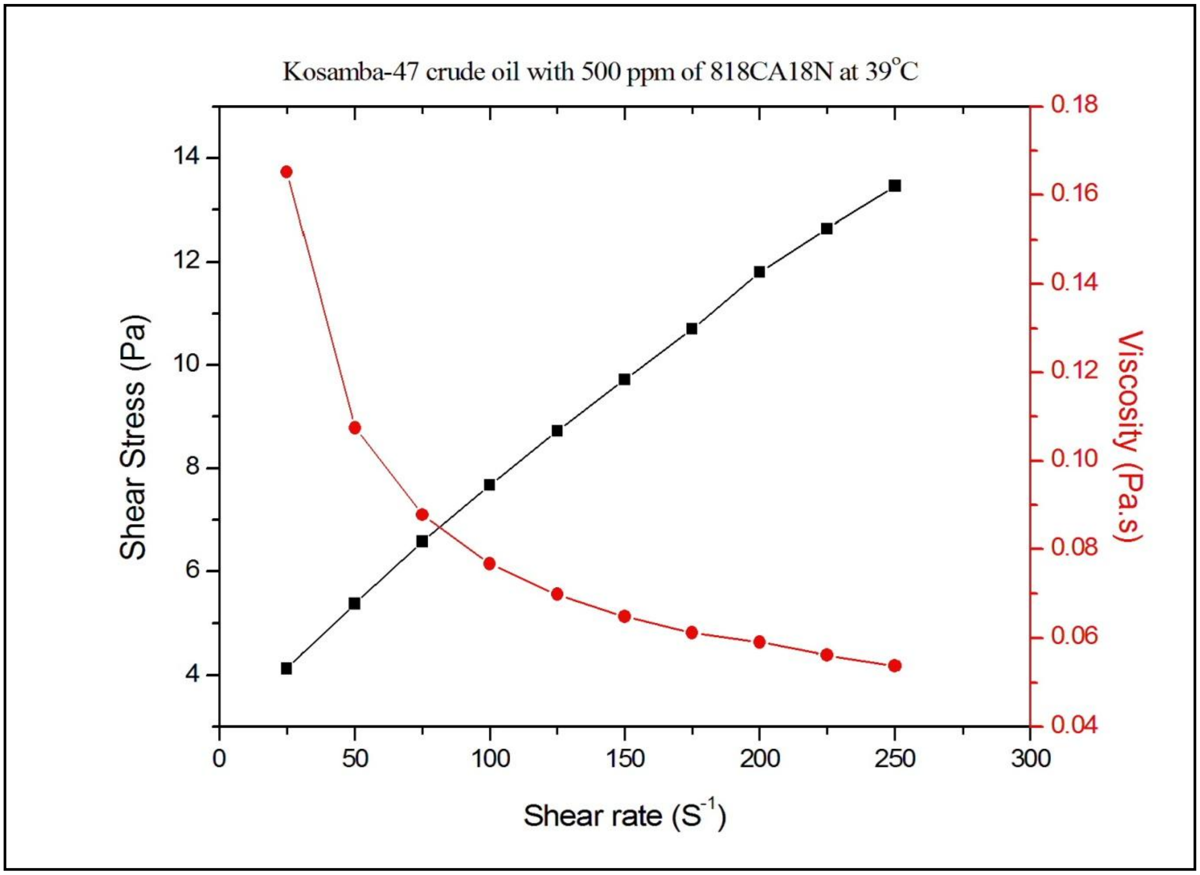

Fig 3.34 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-18CA18N at 39°C

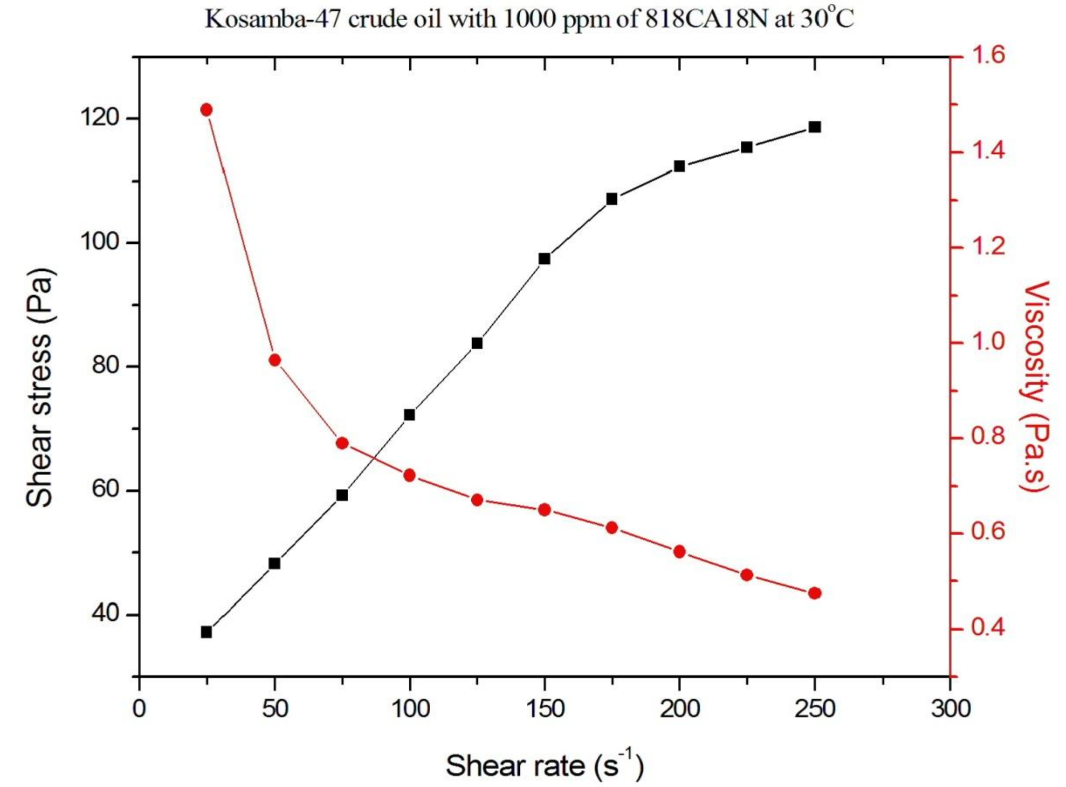

Fig 3.35 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-18CA18N at 30°C

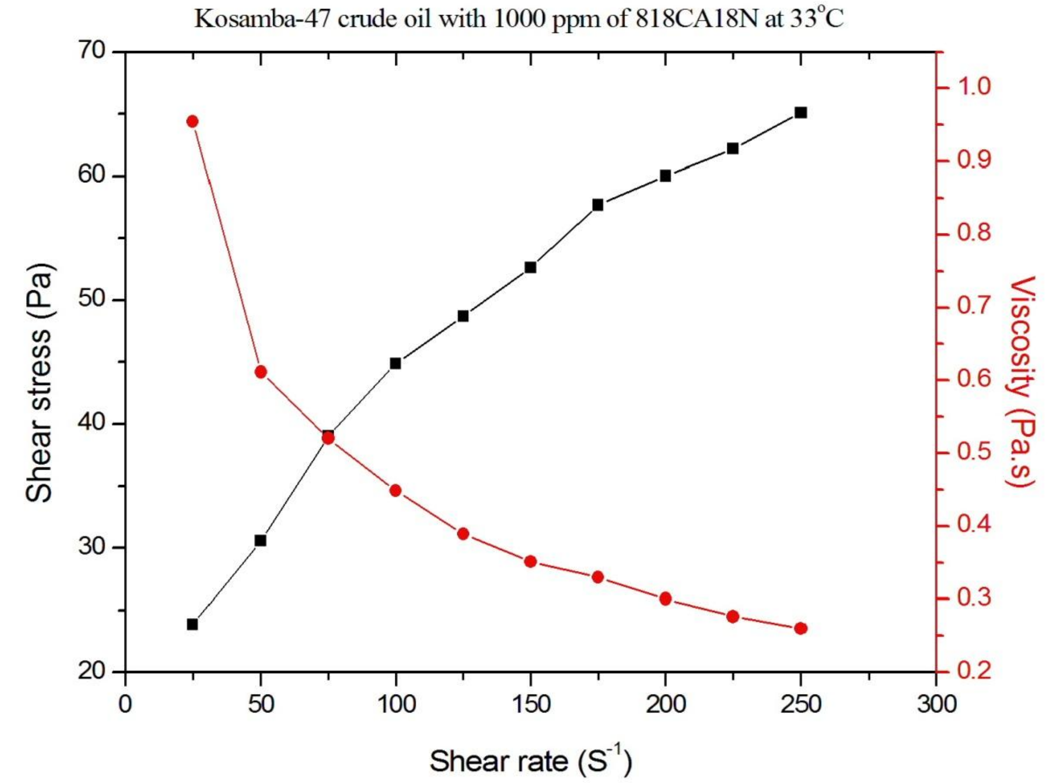

Fig 3.36 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-18CA18N at 33°C

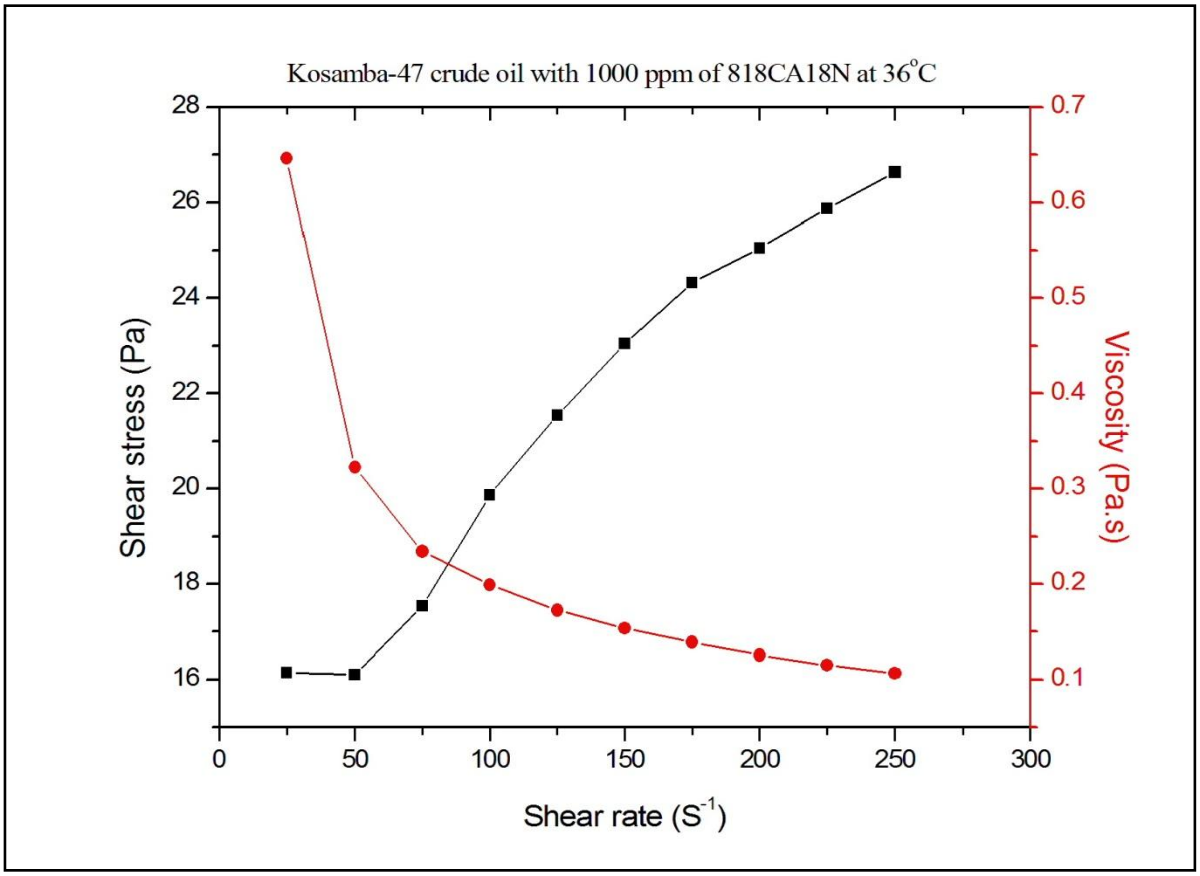

Fig 3.37 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-18CA18N at 36°C

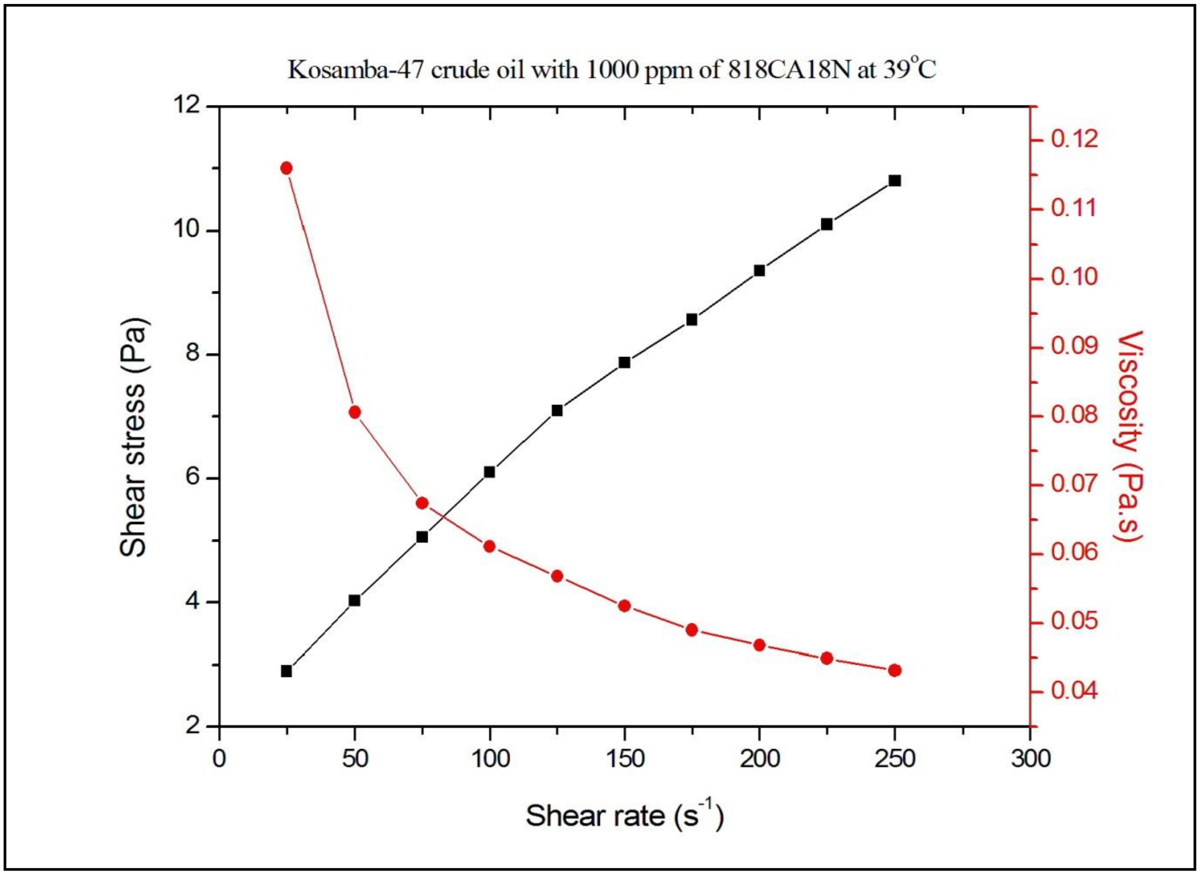

Fig 3.38 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-18CA18N at 39°C

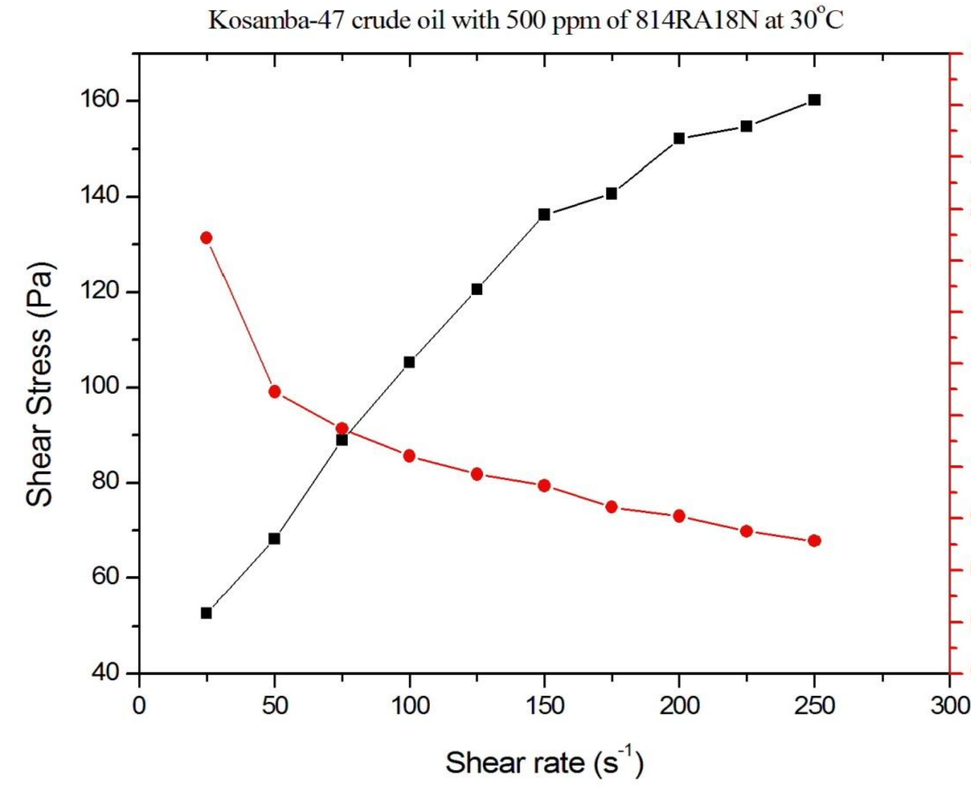

Fig 3.39 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14RA18N at 30°C

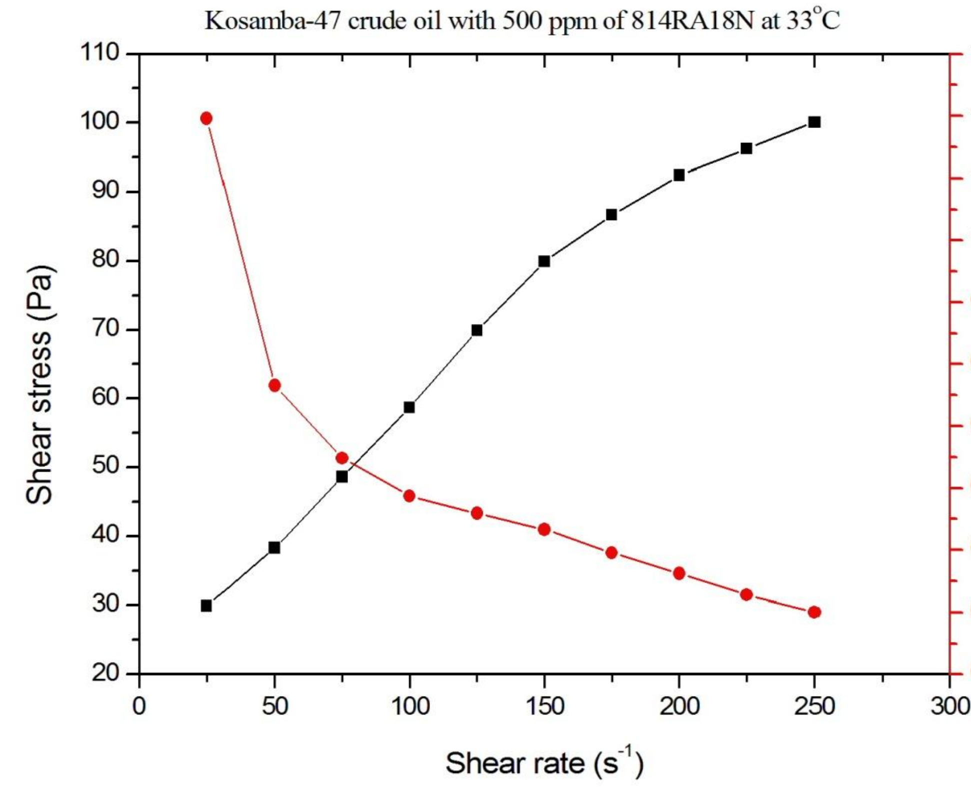

Fig 3.40 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14RA18N at 33°C

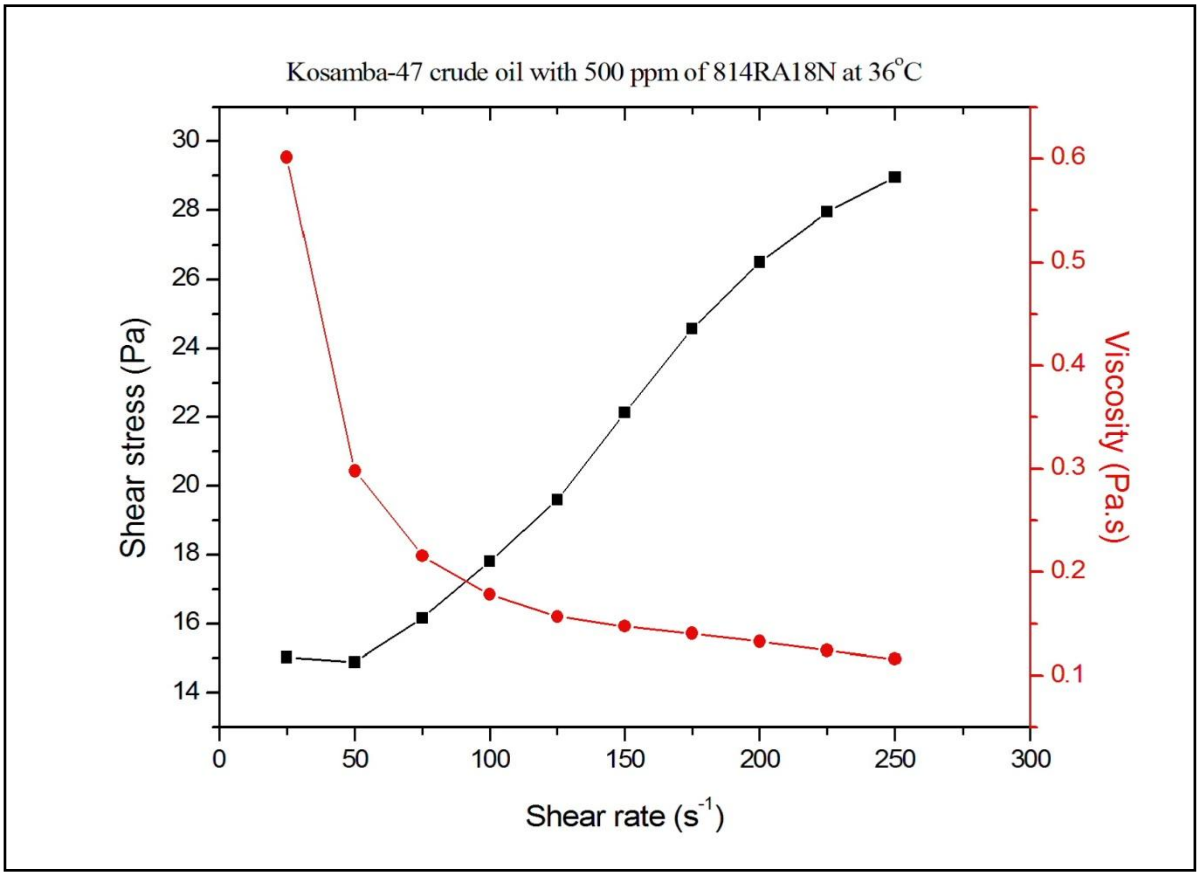

Fig 3.41 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14RA18N at 36°C

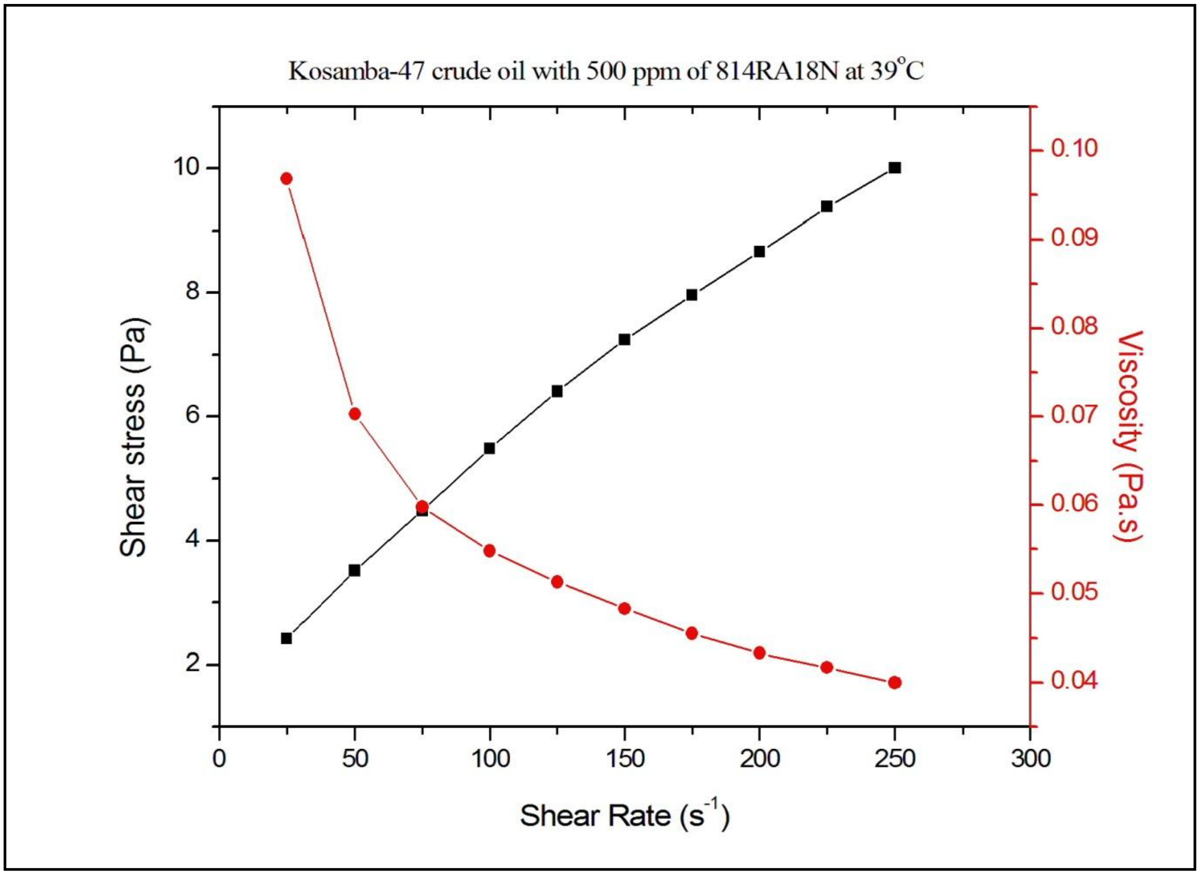

Fig 3.42 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14RA18N at 39°C

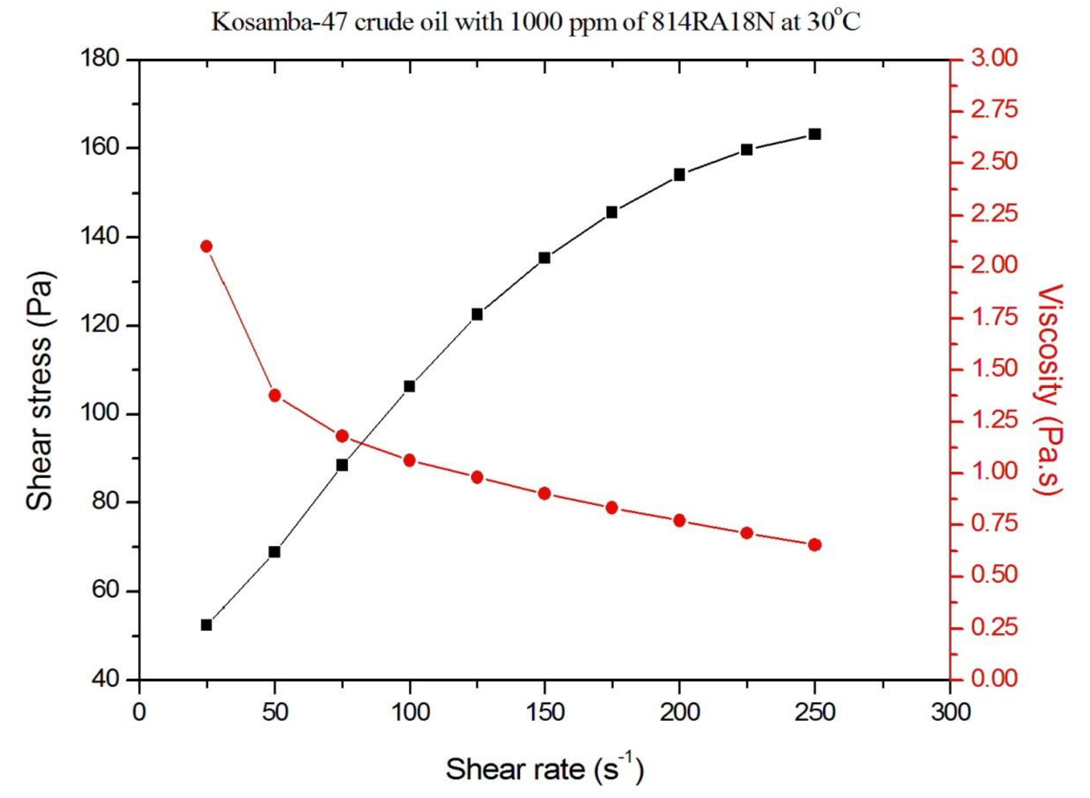

Fig 3.43 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14RA18N at 30°C

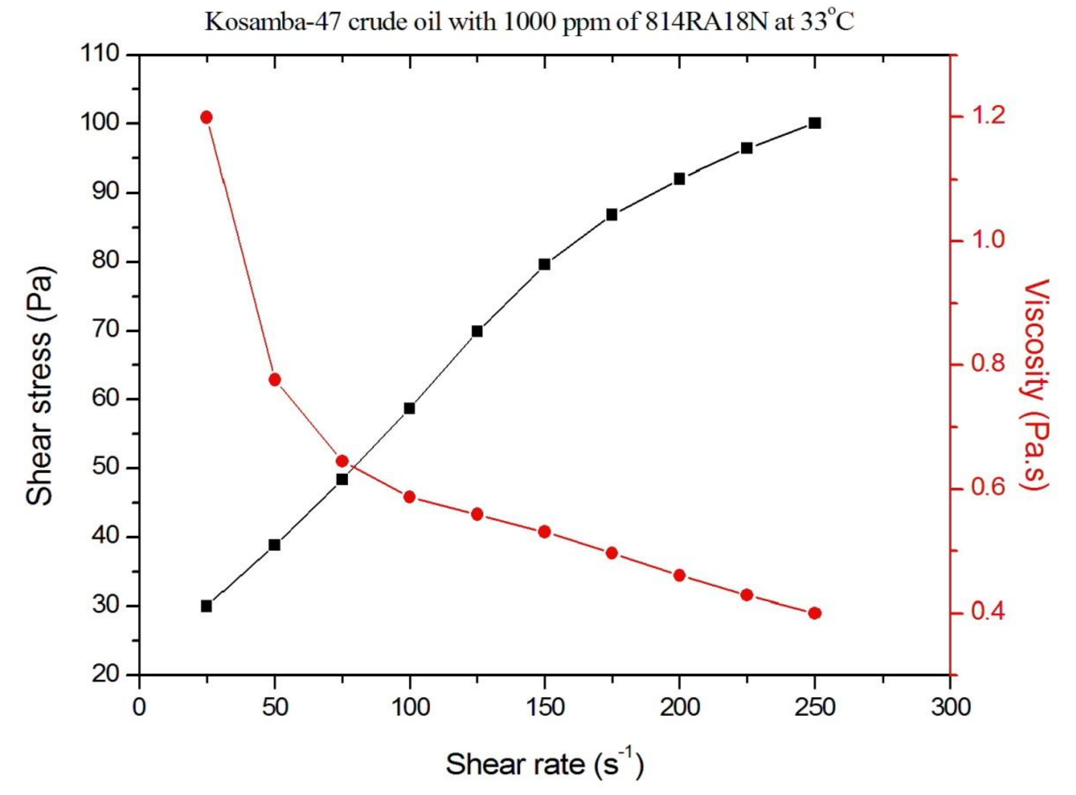

Fig 3.44 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14RA18N at 33°C

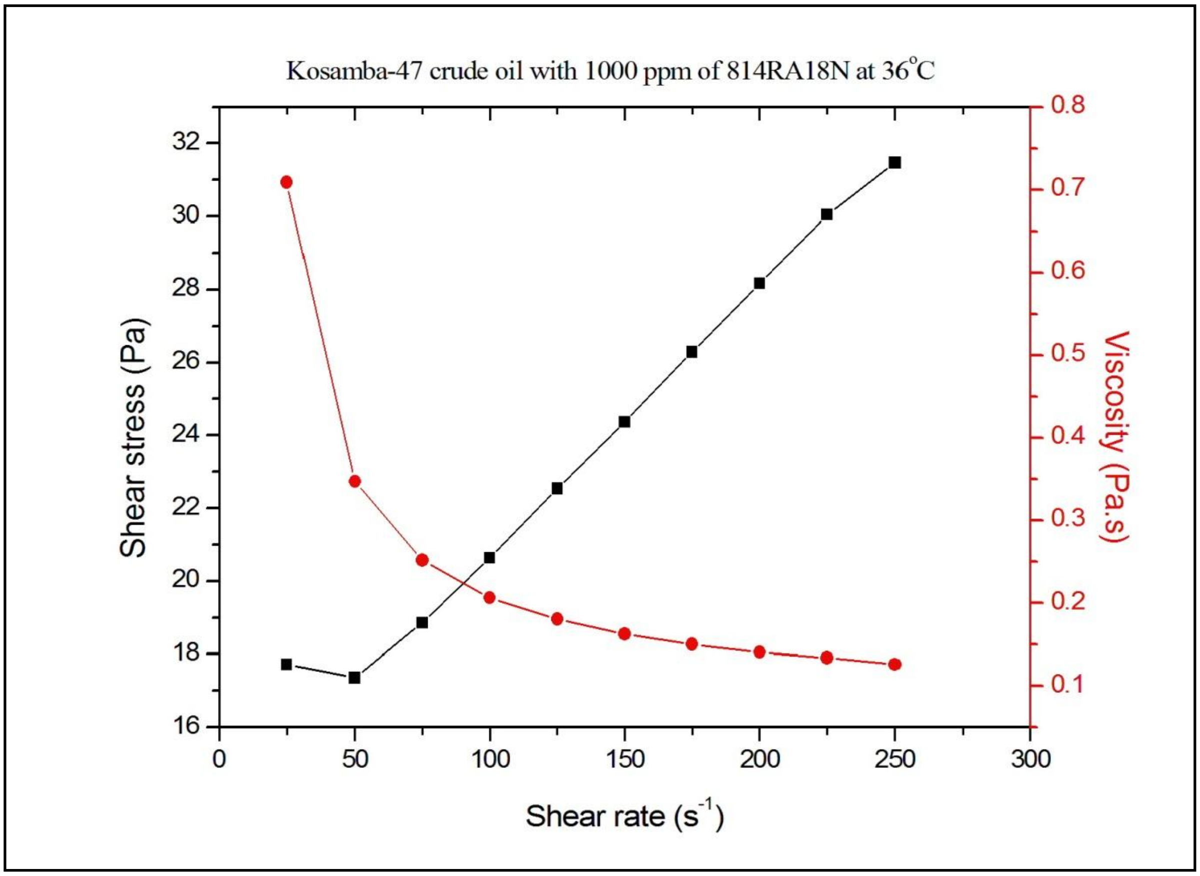

Fig 3.45 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14RA18N at 36°C

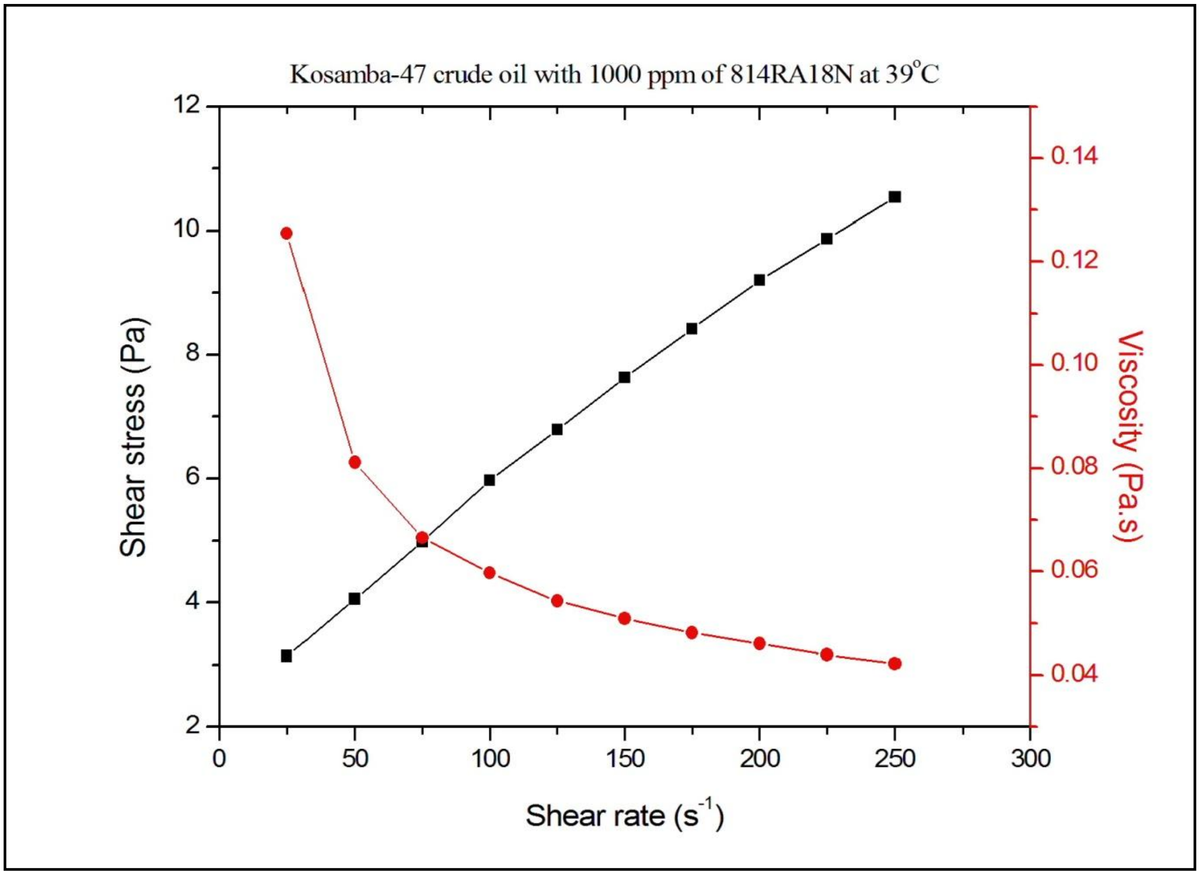

Fig 3.46 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14RA18N at 39°C

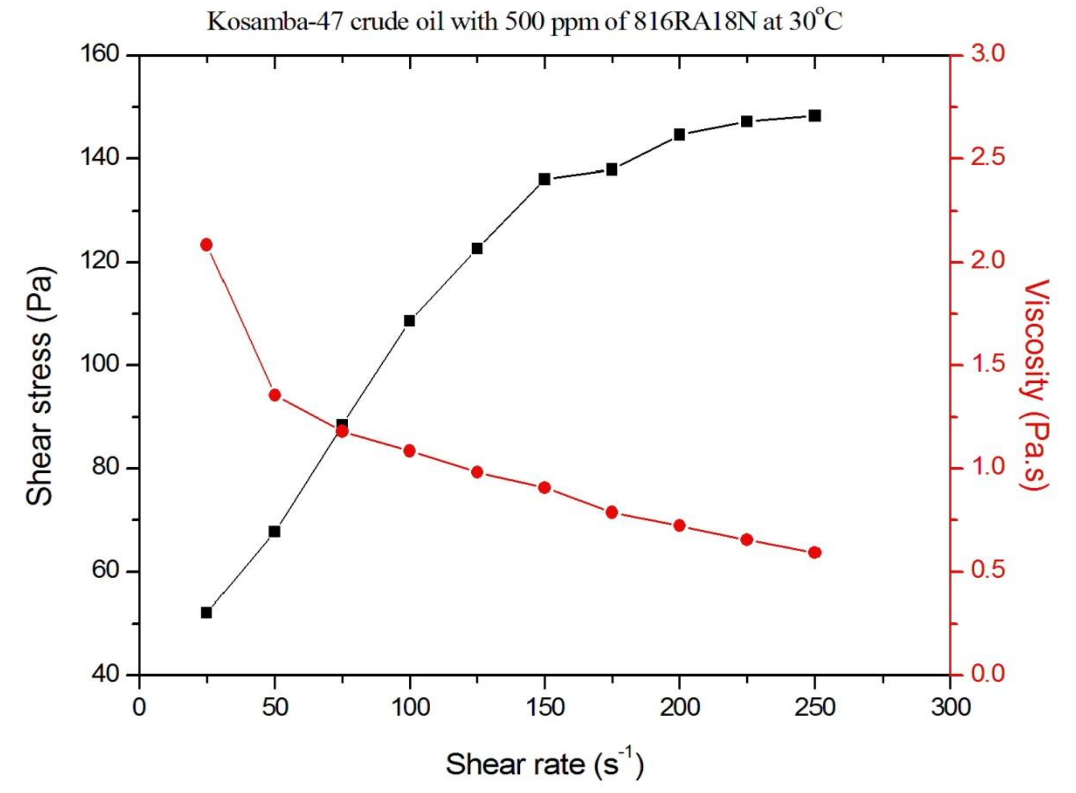

Fig 3.47 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16RA18N at 30°C

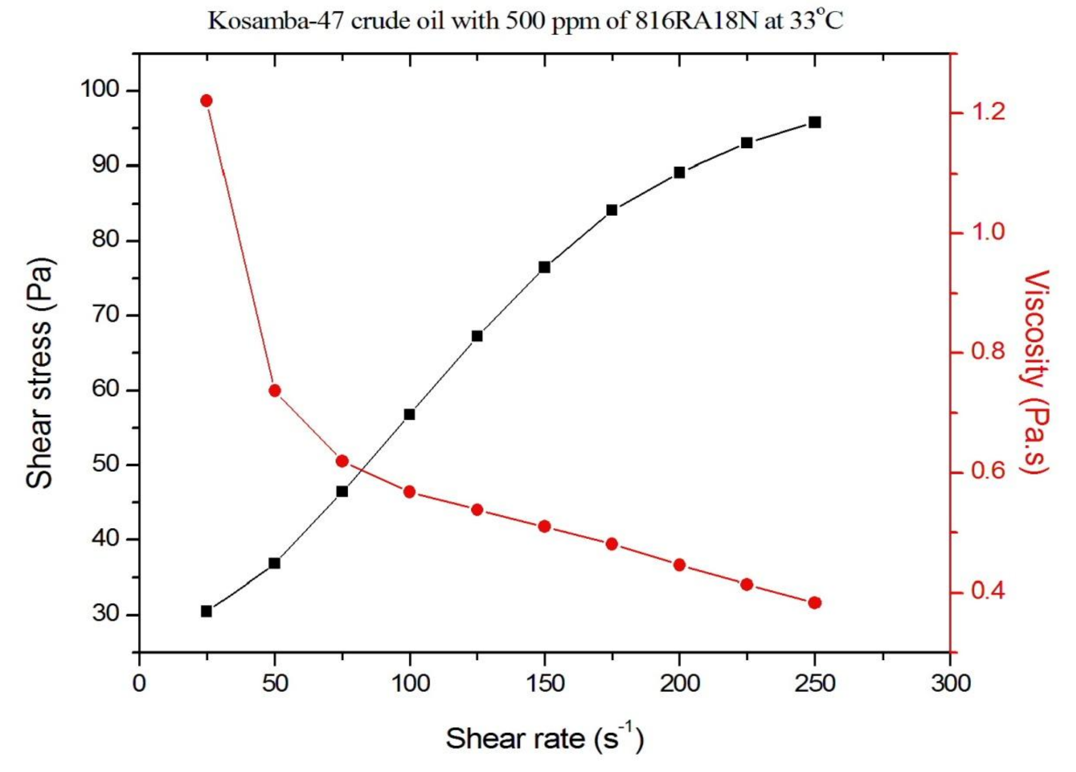

Fig 3.48 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16RA18N at 33°C

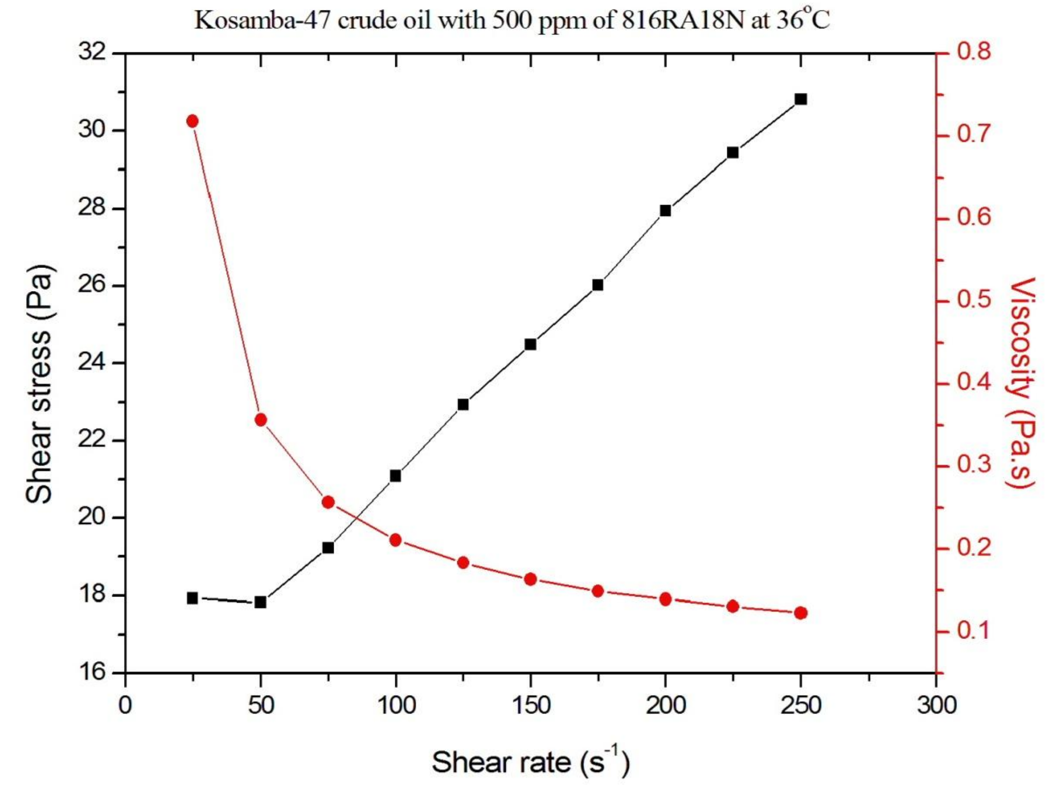

Fig 3.49 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16RA18N at 36°C

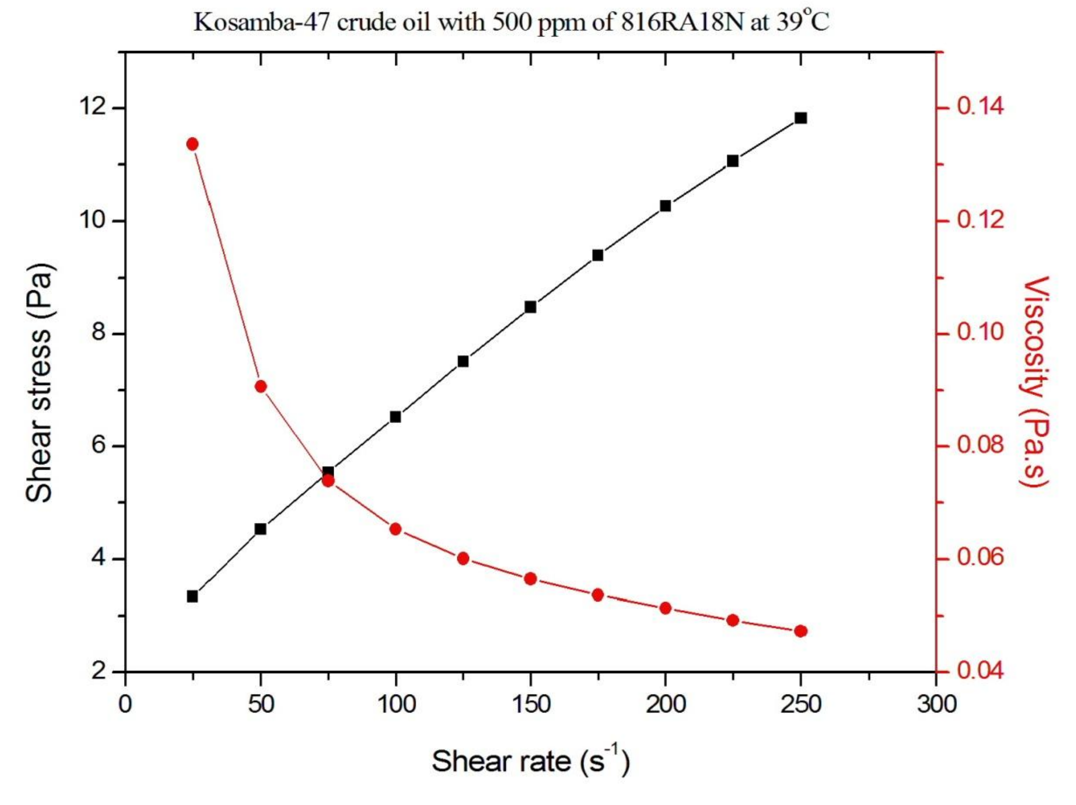

Fig 3.50 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16RA18N at 39°C

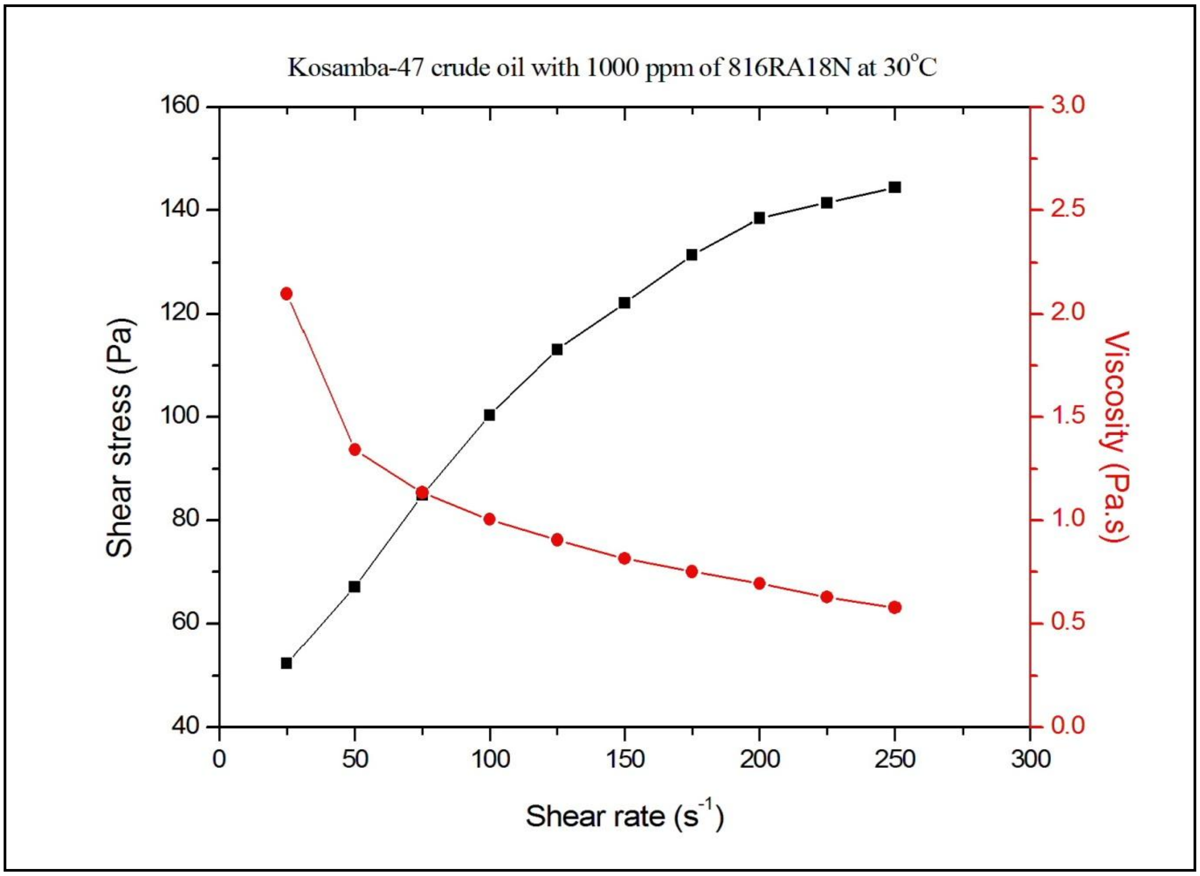

Fig 3.51 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16RA18N at 30°C

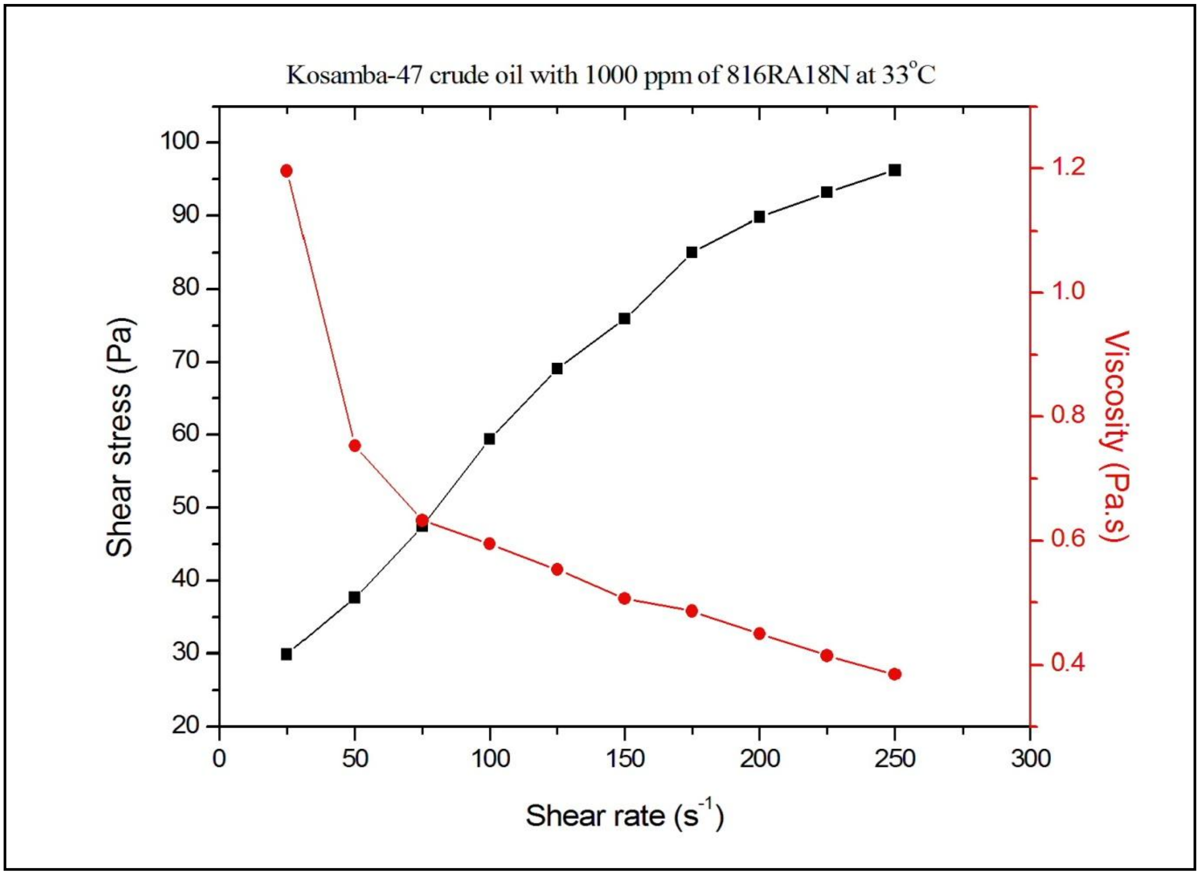

Fig 3.52 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16RA18N at 33°C

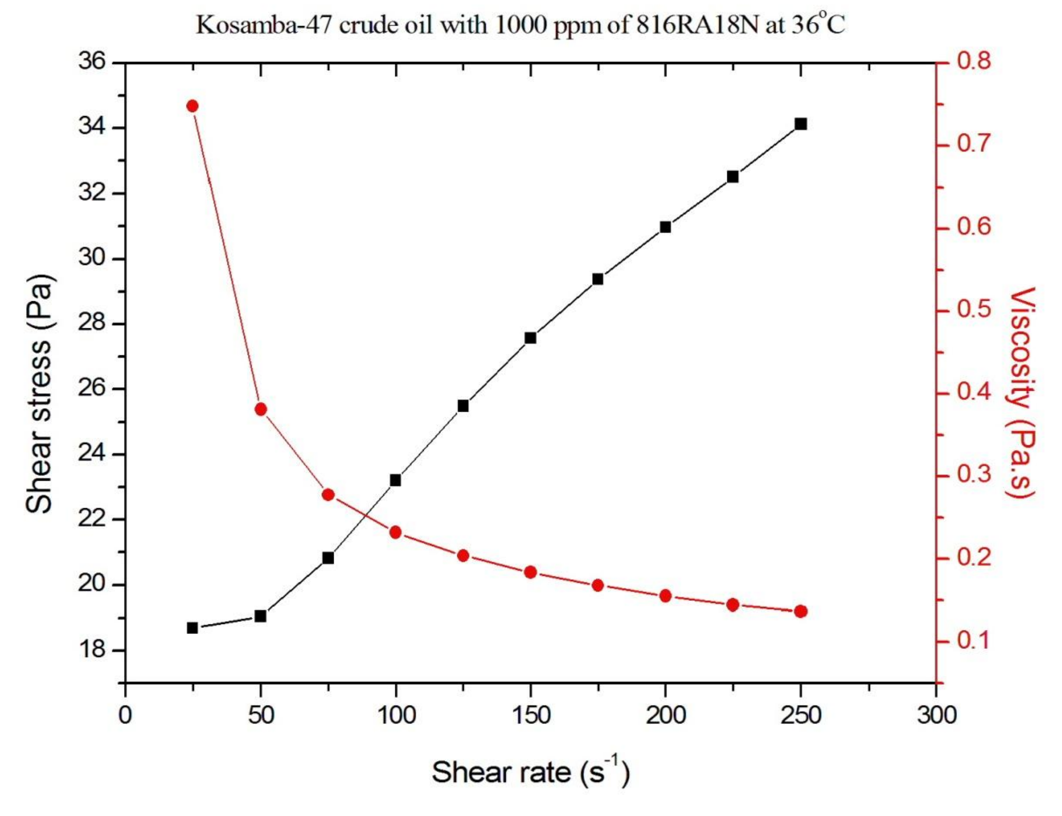

Fig 3.53 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16RA18N at 36°C

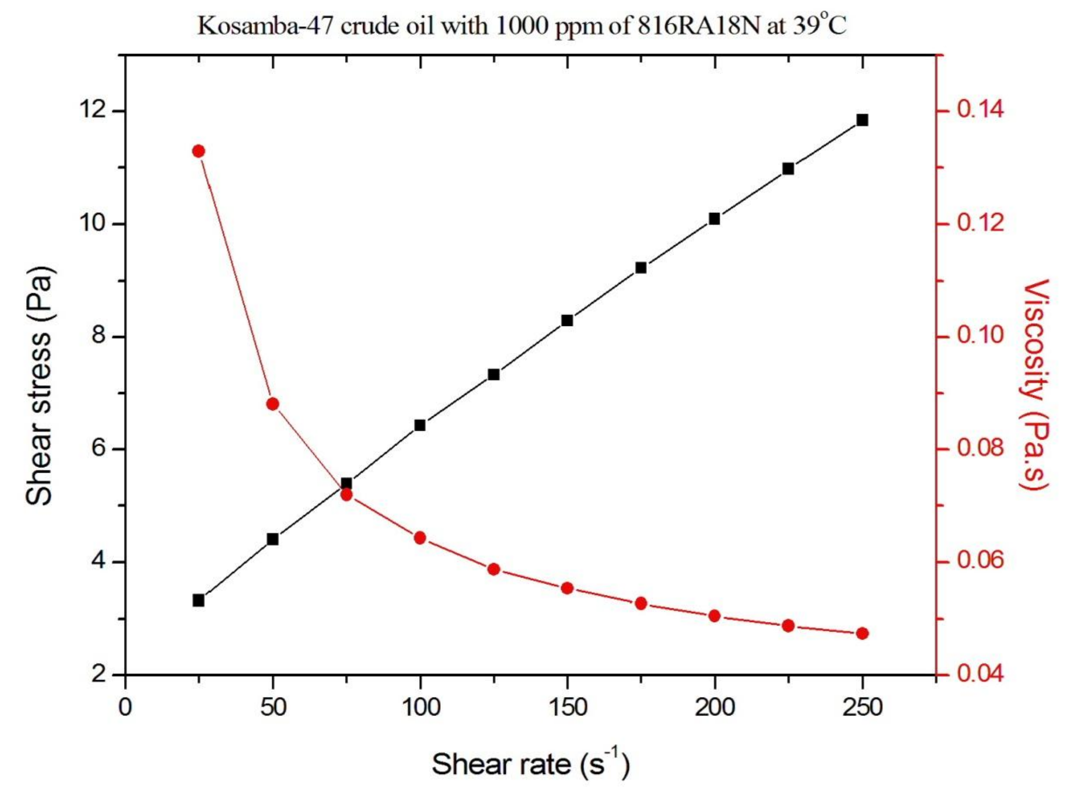

Fig 3.54 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16RA18N at 39°C

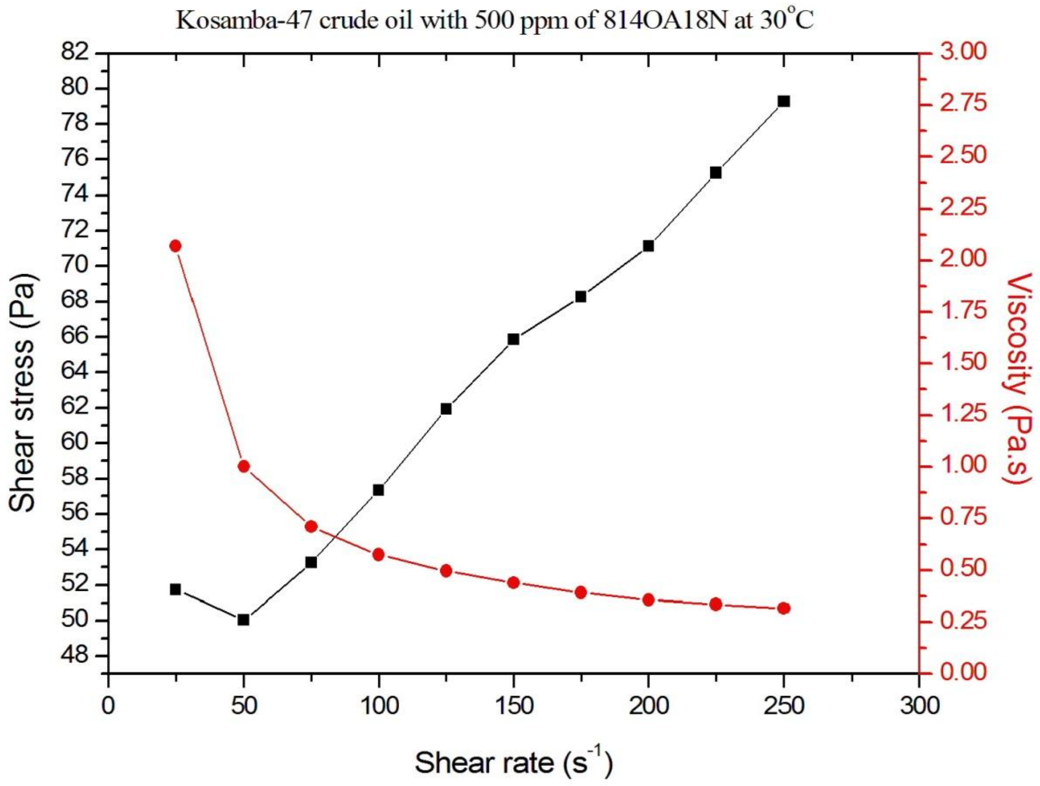

Fig 3.55 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14OA18N at 30°C

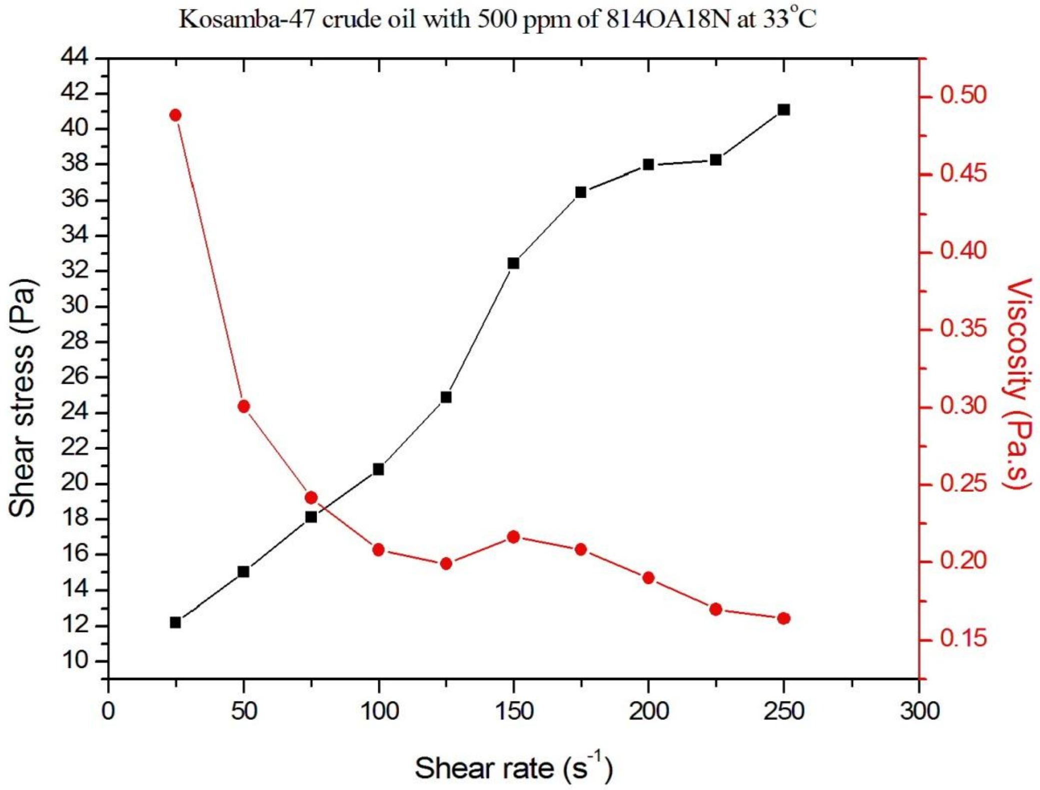

Fig 3.56 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14OA18N at 33°C

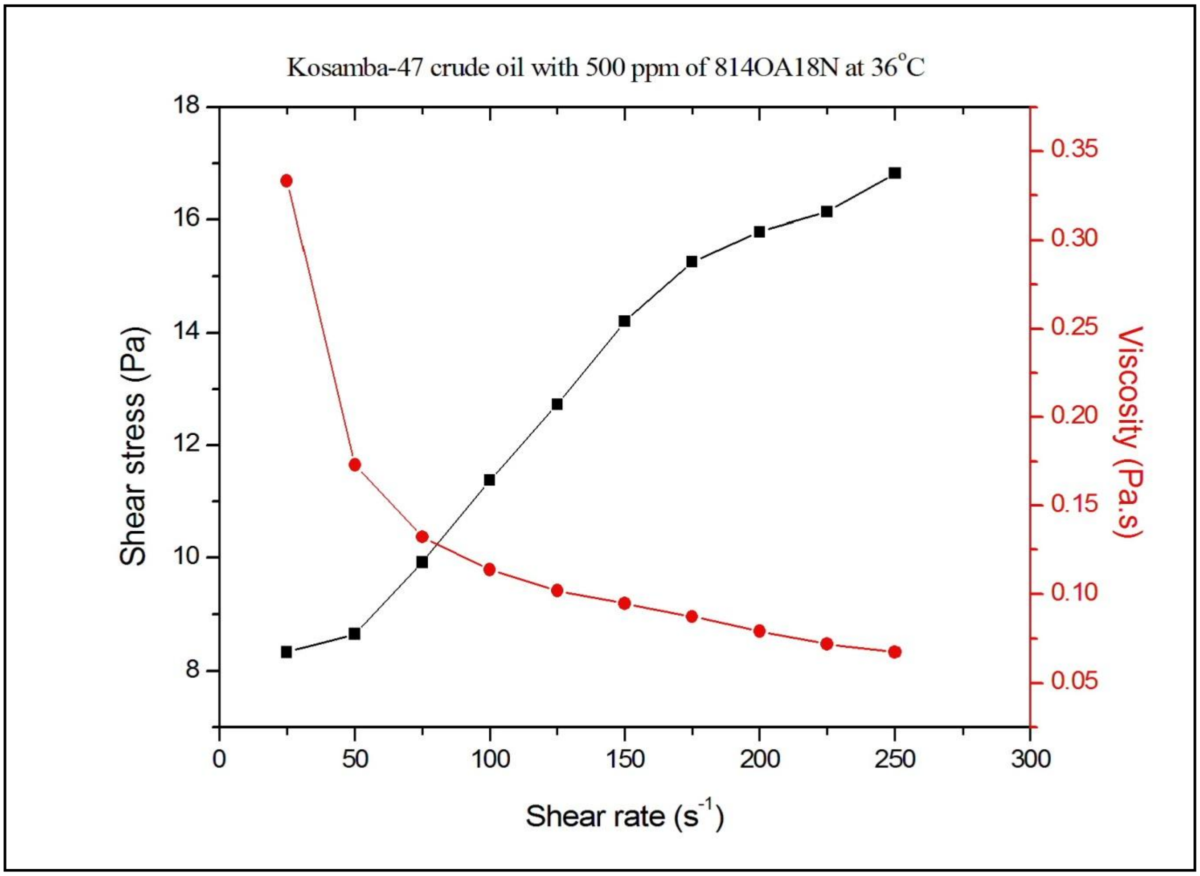

Fig 3.57 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14OA18N at 36°C

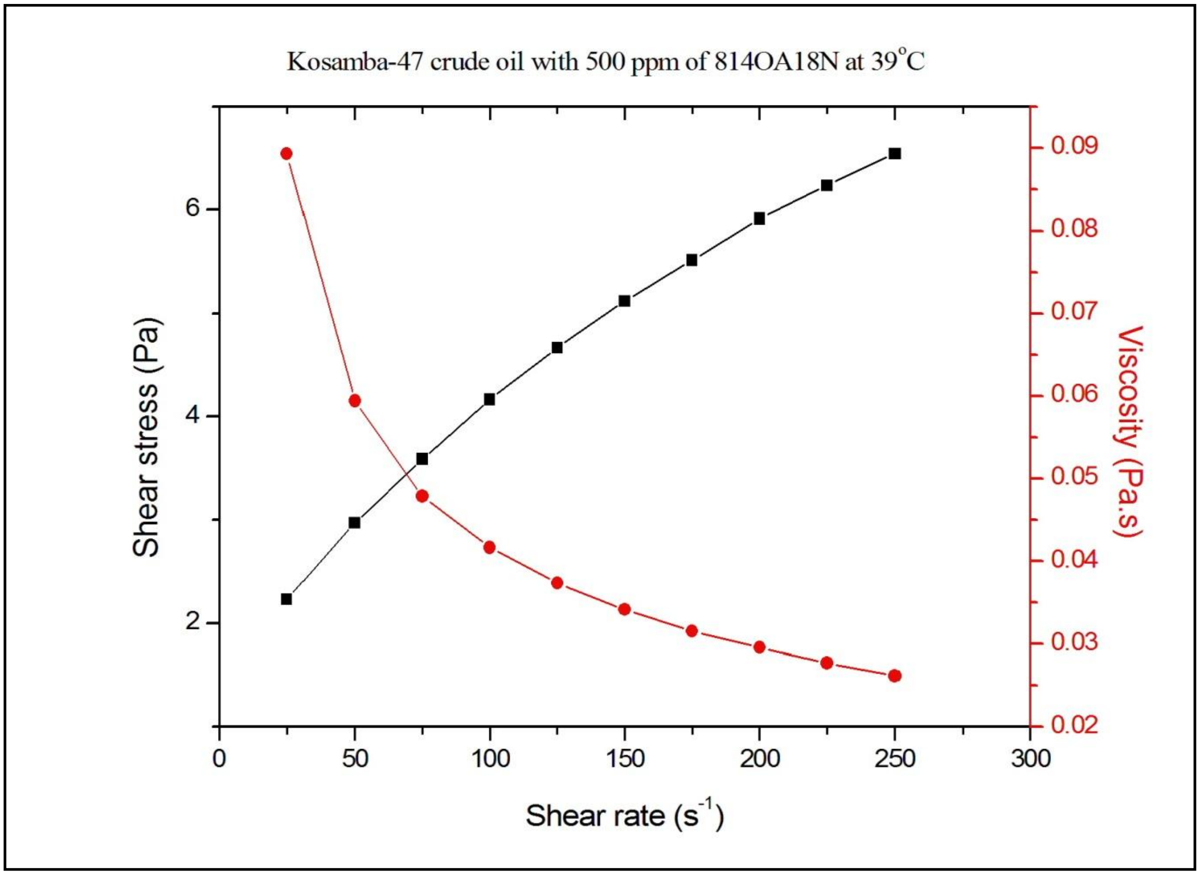

Fig 3.58 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-14OA18N at 39°C

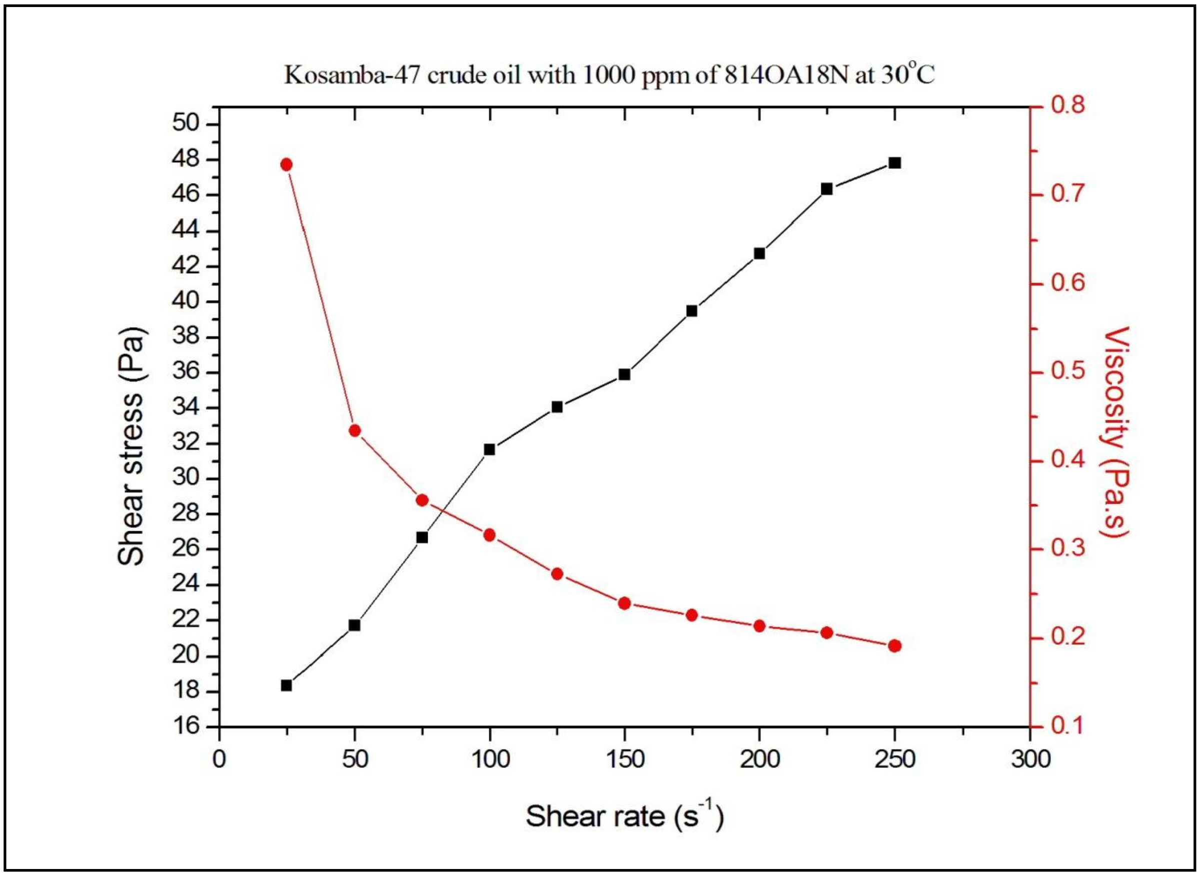

Fig 3.59 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14OA18N at 30°C

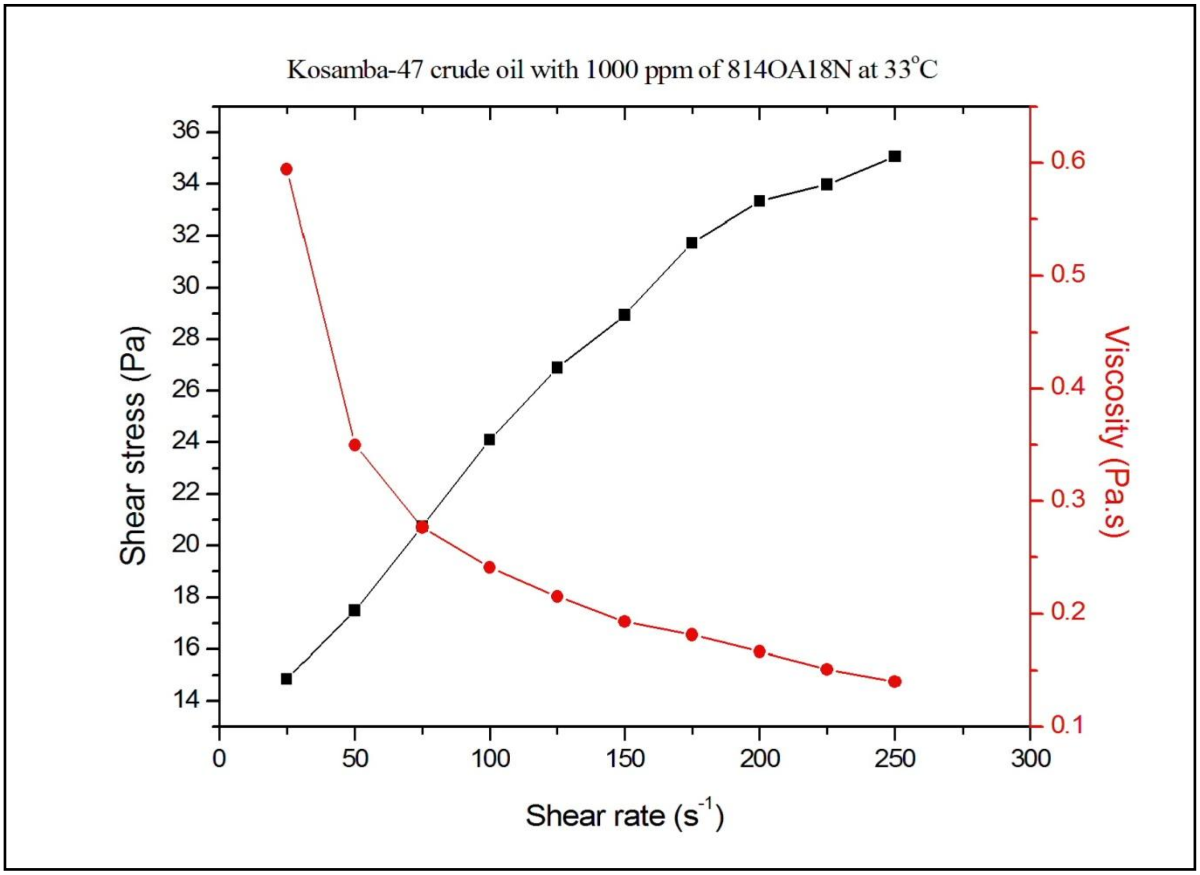

Fig 3.60 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14OA18N at 33°C

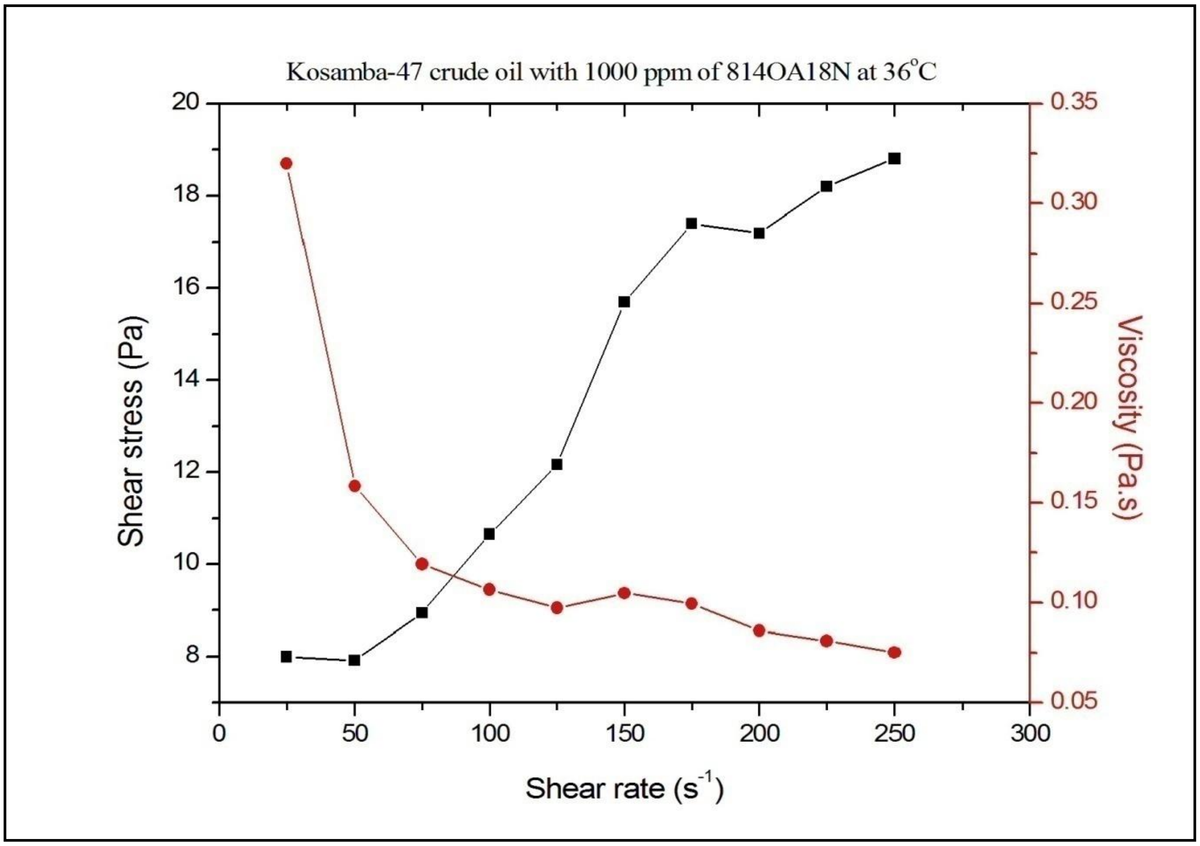

Fig 3.61 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14OA18N at 36°C

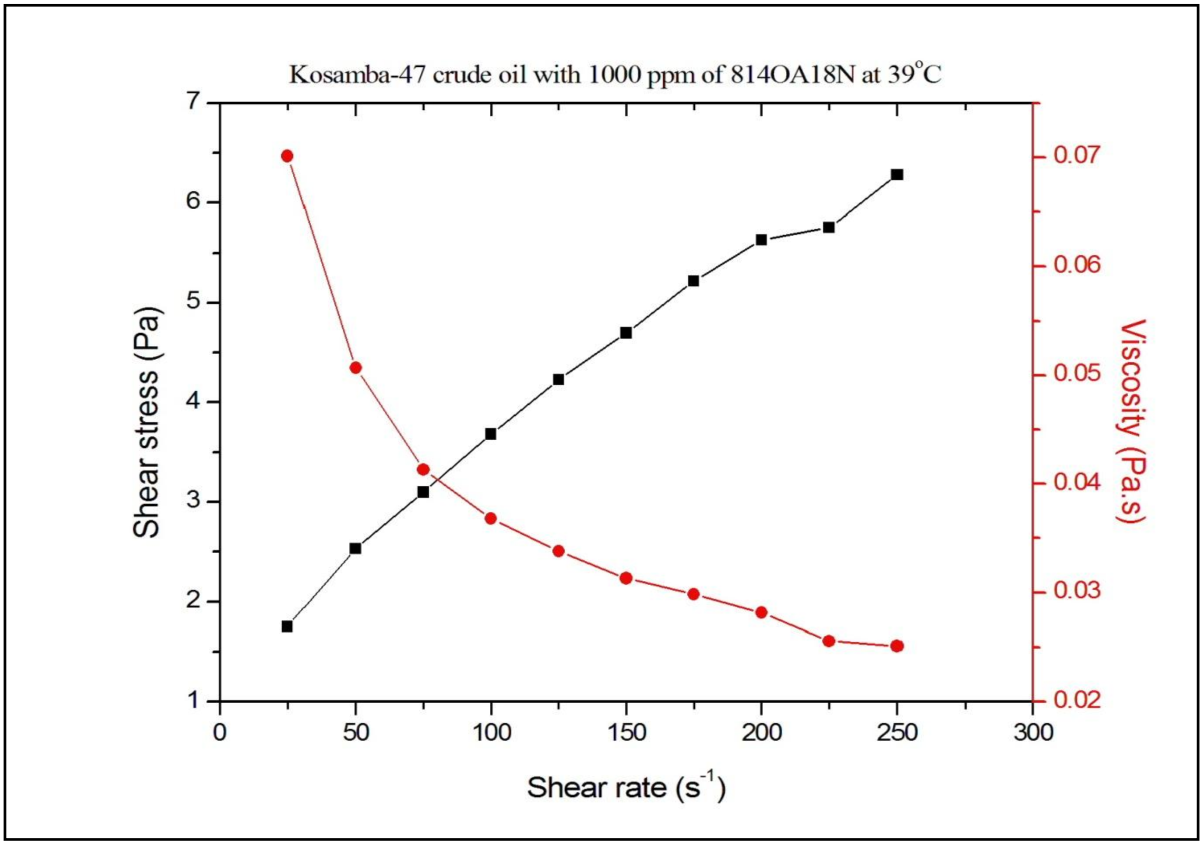

Fig 3.62 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-14OA18N at 39°C

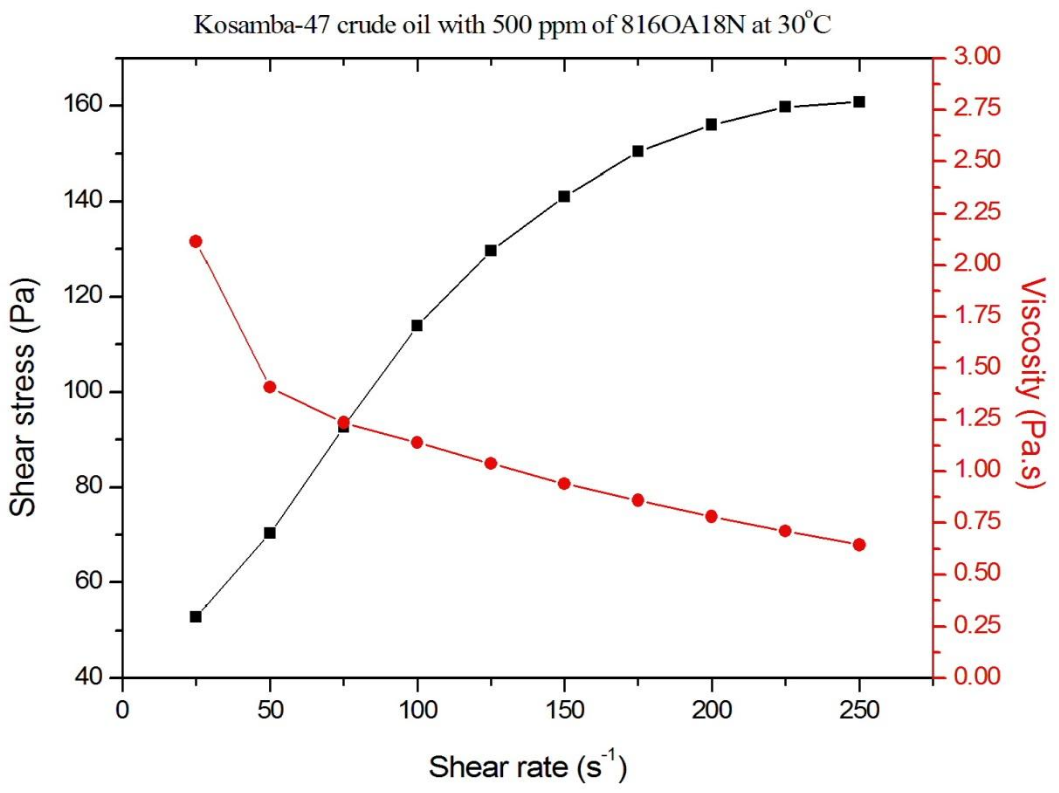

Fig 3.63 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16OA18N at 30°C

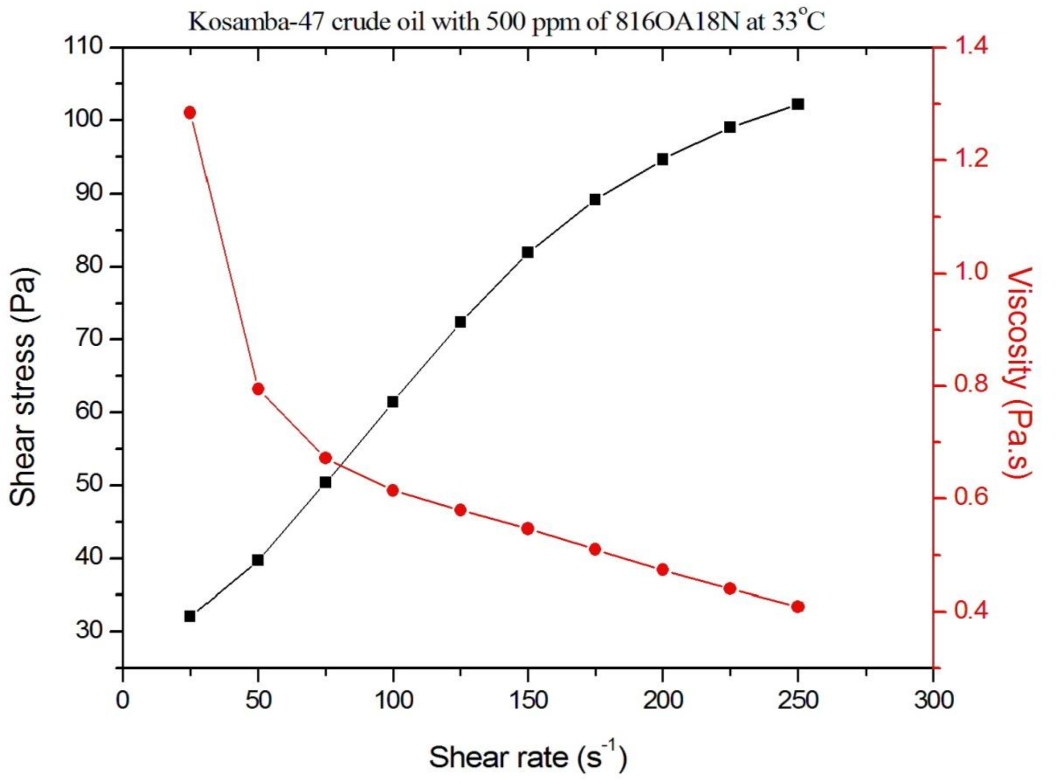

Fig 3.64 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16OA18N at 33°C

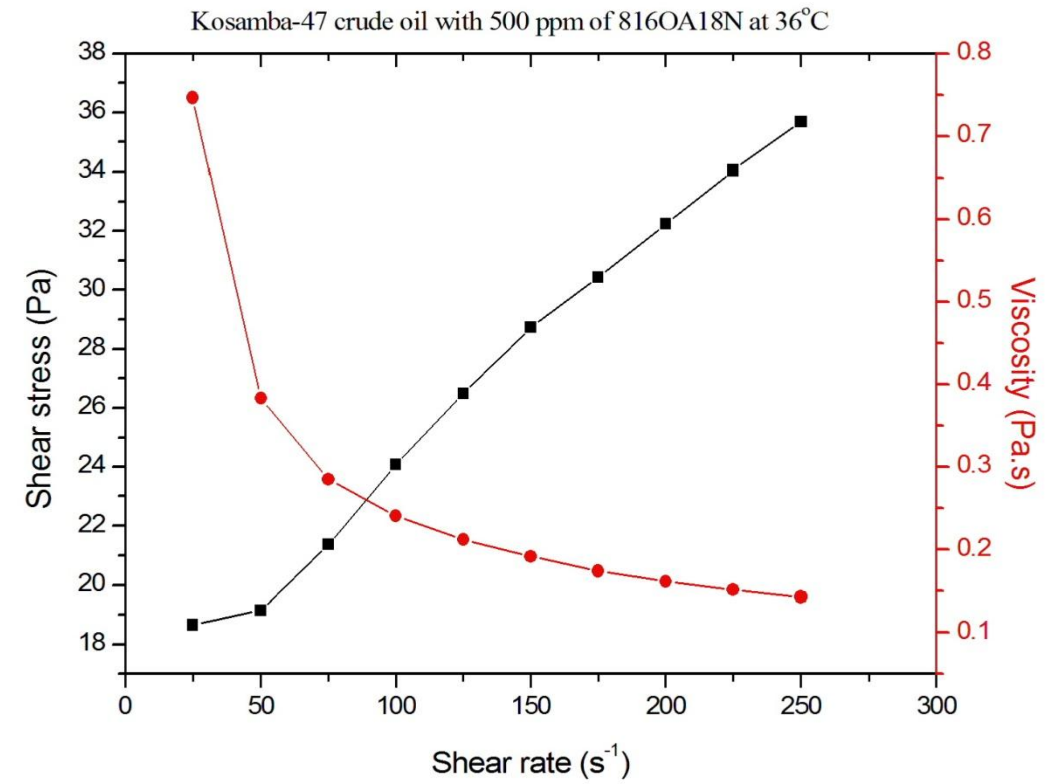

Fig 3.65 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16OA18N at 36°C

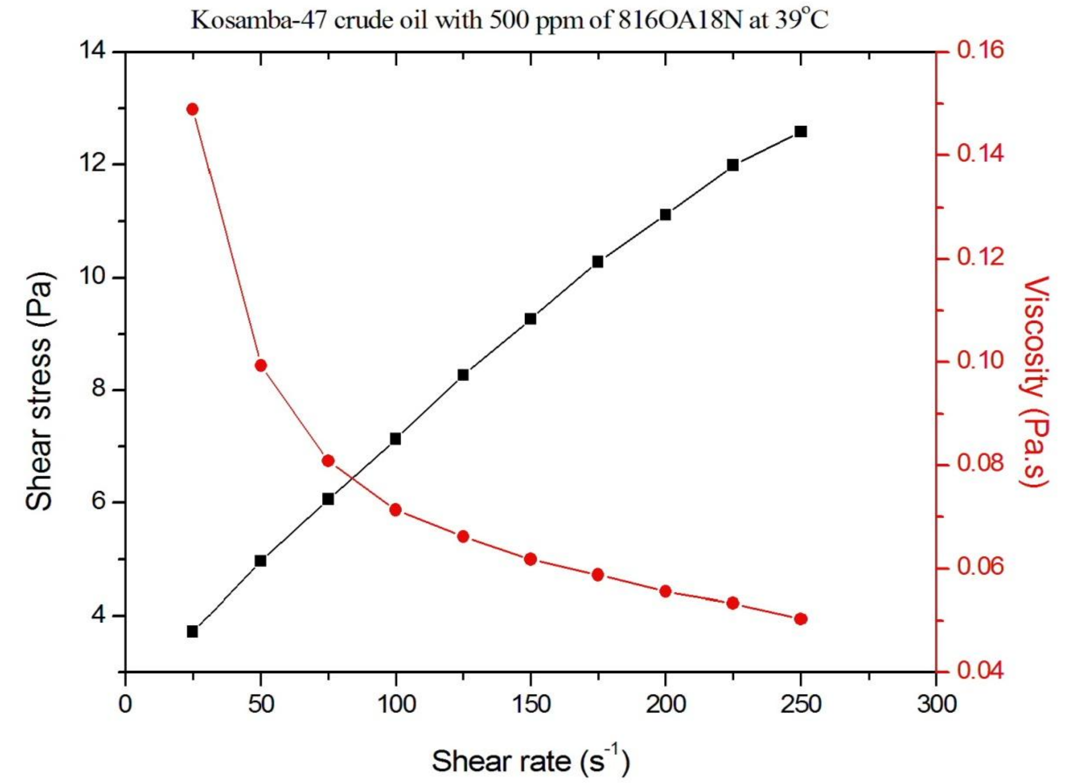

Fig 3.66 Rheogram of Kosamba-47 crude oil with 500 ppm of 8-16OA18N at 39°C

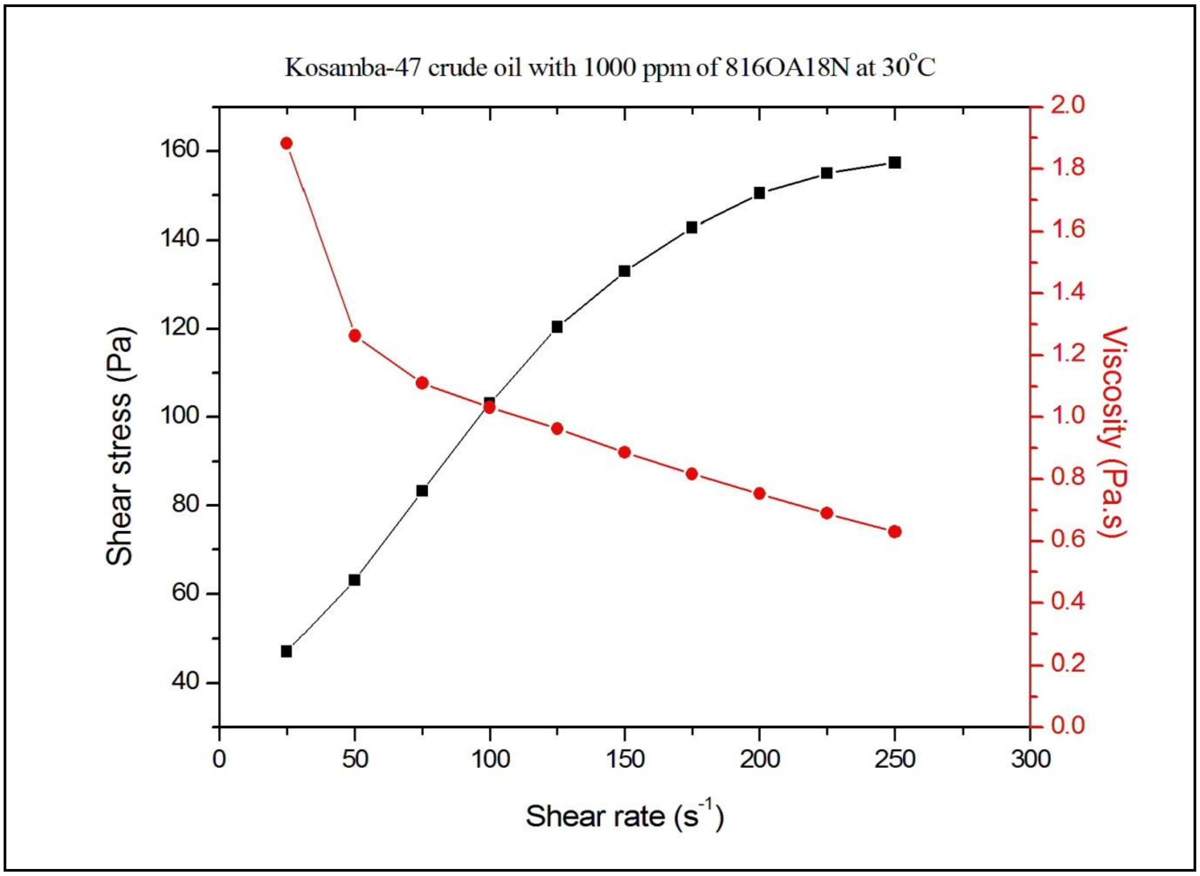

Fig 3.67 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16OA18N at 30°C

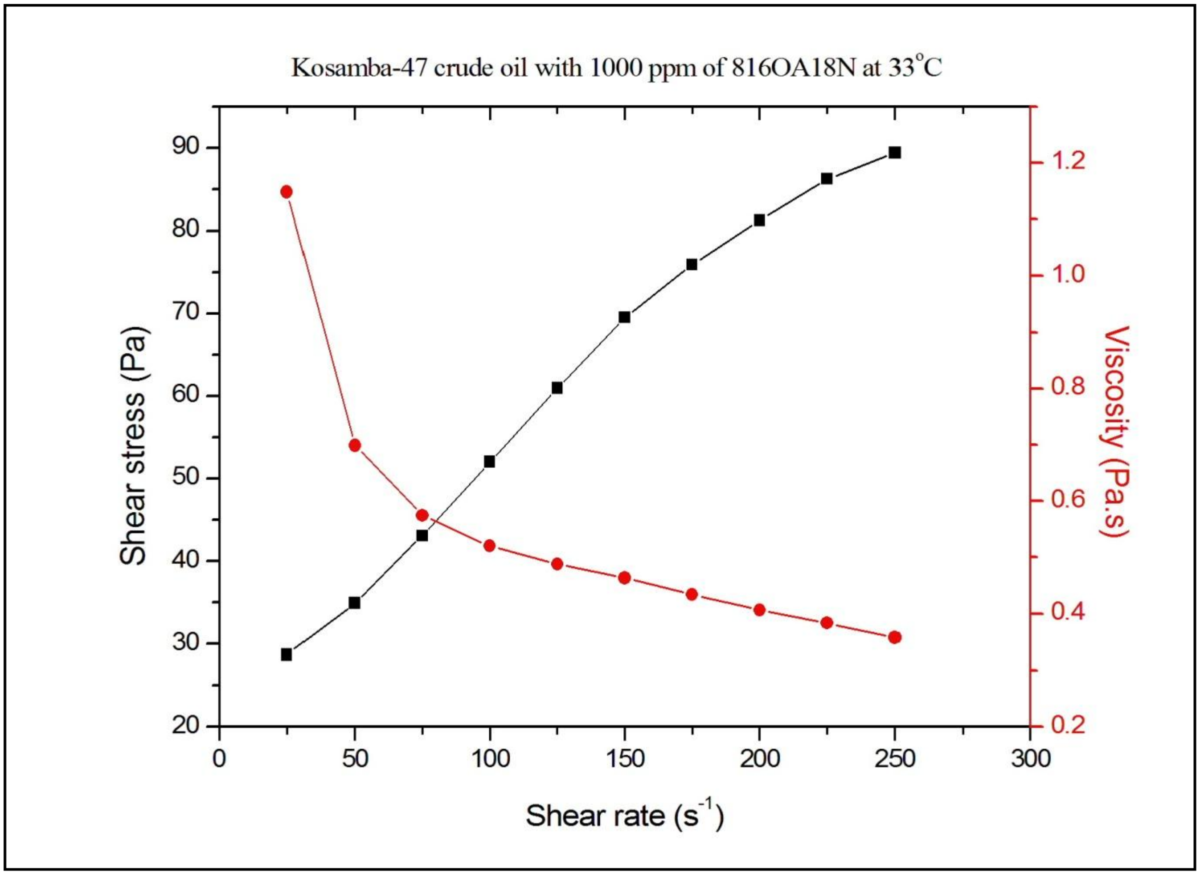

Fig 3.68 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16OA18N at 33°C

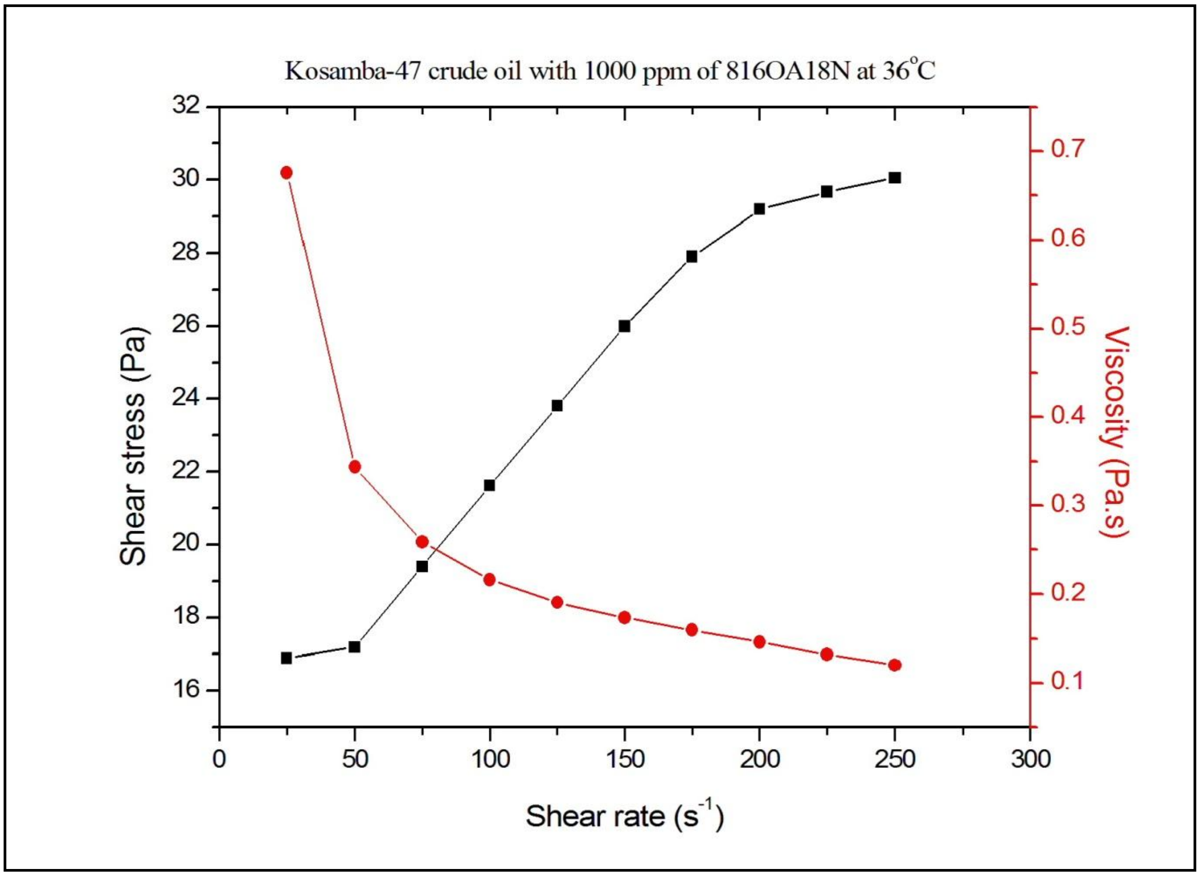

Fig 3.69 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16OA18N at 36°C

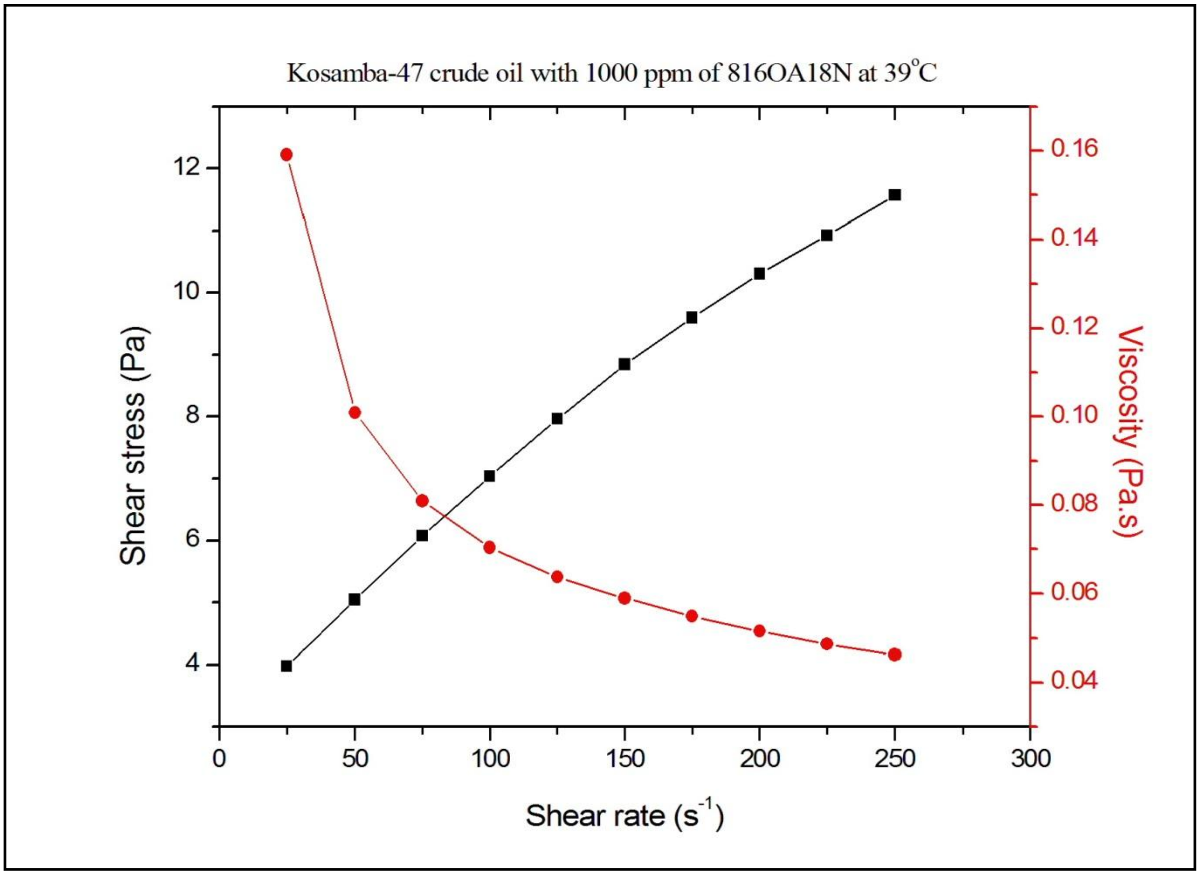

Fig 3.70 Rheogram of Kosamba-47 crude oil with 1000 ppm of 8-16OA18N at 39°C

Yield stress and viscosity values of virgin Kosamba-47 crude oil are as shown in table 3.3. From the shown values, it is clear that at 39^{o}C i.e. pour point of Kosamba-47 crude oil viscosity is 0.0600 Pa.s which increases to 1.1901 Pa.s at 30^{o}C. This clearly reveals that as temperature decreases viscosity increases and vice-versa. Same is the case with yield stress also. It is seen that at 39^{o}C yield stress value is 2.341 Pa which increases to 58.21 Pa at 30^{o}C. So viscosity and yield stress follows same trend in neat conditions.

Rheogram of virgin and additive treated crude oil depicts zigzag nature for plot of shear stress v/s shear rate having constant slope overall. Wax crystals present in crude oil stays in the fluid state and shows Newtonian behavior at higher shear stress but as shear stress reduces, wax crystallize to impart zigzag nature to curve. Figure 3.3 to 3.6 shows Rheogram of virgin Kosamba-47 crude oil at 30^{o}C, 33^{o}C, 36^{o}C and 39^{o}C. Fig. 3.6 shows Newtonian behavior of crude oil at 39^{o}C and beyond it, as shear rate v/s shear stress curve passes through origin and viscosity reduces with rise in shear rate and after shear rate 100 s^{-1} it become almost constant. The figure 3.3, 3.4 and 3.5 clearly shows high value of yield stress as 58.21 Pa, 23.55 Pa and 11.38 Pa respectively. From such values it can be concluded that at temperature below pour point of crude oil it shows non-Newtonian behavior as increase in shear stress is not proportional to shear rate and curve does not pass through origin.

Above mentioned behavior can be explained as follows: at temperatures near pour point and at low shear rates the energy imparted by shear and dispersed energy in crude matrix tends to break down the wax crystals partially. Secondary bonds form among the flocculated wax structure, thus bringing partial decrease of yield stress and drop in viscosity (thinning effect) without any tendency to flow. By increasing the shear rate, the dispersed energy is high enough to overcome yield stress and start flow, which is evident by increasing the shear stress of flow curve. At lower temperature, the dispersed energy is mostly directed to the decrease of progressive yield stress and thus less amount of energy is given to the decrease of viscosity, hence thinning effect is lowered.

On increasing the shear rate, the size of aggregates decreases and this process releases some of the continuous phase originally immobilized within the aggregates. As a result, the effective dispersed phase concentration decreases and brings decrease of viscosity. The viscosity decreases with increasing the shear rate until the aggregates are completely broken down into the basic particles. So the waxy crude oil system shows non-Newtonian characteristic. [32]

The selection of additives from each series of polymers for further rheological studies was done based on its efficiency to reduce pour point at different concentration ranging from 100 to 1000ppm. The additive which showed best performance at all concentrations (i.e. from 100 to 1000ppm) was selected which is as shown by circles in table 3.2.

The selected additives are 8-14UA18N, 8-16UA18N, 8-6CA18N, 8-18CA18N, 8-14RA18N, 8-16RA18N, 8-14OA18N and 8-16OA18N were taken at 39°C, 36°C, 33 °C and 30°C at 500 ppm and 1000 ppm concentrations and their Rheograms are shown from Figure 3.7 to Figure 3.60. From all the above additives employed, 8-16UA18N and 8-14OA18N were capable of reducing rheological parameters of viscosity and yield value to great extent as compared to virgin crude oil at 500 ppm and 1000 ppm concentration respectively.

However, the other additives 8-14UA18N, 8-6CA18N, 8-18CA18N, 8-14RA18N, 8-16RA18N and 8-16OA18N showed reverse behavior by increasing viscosity as well as yield value of Kosamba-47 crude oil to a particular extent.

3.1.5 Conclusion

3.1.5.1 Pour Point of Kosamba-47 crude oil

Pour Point Depressants do not affect crystallization temperature or amount of crystals formed. The mechanism of pour point depressants is adsorption onto the crystals formed to modify crystal formation and by co-crystallization to form smaller crystals. The efficacy of PPD depends on its chemical composition, its structural features and length of alkyl side chain. The length pendant chain governs the overall efficacy of PPD to a great extent. Another crucial parameter is extent of interaction between polymeric additives and wax distribution in crude oil. PPDs perform best when they match very well with wax distribution of crude oil [43]. So the additives having C_{11} to C_{20} pendant alkyl chains are more efficient PPDs for Kosamba-47 crude oil. C_{22} and above pendant alkyl chains make polymeric chain bulky leading to decrease in its efficiency. Adsorption tendency of additive on wax is mainly governed by length of pendant alkyl chain length. The longer alkyl polymers are efficient in depressing the pour point of high pour oils, while shorter alkyl polymers are efficient in low pour oils. In additives having very short alkyl pendant chain tends to get adsorbed on wax below pour point of oil and proved to be ineffective as PPDs. On the other hand, if very long pendant alkyl chains are present then the polymeric additive tends to crystallize out from oil solution at a temperature above pour point of the oil. All additives are found to depress pour point of crude oil. The higher dispersing activity of these additives can be attributed to presence of Nitrogen containing group in the polymeric structure i.e. imide linkage. The need of polar group in polymeric backbone is satisfied by imide linkage. Hence the non-polar chains co-crystallize with wax to form aggregates and their morphology can be modified by the presence of polar group along the polymeric backbone. Hence, it can be concluded that the functional groups present have more influence on the performance of additive when it matches better with wax composition and structure. Additives 8-6CA18N and 8-18CA18N could reduce the pour point of Kosamba-47 crude oil by 12^{o}C and were found to be best performer among the tested ones. Such high performance can be attributed to the presence of asphaltenes in Kosamba-47 crude oil which serves as natural PPD and benzene ring found in the polymeric backbone of these additives. These asphaltenes present co-precipitates with waxes and prevent agglomeration of wax crystals. Hence it improves the performance of additives having aromatic (benzene) parts in their pendant chain. Hence it can be understood that aromatic part of the pendant chains acts as nucleating sites for asphaltenes. The planar aromatic portion of asphaltene communicates well with planar aromatic rings of pendant chain of the additive with attractive forces such as π-π stacking. The aliphatic pendant chains present in the same polymeric additive act as nucleating sites for waxes found in the crude oil. Hence, it can be easily envisaged that the wax crystals cannot interlock with each other and form house of card type structure because of presence of asphaltenes and remain in crude as suspended particles. [50] For other additives like 8-14UA18N, 8-16UA18N, 8-14RA18N, 8-16RA18N, 8-14OA18N and 8-16OA18N, high efficiency as PPD can be attributed to possible presence of wax components falling in C_{11} to C_{20} range. All the above mentioned additives configure well with wax components of Kosamba-47 crude oil.

3.1.5.2 Rheological Studies

Rheological behavior of virgin and some additive treated crude oil at various concentration and temperature were studied. The Rheogram shows alteration in viscosity due to additive treatment at different temperatures and shear rates. The results obtained clearly depict that some of additives like 8-16UA18N, 8-14OA18N brought significant reduction in viscosity of Kosamba-47 crude oil. Also, as viscosity of crude oil decreases then the yield stress needed to start flow also decreases and so it is possible to keep crude oil in flowing condition even at low temperature. 8-16UA18N at 500 ppm reduced viscosity to 0.0390, 0.0939, 0.1190 and 0.1991 Pa-s at 39^{o}C, 36^{o}C, 33^{o}C and 30^{o}C respectively. Also at 1000 ppm concentration the viscosity values registered are 0.0227, 0.0412, 0.0868 and 0.2266 Pa-s at 39^{o}C, 36^{o}C, 33^{o}C and 30^{o}C respectively. Also for 8-

14OA18N at 500 ppm concentration 0.0424, 0.1254, 0.2387 and 0.6686 Pa-s viscosity values were reported at 39°C, 36°C, 33°C and 30°C respectively. When concentration increased to 1000 ppm 0.0372, 0.1247, 0.2509 and 0.3190 Pa-s at 39°C, 36°C, 33°C and 30°C respectively were observed. For 8-16UA18N additive, the values of yield stress are also in the range of 1.955 Pa to maximum 10.05 Pa. And for 8-14OA18N additive, the yield stress values found to be in range of 1.586 to 16.38 Pa. Both the values of viscosity and yield stress for above additives observed are pretty low as compared to virgin crude oil. Hence, these additives can be successfully employed for Kosamba-47 crude oil.

This behavior may be explained by the two reasons: on one hand, PPD have changed the morphology of paraffins in crude oil, resulting in decrease of pour point, thereby reducing temperature at which viscosity increases. On the other hand, intermolecular forces between paraffins, asphaltenes and resins become weaker when PPDs are added because of nucleation in case of paraffins and H-bonds between PPDs, asphaltenes, resins which keeps these molecules in dispersed phase. As a result, viscosity is reduced.

Now, the other additives coded 8-14UA18N, 8-6CA18N, 8-18CA18N, 8-14RA18N, 8-16RA18N, and 8-16OA18N have given reverse results that is increased the viscosity of Kosamba-47 crude oil. It can be observed from the table 3.3 that with increase in pendant alkyl chain length and concentration of additive the viscosity and yield stress has been increased. Flow behavior is reduced to considerable extent. The yield stress has increased to as high as 58.63Pa indicating reverse effect of additive. So, it is very much clear that above mentioned additives are not suitable for Kosamba-47 crude oil.

The reason for such high values of rheological parameters may be such that the polymer additive becomes insoluble in crude oil and forms aggregates, which precipitate out from the crude along with wax crystal without being properly adsorbed on the surface. Due to this, they cannot make a change in the crystal structure but instead, the pendant chains of polymers interlock into one another like a zipper. Now the polymer molecules cannot slide over one another which results in an increase in viscosity and yield value of the crude oil. [25, 35]

CHAPTER-3 (II)

EVALUATION OF POLYMERIC FLOW IMPROVERS OR POUR POINT DEPRESSENTS ON KOSAMBA-33 (GUJARAT, INDIA) CRUDE OIL

3.2.1 Physico-chemical properties of Kosamba-33 crude oil

Kosamba-33 crude oil is medium to high density oil. The sample taken is from a particular well from Kosamba field. Kosamba-33 crude oil is highly waxy as it has almost 20 % of wax and shows pour point of 39 °C which is a problem in summer season also. This amplifies in winter season when temperature goes below 20°C and makes it difficult to handle. The Physico-chemical Properties of Kosamba-33 crude oil is as shown in Table 3.4.

Table 3.4: Physico-Chemical Properties of Kosamba-33 Crude Oil

S. No.	Parameter	Method	Unit	Result
1	Free water	-	%	Nil
2	Water content	IP-358	%	1.0
3	Density at 15°C	IP-160	Kg/l	0.8747
4	Specific Gravity	IP-200	-	0.8752
5	API Gravity	-	-	30.18
6	Pour Point	IP-15	°C	39
7	Wax content	UOP-46-64	%	20.80
8	Asphaltenes Content	IP-143	%	0.46
9	Saturate	-	%	69.23
10	Aromatic	-	%	23.41
11	Resin Content	-	%	6.90

3.2.2 Pour Point Determination

The pour point determination was done by the standard method ASTM D-97/IP-15 as described in section-3.1.2 (Chapter-3, Part-1). The pour point results of virgin Kosamba-33 crude oil and additive doped crude oil is as shown in Table 3.4.

3.2.3 Rheological Studies

The rheological studies were performed by the method described in section 3.1.3 (Chapter-3, Part-1). The rheological data is as shown in Table 3.5.

3.2.4 Results and Discussions

3.2.4.1 Evaluation of Polymeric Additives as Pour Point Depressants

Table 3.5 Pour Point Data of Neat and Treated Kosamba-33 crude oil

Kosamba-47	Temperature (^{o}C)							
Sample Code	Virgin Crude	100 ppm	200 ppm	400 ppm	500 ppm	1000 ppm	Maximum depression in pour point	Extent of pour point depression
8-6UA18N	39	36	36	36	36	36	36	03
8-10UA18N	39	39	39	36	36	33	33	06
8-12UA18N	39	33	33	33	30	33	30	09
8-14UA18N	39	36	36	33	33	33	33	06
8-16UA18N	39	33	33	33	33	33	33	06
8-18UA18N	39	36	33	33	33	33	33	06
8-22UA18N	39	36	36	36	36	36	36	03
8-6CA18N	39	33	33	33	33	33	33	06
8-10CA18N	39	30	30	30	30	30	30	09
8-12CA18N	39	33	30	30	30	30	30	09
8-14CA18N	39	30	30	30	30	27	27	12
8-16CA18N	39	36	33	33	33	33	33	06
8-18CA18N	39	33	33	33	33	36	33	06
8-22CA18N	39	33	33	33	33	36	33	06
8-6RA18N	39	36	36	36	36	36	36	03
8-10RA18N	39	39	39	36	36	36	36	03
8-12RA18N	39	36	33	33	30	30	30	09
8-14RA18N	39	33	30	30	30	30	30	09
8-16RA18N	39	36	36	36	33	33	33	06
8-18RA18N	39	39	36	36	36	33	33	06
8-22RA18N	39	36	36	36	36	36	36	03
8-6OA18N	39	39	39	39	36	36	36	03
8-10OA18N	39	36	33	33	33	30	30	09
8-12OA18N	39	39	36	36	36	36	36	03
8-14OA18N	39	36	36	33	33	33	33	06
8-16OA18N	39	36	36	33	33	30	30	09
8-18OA18N	39	36	36	36	36	36	36	03
8-22OA18N	39	39	36	36	36	36	36	03

Pour Point Depressants or Flow improvers make crystal size smaller and volumes higher by co-crystallizing on the growing faces of wax molecules and block interlocking and intergrowing of wax crystal. The pour point depressants change wax crystal size and shape and put oil in flowing state. Wax crystal habitat depends on crude oil source and other factors like rate of cooling and degree of agitation during cooling. For getting best results, the optimum concentration of additive dose is required.

Kosamba-33 crude oil was treated with each of various polymers synthesized successively. Results are depicted in Table 3.5 which indicate that most of the additives are showing activity towards pour point depression. Table 3.5 shows that 8-12UA18N, 8-16UA18N, 8-10CA18N, 8-14CA18N, 8-12RA18N, 8-14RA18N, 8-10OA18N and 8-16OA18N show good tendency to decrease pour point of Koamba-33 crude oil.

In class of poly (octyl cinnamate-co-octadecyl maleimide-co-alkyl cinnamate) additives, 8-14CA18N produced higher depression of pour point by 12°C at 1000 ppm followed by 8-10CA18N which in turn followed by others. For this class of polymers, increase in pendent chain length has less impact on pour point depression. Also, rise in concentration does not improve the efficiency of additives.

In poly (octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate) class of polymers, 8-12UA18N showed a drop of 9°C at 500 ppm. 8-16UA18N showed a drop of 6°C. In this case, increase in additive concentration does not affect the pour point depression efficiency. 8-10UA18N, 8-14UA18N and 8-18UA18N could decrease the pour point by 6°C only. While 8-6UA18N and 8-22UA18N brought 3°C change in pour point. This indicates that very short pendant chain polymers or long pendant chain polymers have limited effect on pour point depression.

In poly (octyl ricinolate-co-octadecyl maleimide-co-alkyl ricinolate) class of polymers 8-12RA18N and 8-14RA18N are additives showing good pour point depression tendency. 8-12RA18N decreased pour point up to 30°C at 500 ppm while 8-14RA18N showed pour point drop to 30°C at 200 ppm. 8-14RA18N showed same drop but at lower concentration of additive. 8-16RA18N and 8-18RA18N could decrease the pour point up to 33°C only. The least drop in pour point was shown by 8-6RA18N and 8-22RA18N where a decrease of only 3°C was reported.

Lastly, in poly (octyl oleate-co-octadecyl maleimide-co-alkyl oleate) class of polymers, 8-10OA18N and 8-16OA18N additives could decrease the pour point of Kosamba-33 crude oil from 39°C to 30°C. 8-14OA18N could depress the pour point from 39°C to 36°C only. Polymeric additives 8-6OA18N, 8-12OA18N, 8-18OA18N, 8-22OA18N were found to be less effective as pour point depressants.

3.2.4.2 Evaluation of Polymeric Additives on Rheological Parameters

Table 3.6 Effect of Additive Concentration on Rheological Parameters of Kosamba-33 Crude Oil

Code	Additive Concentration (ppm)	Temperature (^oC)	Viscosity (Pa-s)	Yield Stress (Pa)
Blank	0	39	0.0710	2.540
		36	0.2380	11.75
		33	0.5640	24.10
		30	1.4000	60.44
8-12UA18N	500	39	0.0960	4.680
		36	0.2890	18.05
		33	0.6495	27.90
		30	1.2050	56.50
8-12UA18N	1000	39	0.0970	4.350
		36	0.2680	16.50
		33	0.6775	28.70
		30	1.2365	58.83
8-16UA18N	500	39	0.0410	1.995
		36	0.0979	5.001
		33	0.1260	6.905
		30	0.2010	10.65
8-16UA18N	1000	39	0.0499	2.630
		36	0.1199	6.67
		33	0.1885	8.50
		30	0.3768	13.10
8-10CA18N	500	39	0.0804	2.777
		36	0.2503	14.49
		33	0.5664	28.10
		30	0.8494	40.06
8-10CA18N	1000	39	0.0410	1.210
		36	0.2060	13.95
		33	0.3399	18.77
		30	0.6055	22.66
8-14CA18N	500	39	0.0337	0.94
		36	0.1876	13.95
		33	0.3501	18.08
		30	0.6638	30.76
8-14CA18N	1000	39	0.0347	1.051
		36	0.2330	15.34
		33	0.4196	27.82
		30	0.8979	43.80

Code	**Additive Concentration (ppm)**	**Temperature (^oC)**	**Viscosity (Pa-s)**	**Yield Stress (Pa)**
8-12RA18N	500	39	0.02792	0.5251
		36	0.2076	11.63
		33	0.5256	25.56
		30	0.9527	51.24
8-12RA18N	1000	39	0.0407	1.187
		36	0.2479	14.23
		33	0.5447	26.95
		30	1.0624	58.29
8-14RA18N	500	39	0.0305	0.6907
		36	0.2136	11.95
		33	0.3992	21.74
		30	0.8338	47.72
8-14RA18N	1000	39	0.0356	1.027
		36	0.2186	13.29
		33	0.4323	21.86
		30	0.8963	53.02
8-10OA18N	500	39	0.0583	1.884
		36	0.3022	16.14
		33	0.5847	38.30
		30	1.1522	69.53
8-10OA18N	1000	39	0.0860	4.077
		36	0.2788	15.08
		33	0.5454	36.95
		30	0.9384	59.46
8-16OA18N	500	39	0.0893	3.518
		36	0.3398	18.83
		33	0.7114	38.13
		30	1.2439	65.70
8-16OA18N	1000	39	0.0735	3.065
		36	0.3006	18.59
		33	0.5387	31.88
		30	0.9179	56.20

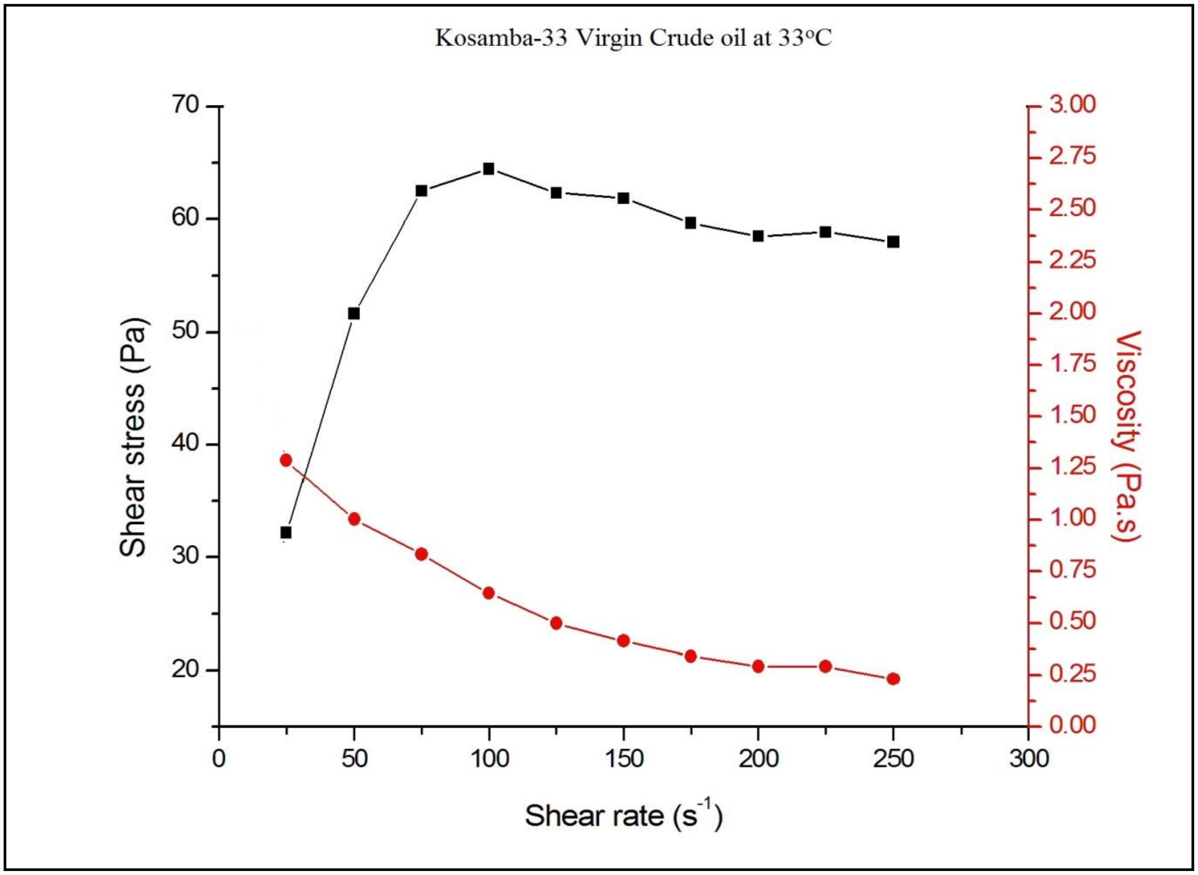

Fig. 3.71 Rheogram of Virgin Kosamba-33 crude oil at 33°C

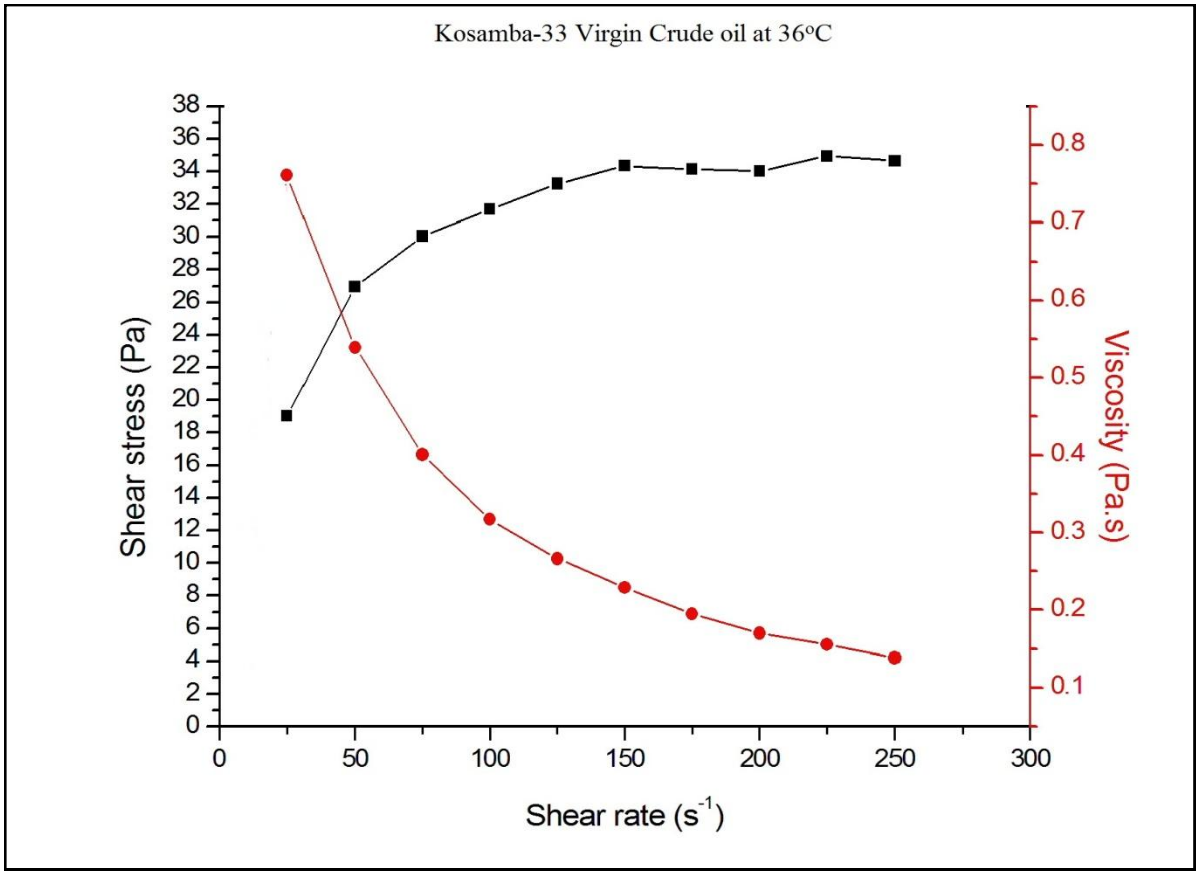

Fig 3.72 Rheogram of Virgin Kosamba-33 crude oil at 36°C

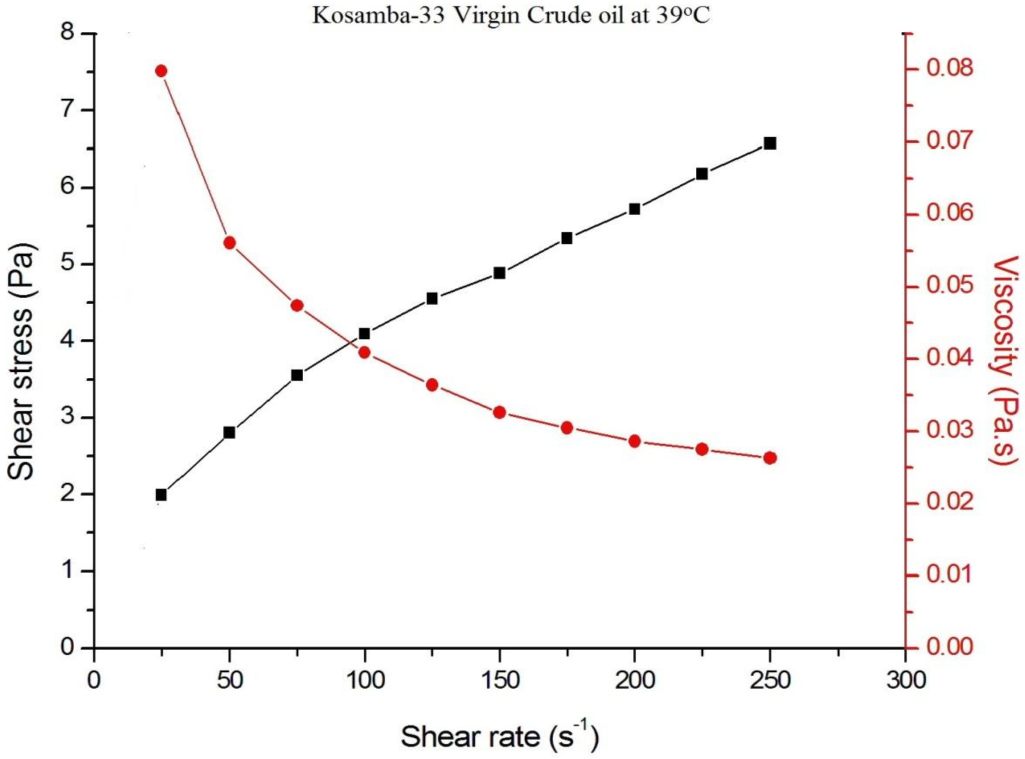

Fig 3.73 Rheogram of Virgin Kosamba-33 crude oil at 39°C

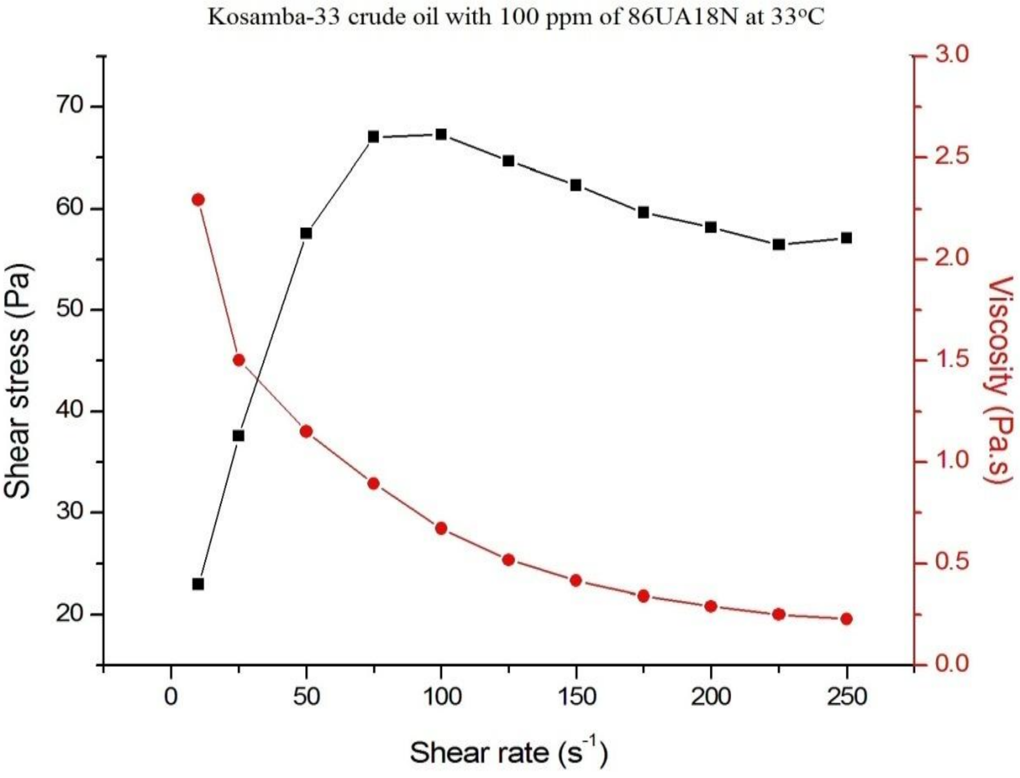

Fig 3.74 Rheogram of Kosamba-33 crude oil with 100 ppm of 8-6UA18N at 33°C

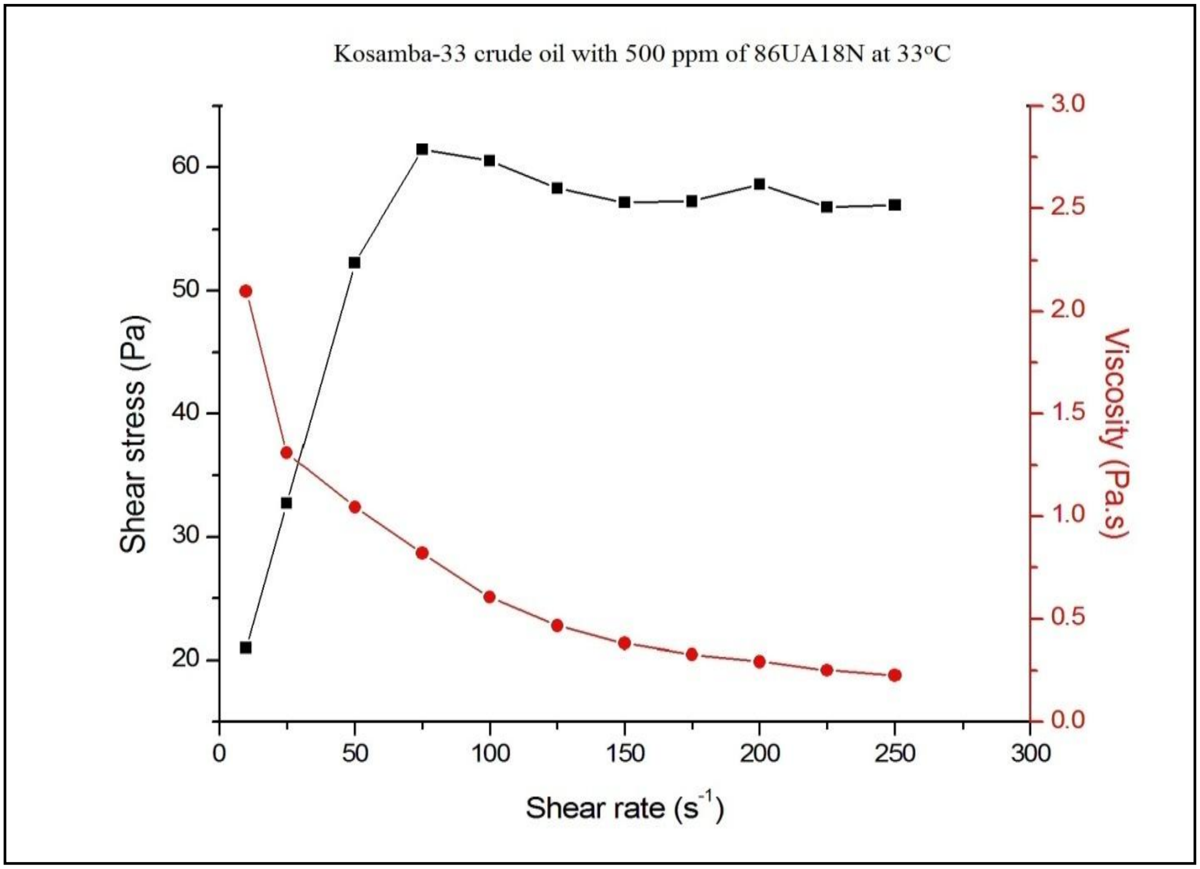

Fig 3.75 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-6UA18N at 33°C

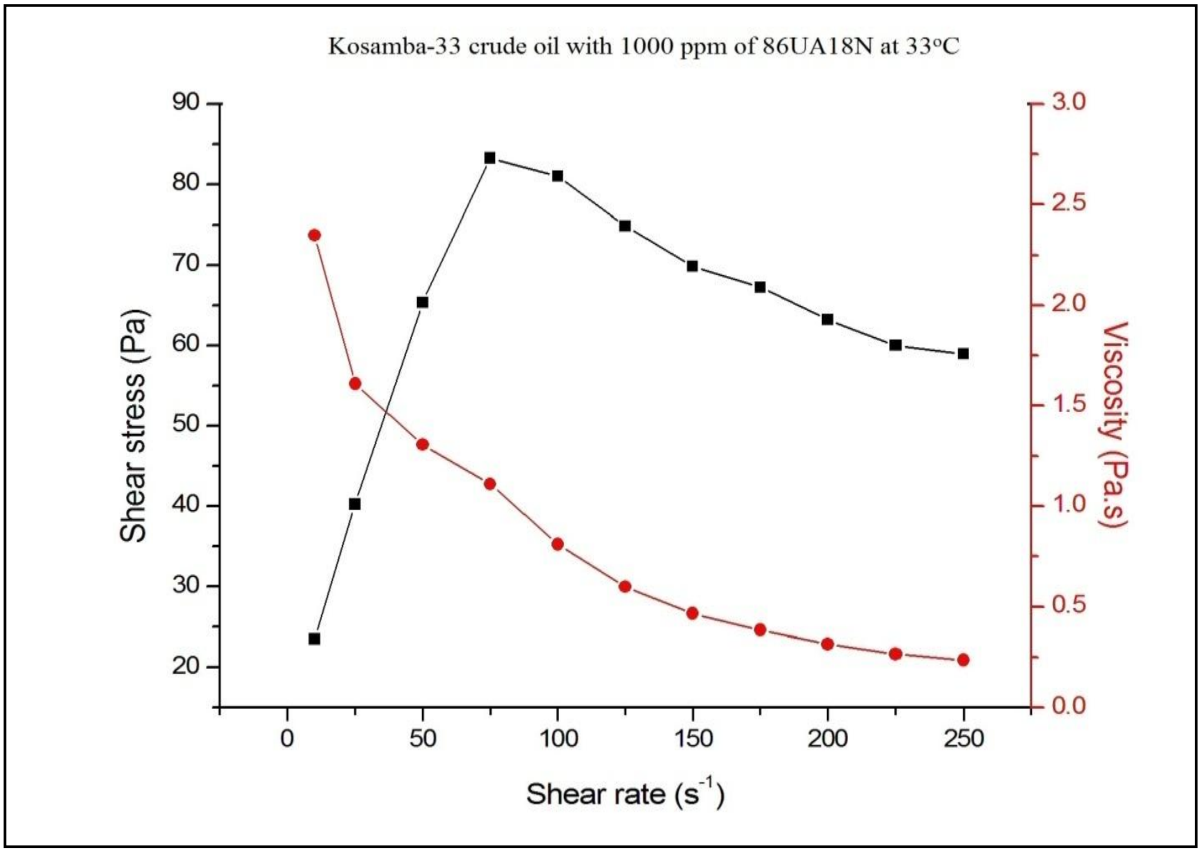

Fig 3.76 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-6UA18N at 33°C

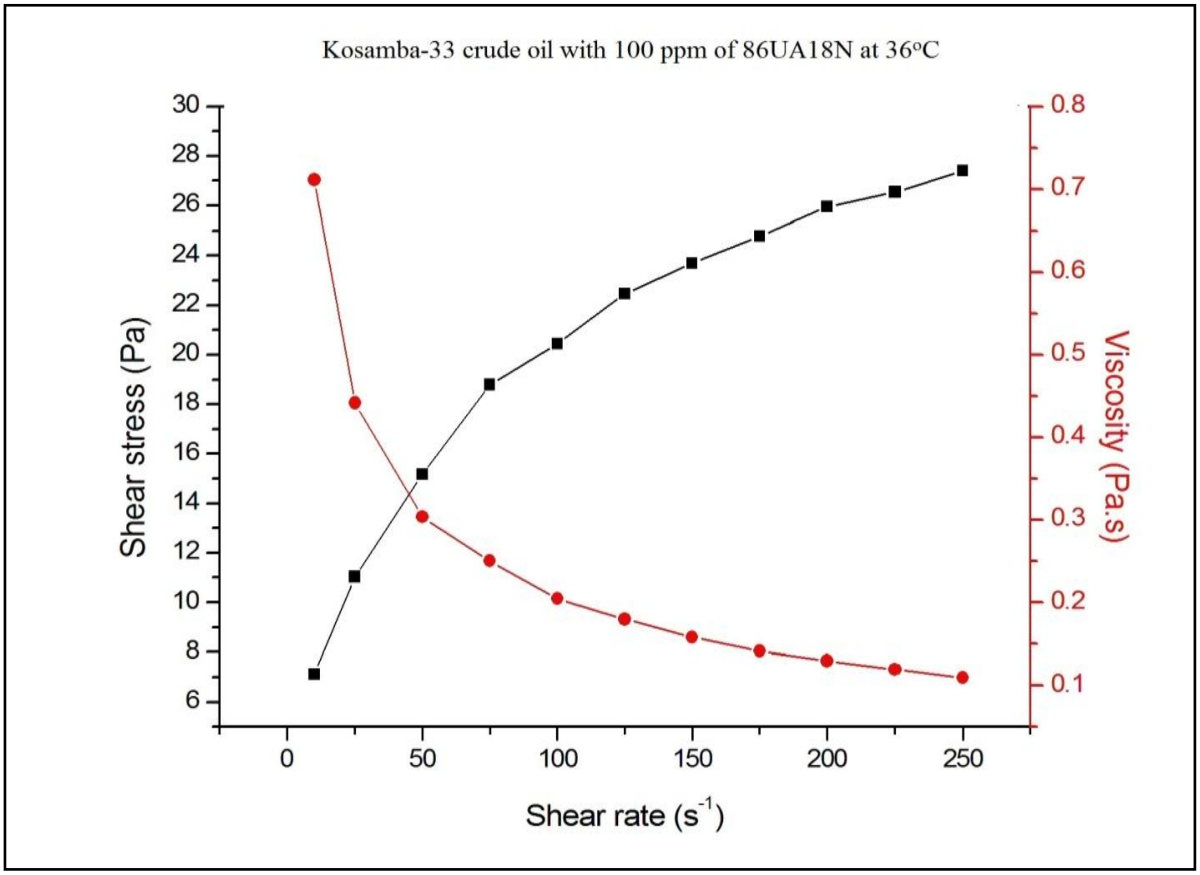

Fig 3.77 Rheogram of Kosamba-33 crude oil with 100 ppm of 8-6UA18N at 36^{o}C

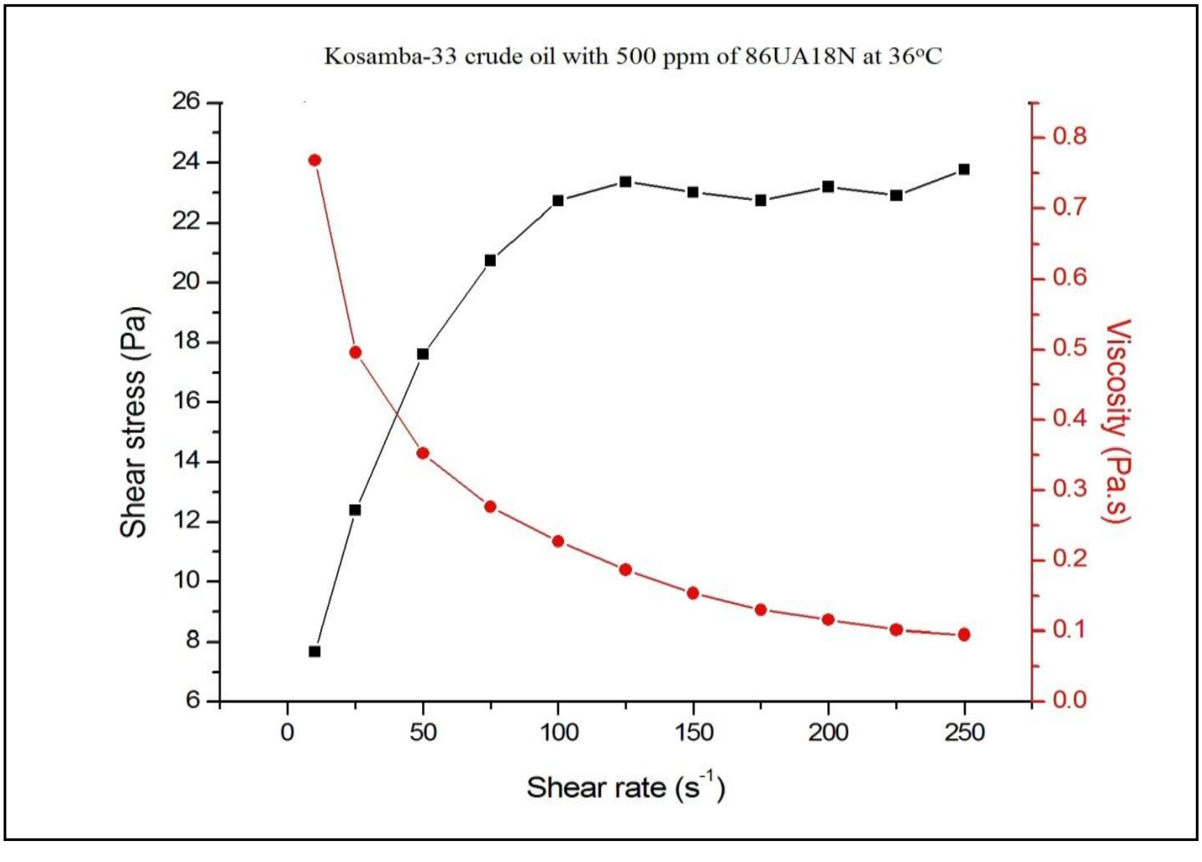

Fig 3.78 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-6UA18N at 36^{o}C

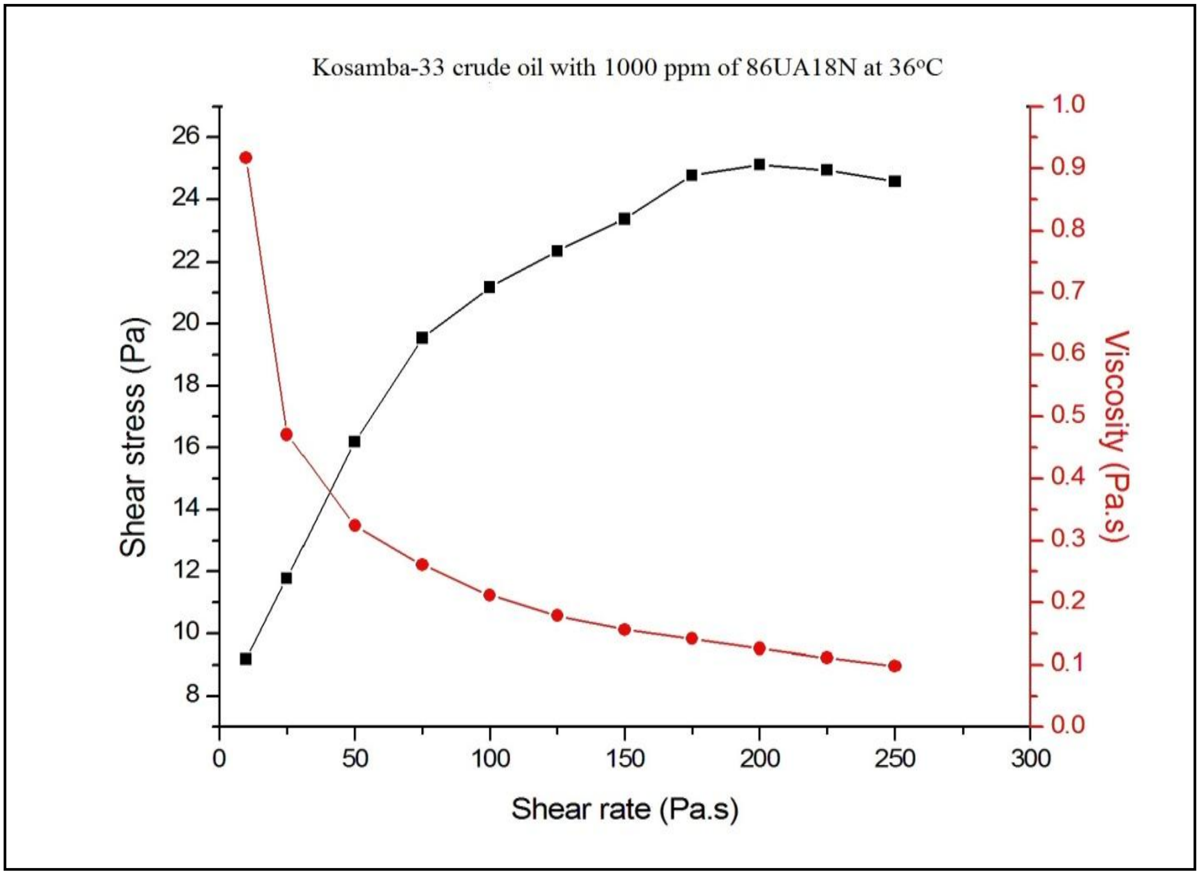

Fig 3.79 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-6UA18N at 36°C

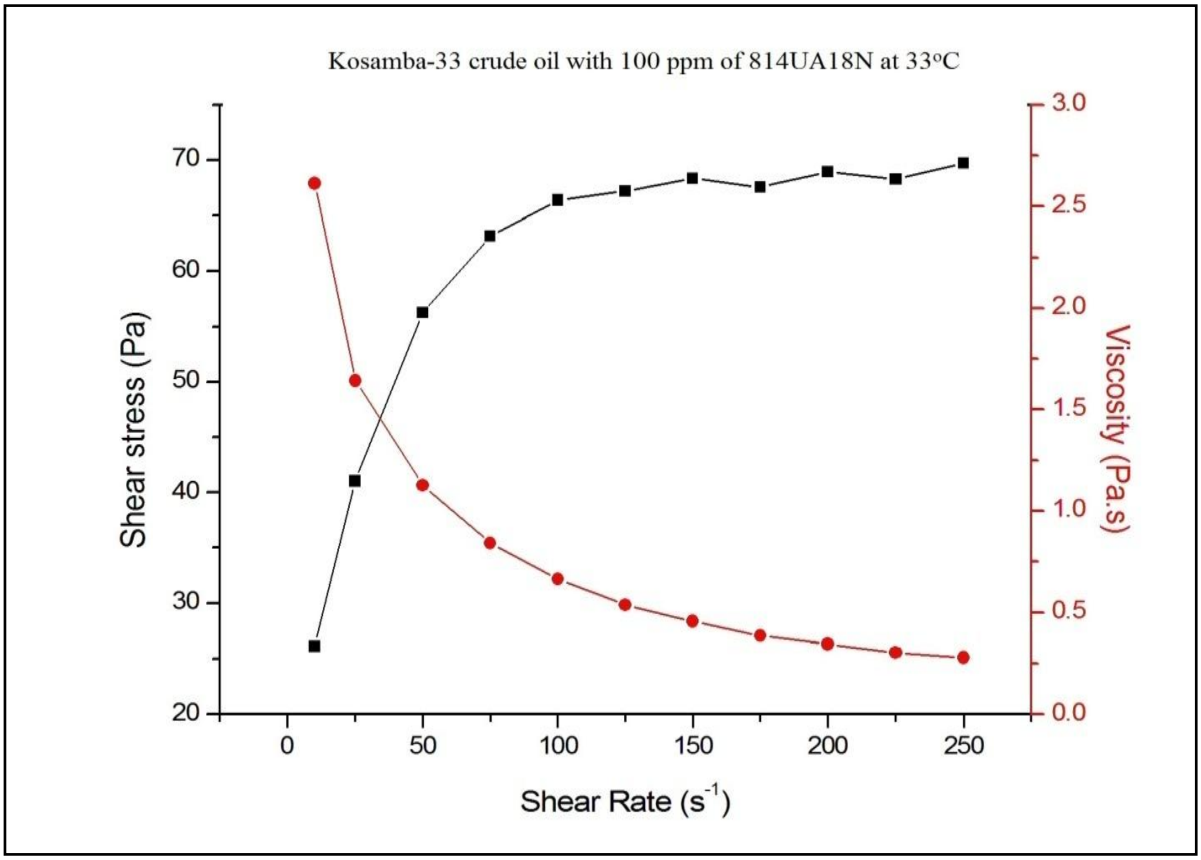

Fig 3.80 Rheogram of Kosamba-33 crude oil with 100 ppm of 8-14UA18N at 33°C

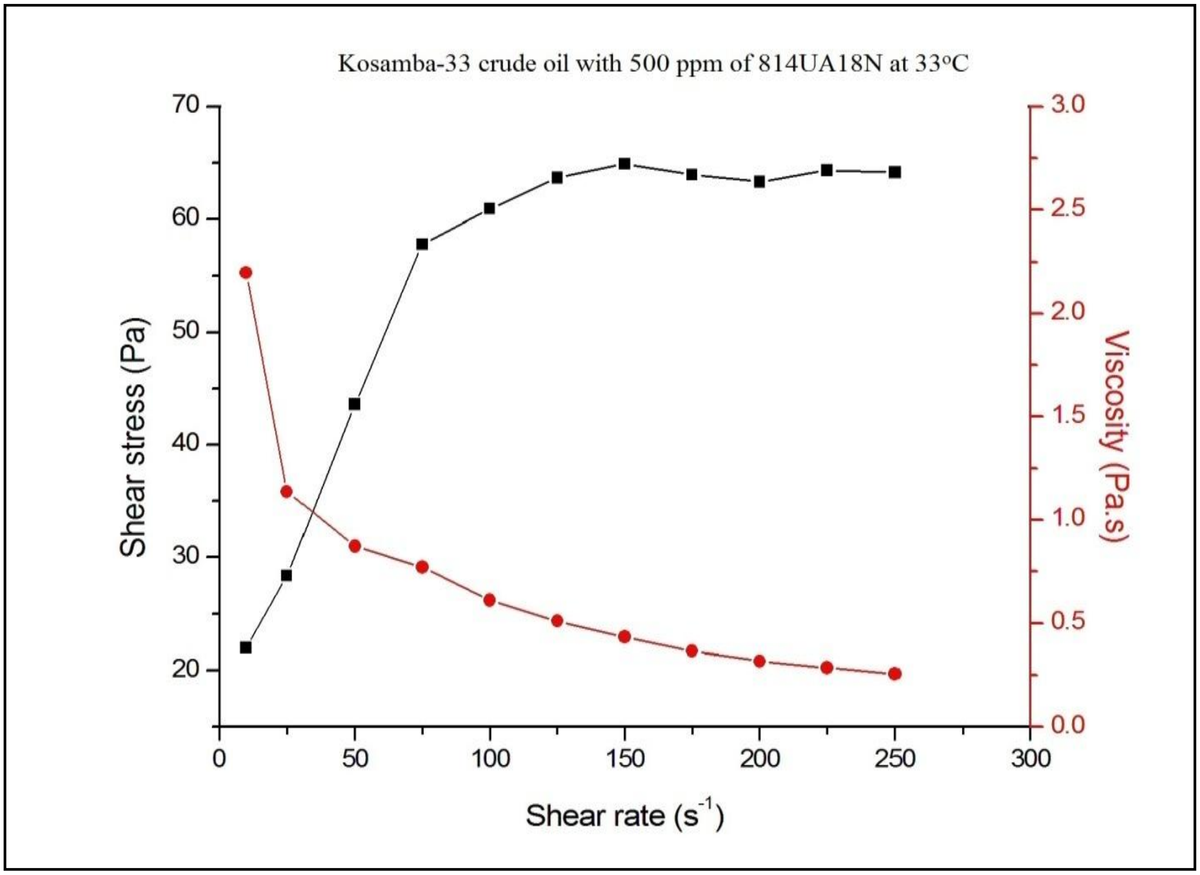

Fig 3.81 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-14UA18N at 33°C

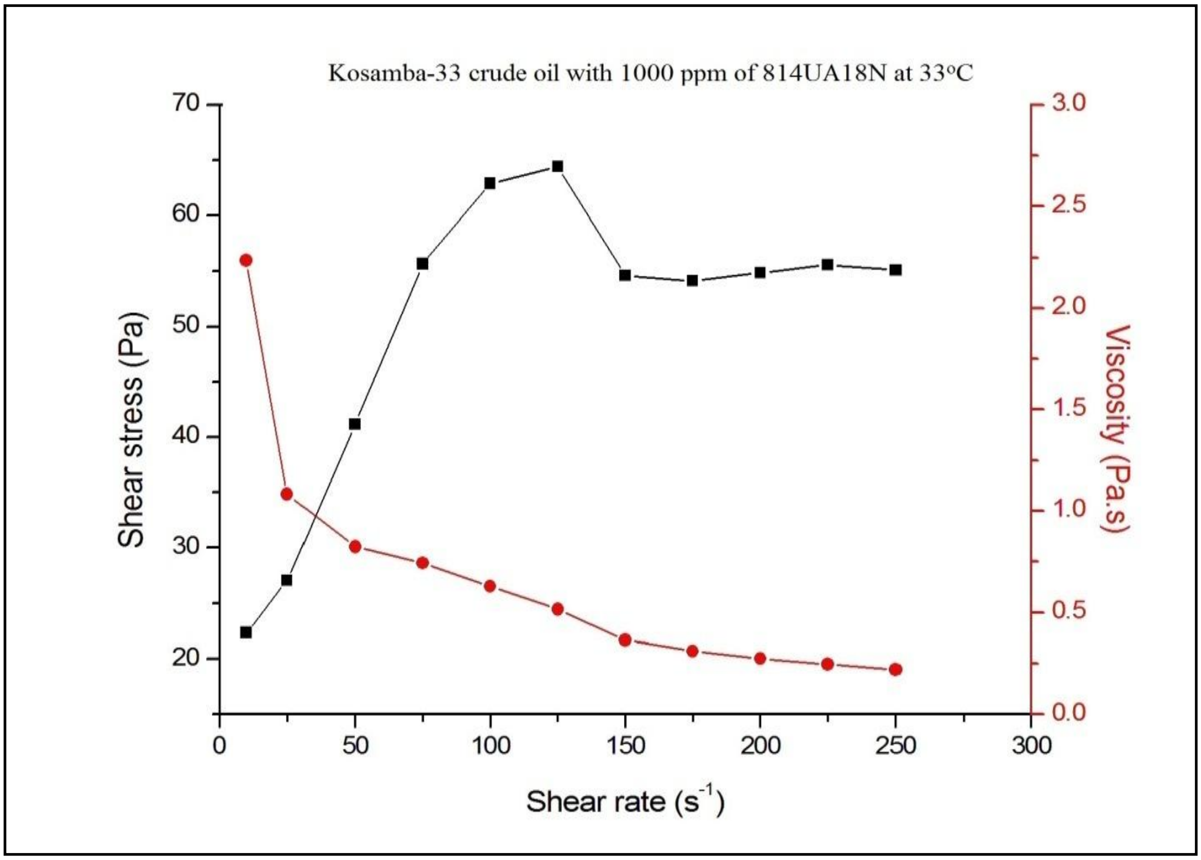

Fig 3.82 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-14UA18N at 33°C

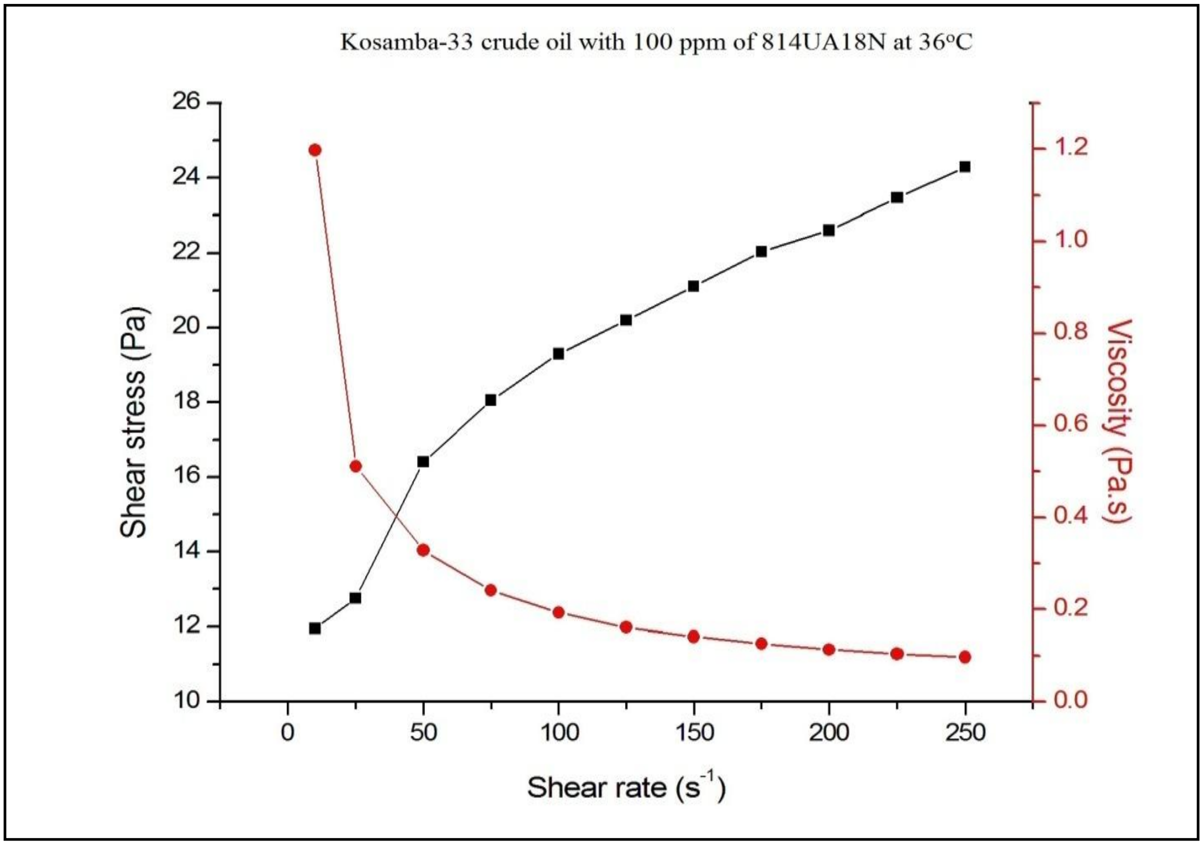

Fig 3.83 Rheogram of Kosamba-33 crude oil with 100 ppm of 8-14UA18N at 36^{o}C

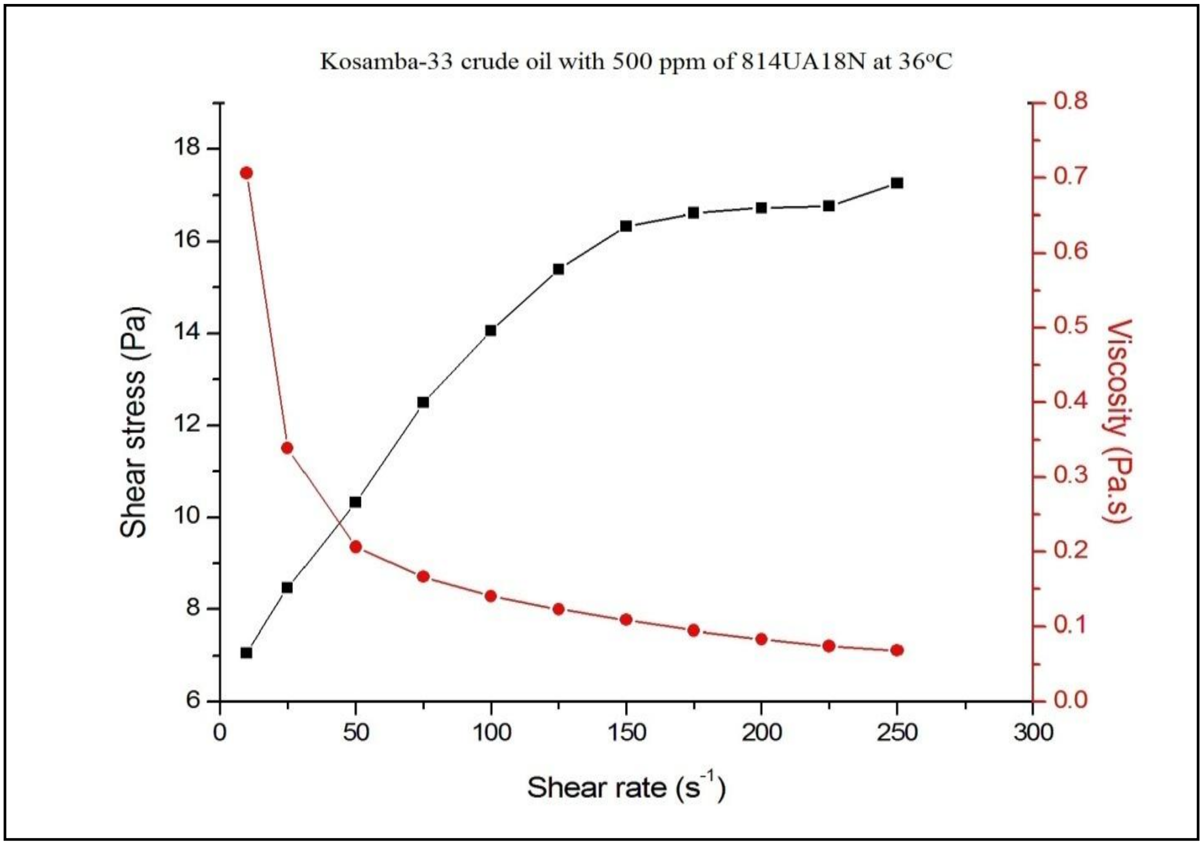

Fig 3.84 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-14UA18N at 36^{o}C

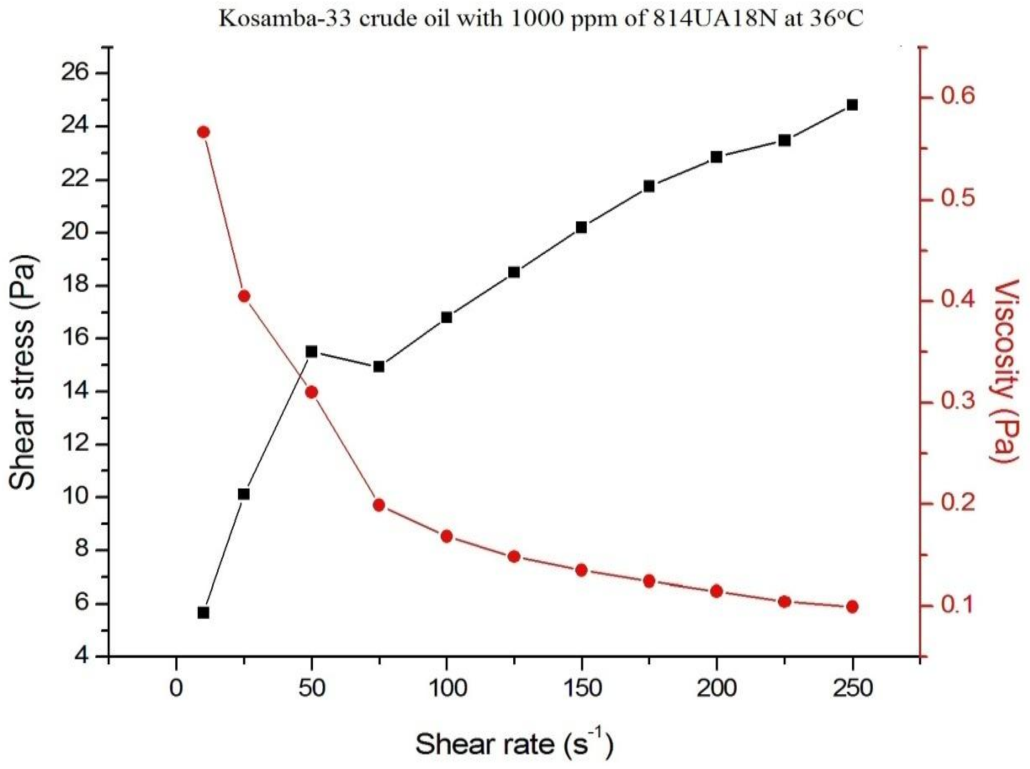

Fig 3.85 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-14UA18N at 36^{o}C

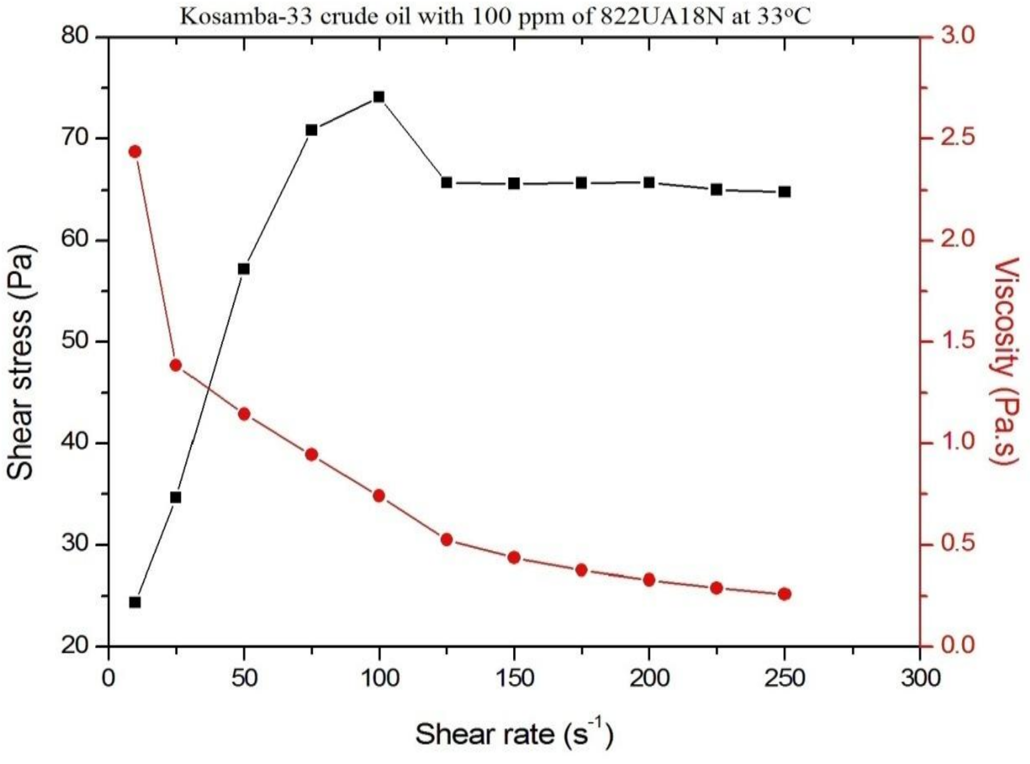

Fig 3.86 Rheogram of Kosamba-33 crude oil with 100 ppm of 8-22UA18N at 33^{o}C

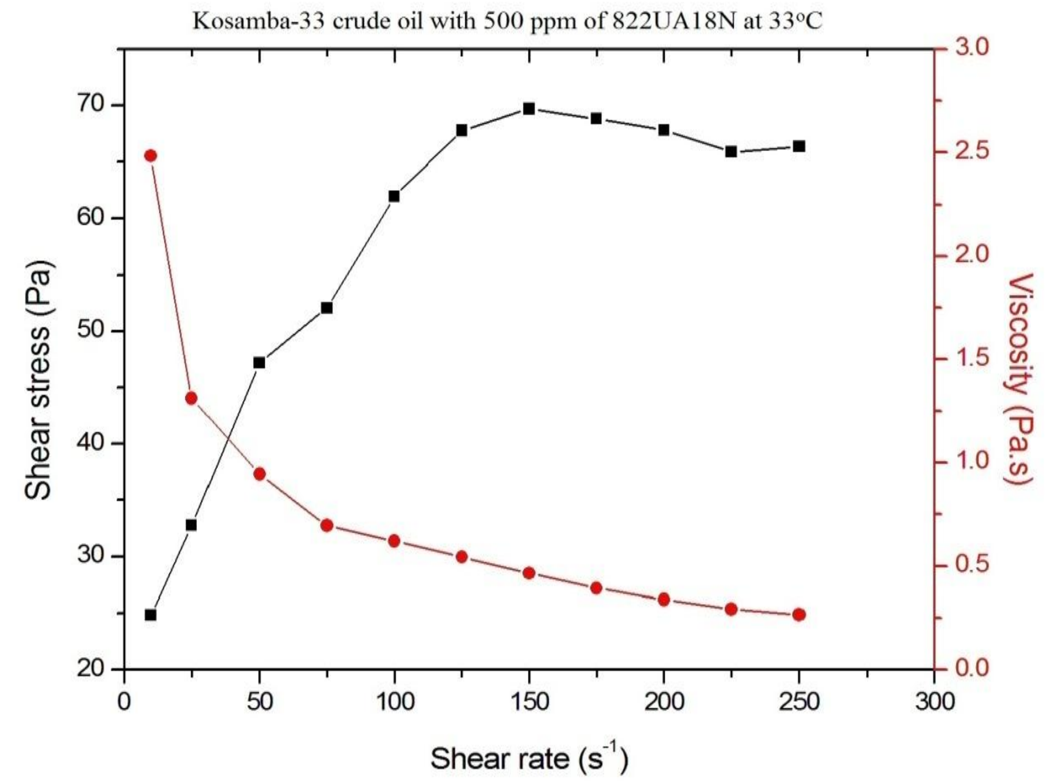

Fig 3.87 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-22UA18N at 33°C

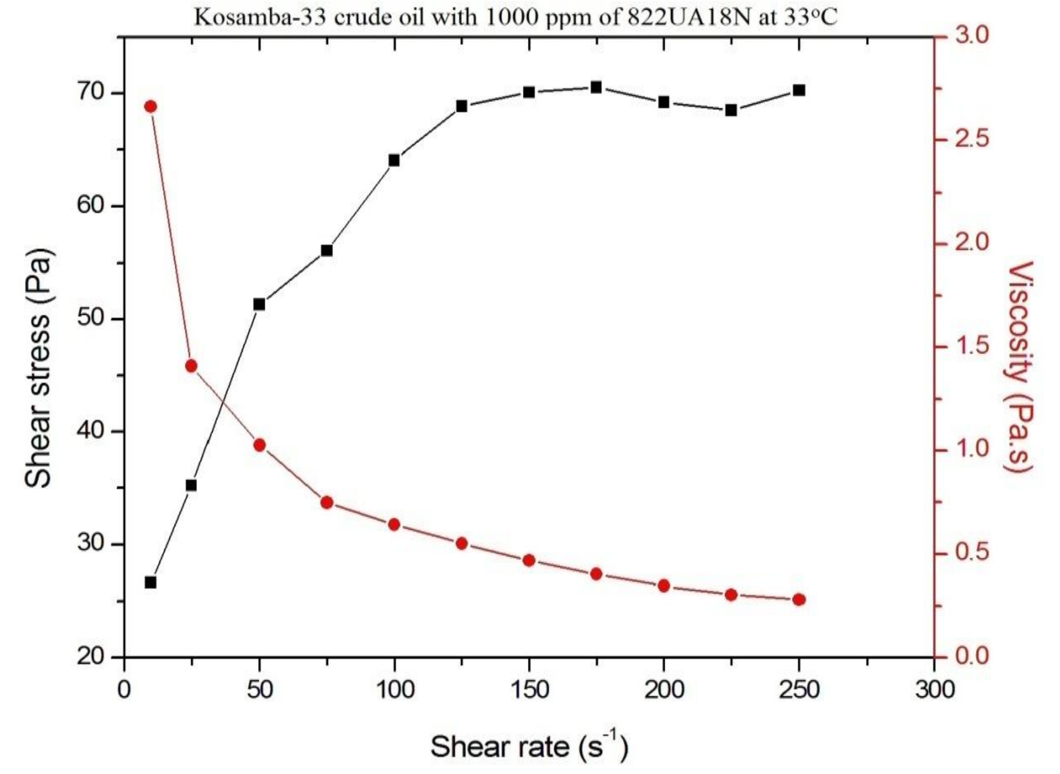

Fig 3.88 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-22UA18N at 33°C

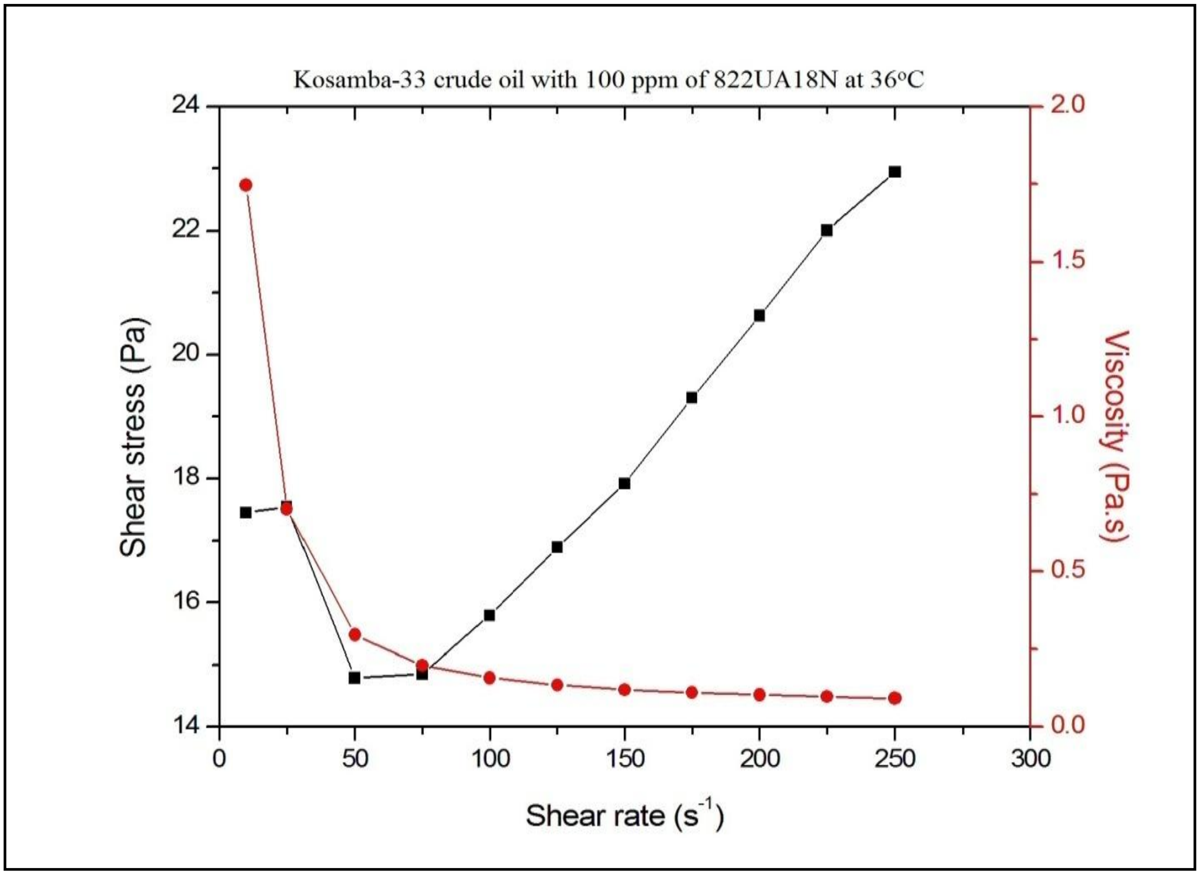

Fig 3.89 Rheogram of Kosamba-33 crude oil with 100 ppm of 8-22UA18N at 36^{o}C

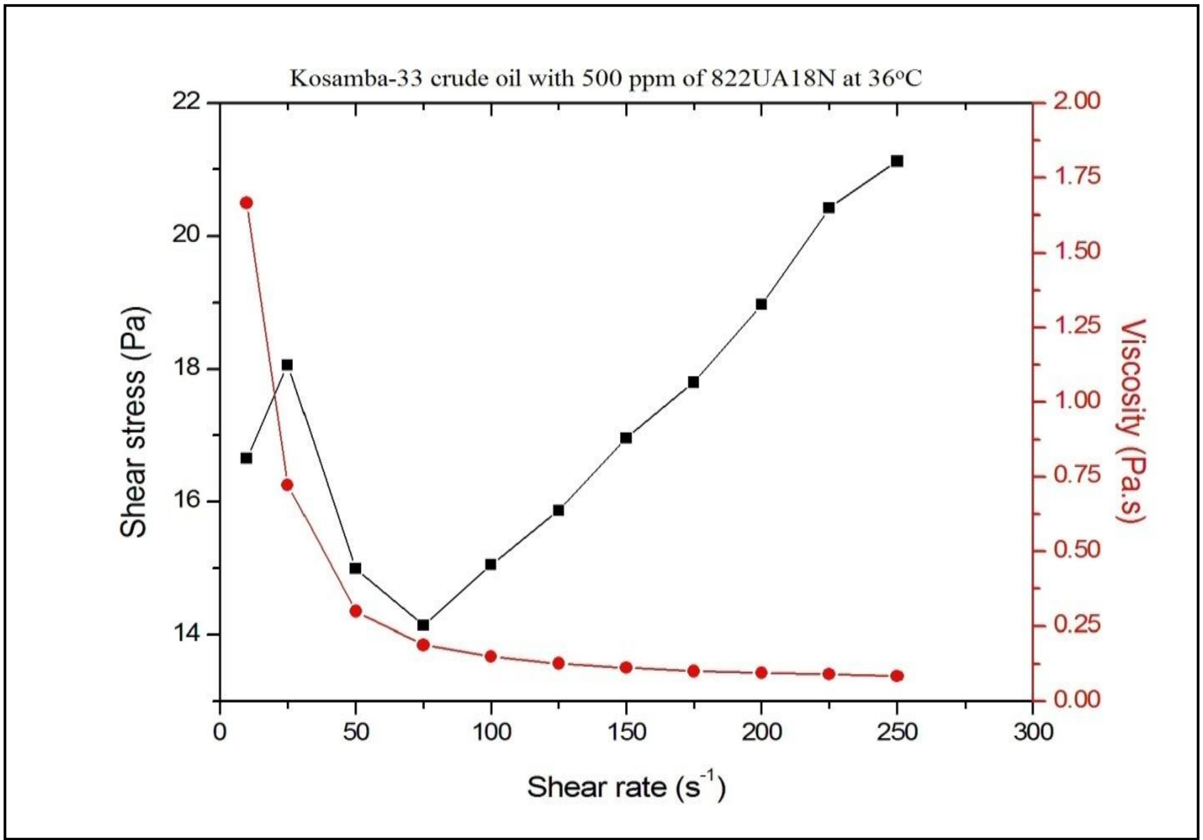

Fig 3.90 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-22UA18N at 36^{o}C

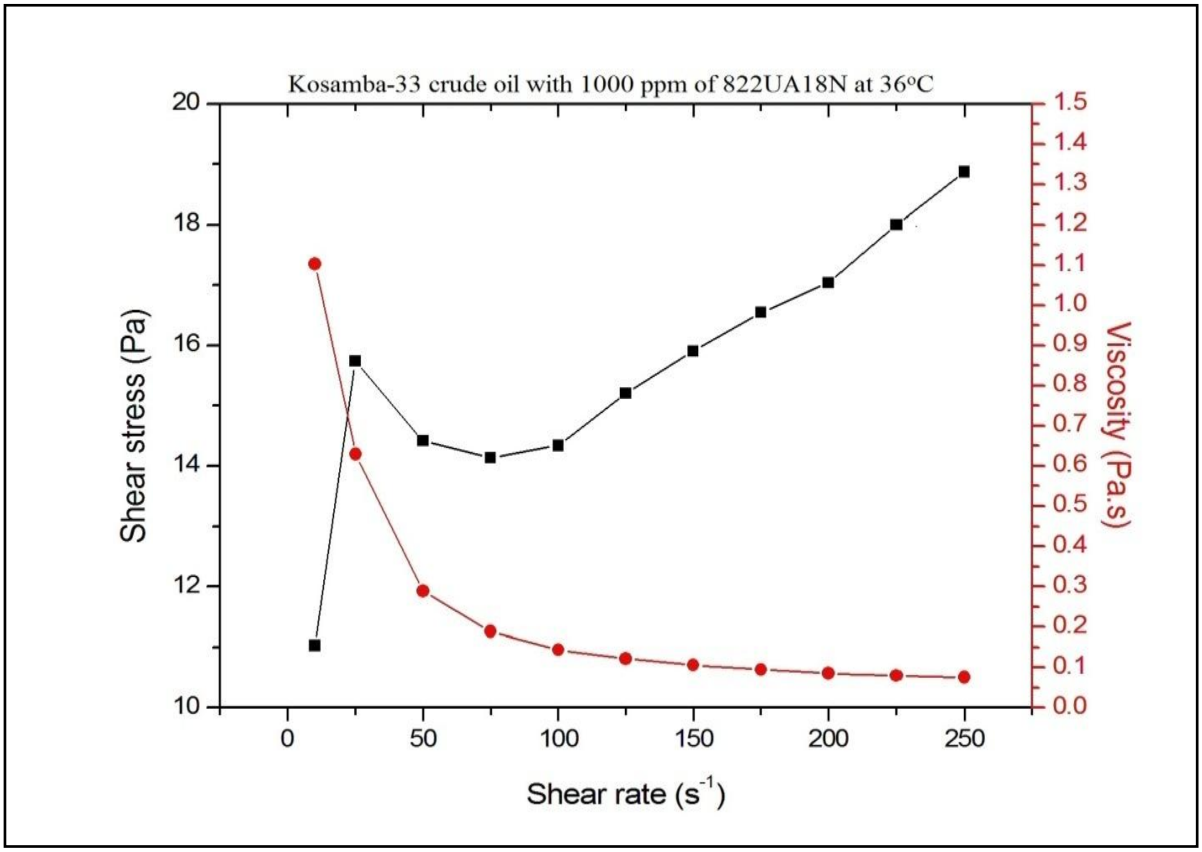

Fig 3.91 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-22UA18N at 36°C

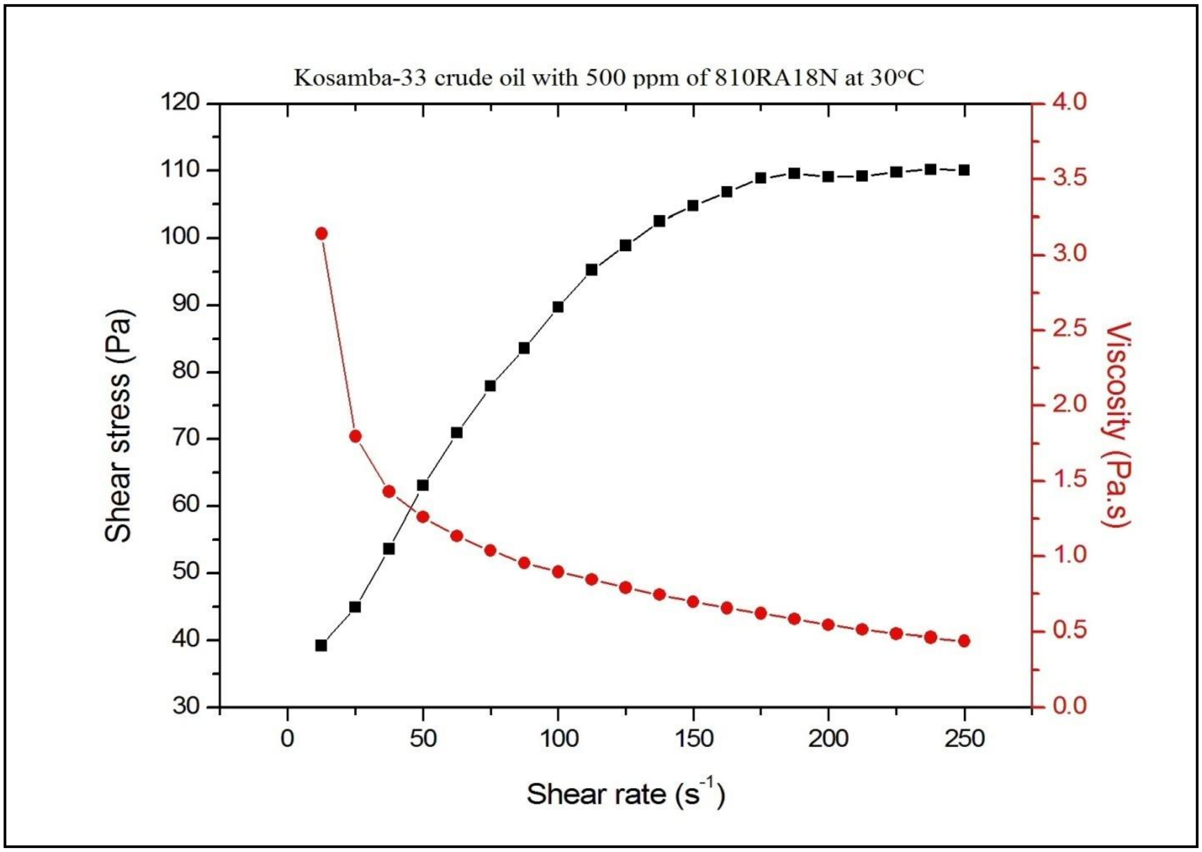

Fig 3.92 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10RA18N at 30°C

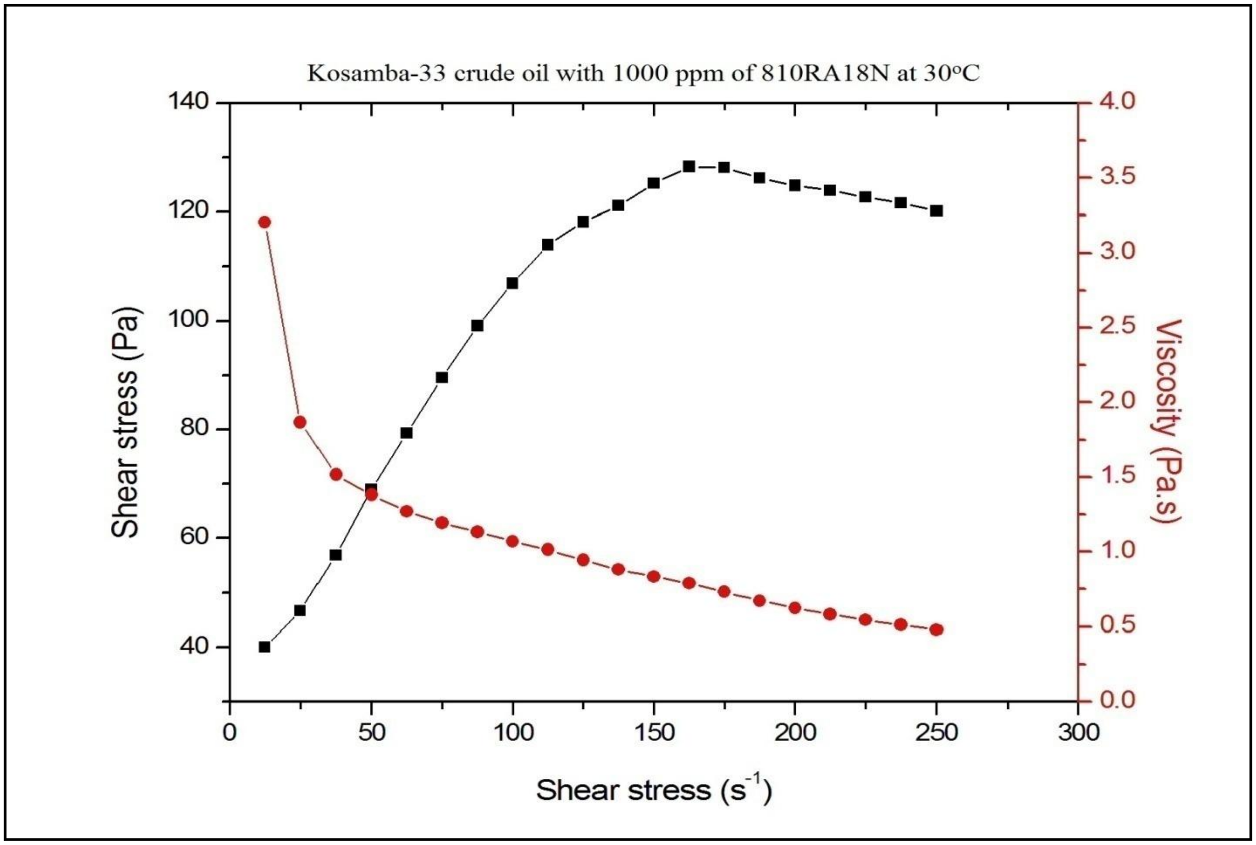

Fig 3.93 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10RA18N at 30°C

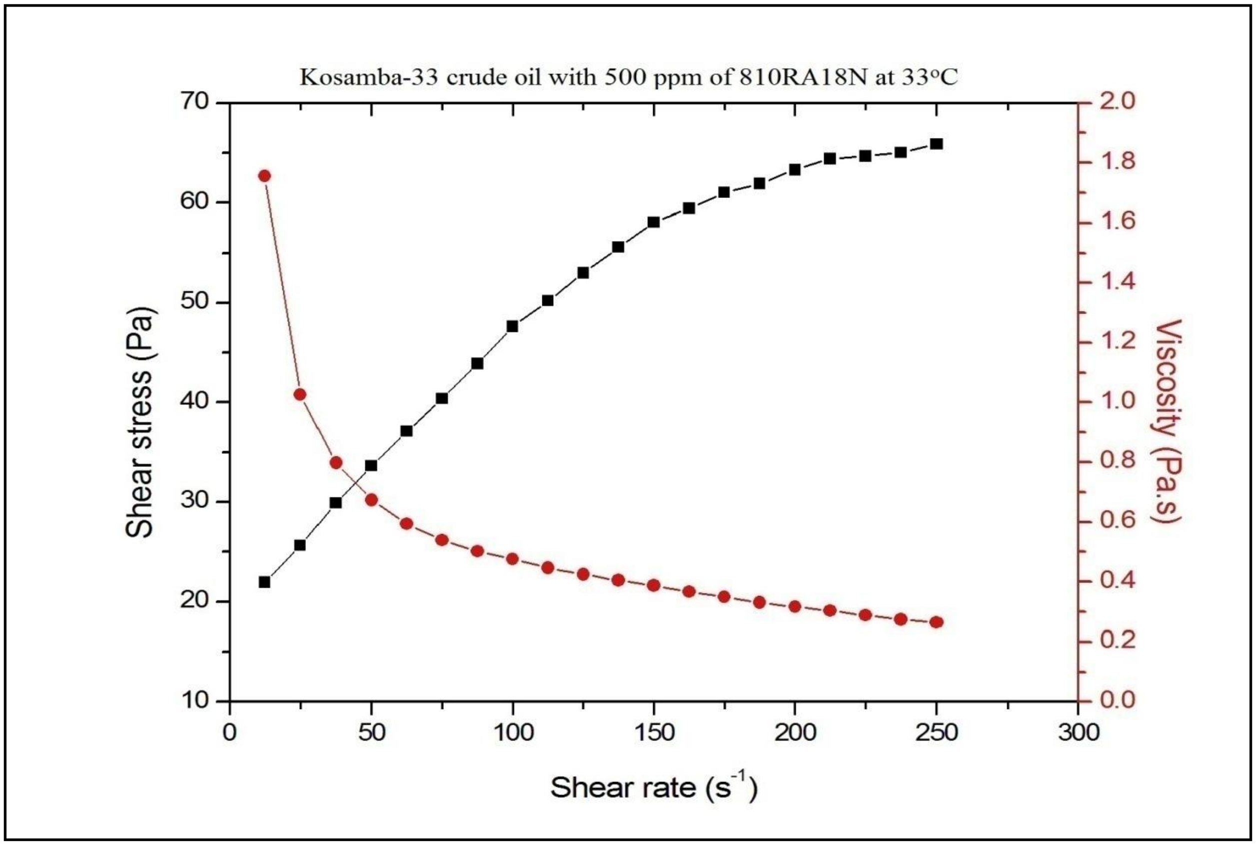

Fig 3.94 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10RA18N at 33°C

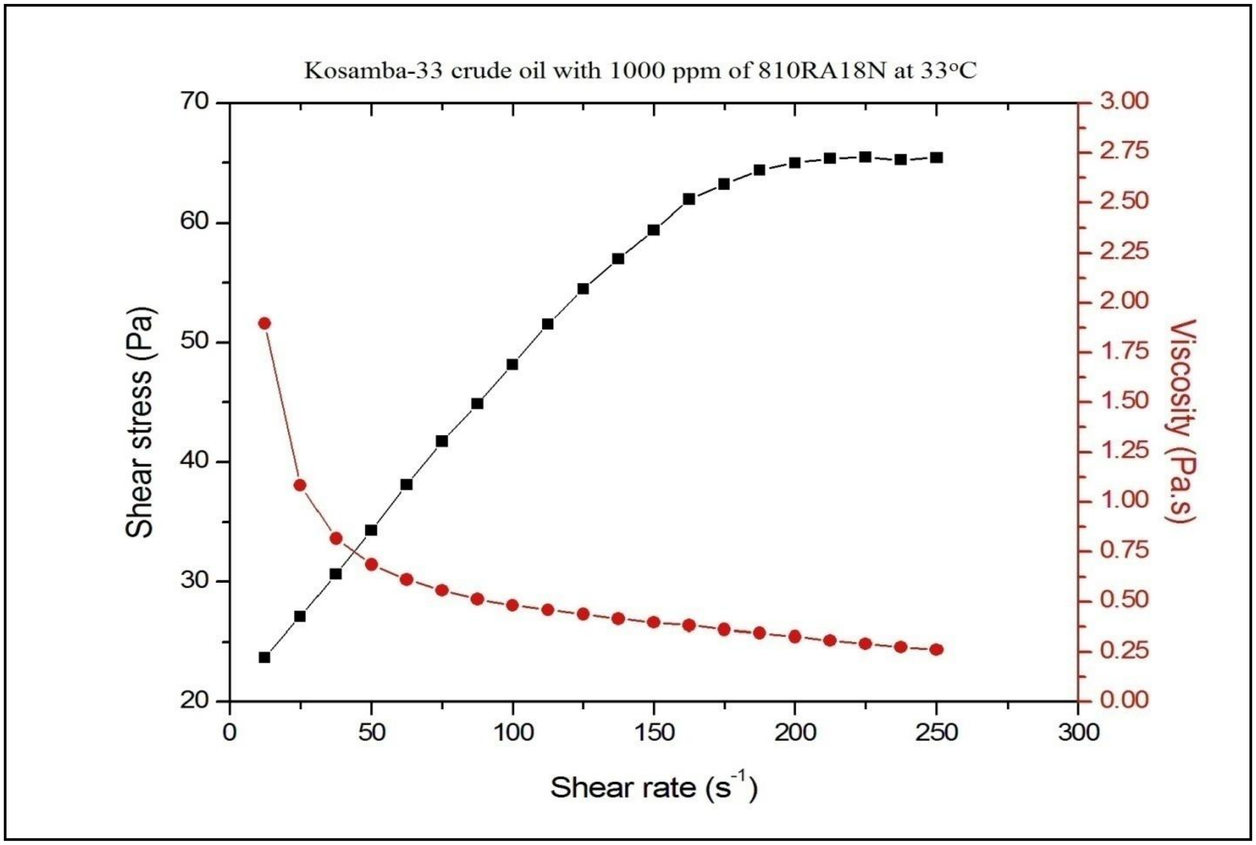

Fig 3.95 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10RA18N at 33°C

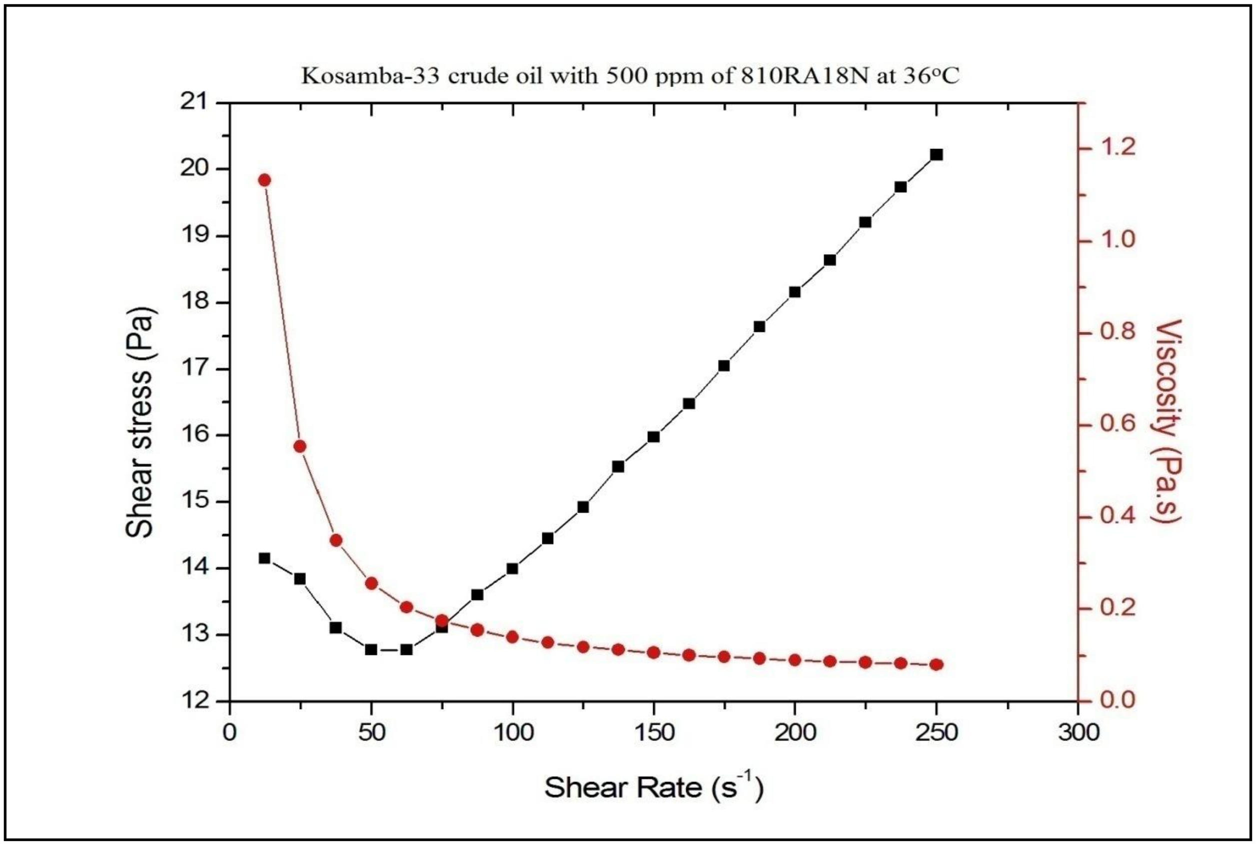

Fig 3.96Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10RA18N at 36°C

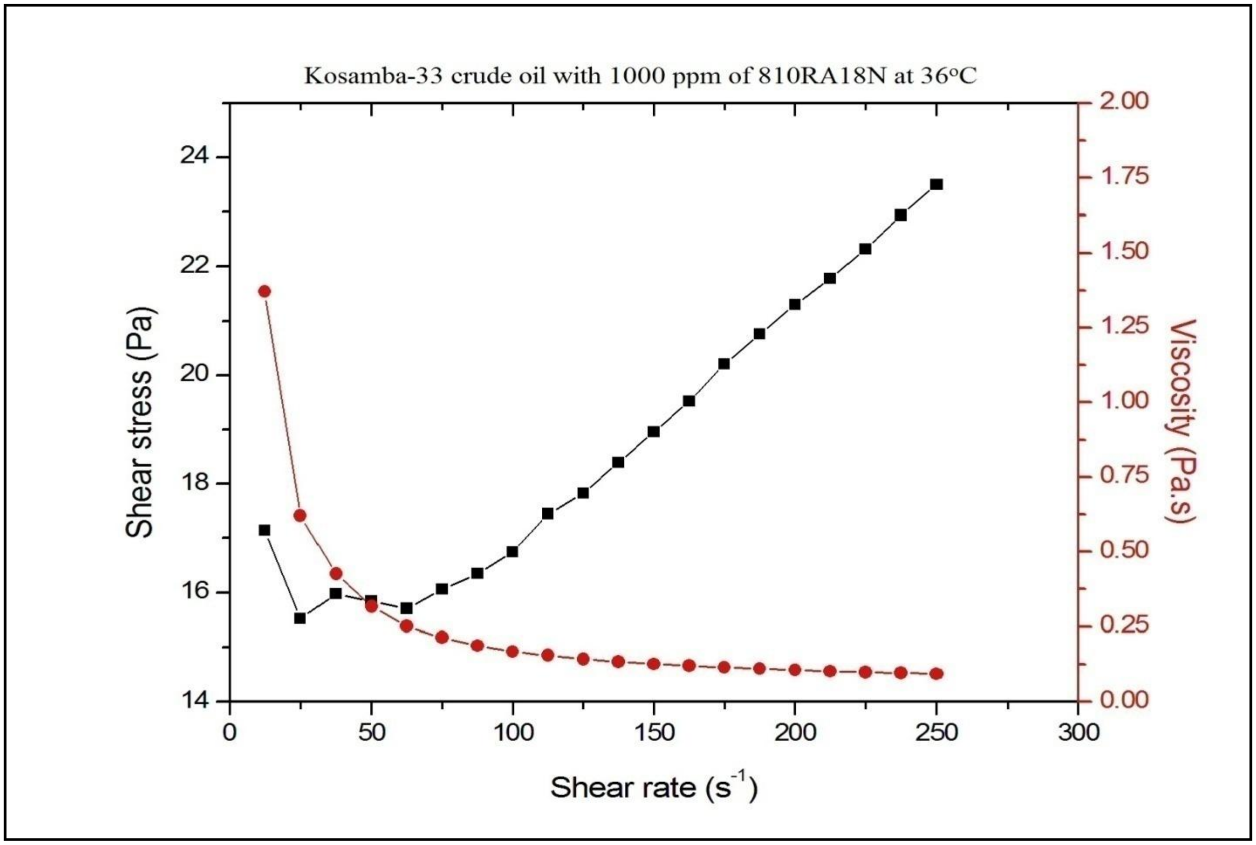

Fig 3.97 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10RA18N at 36°C

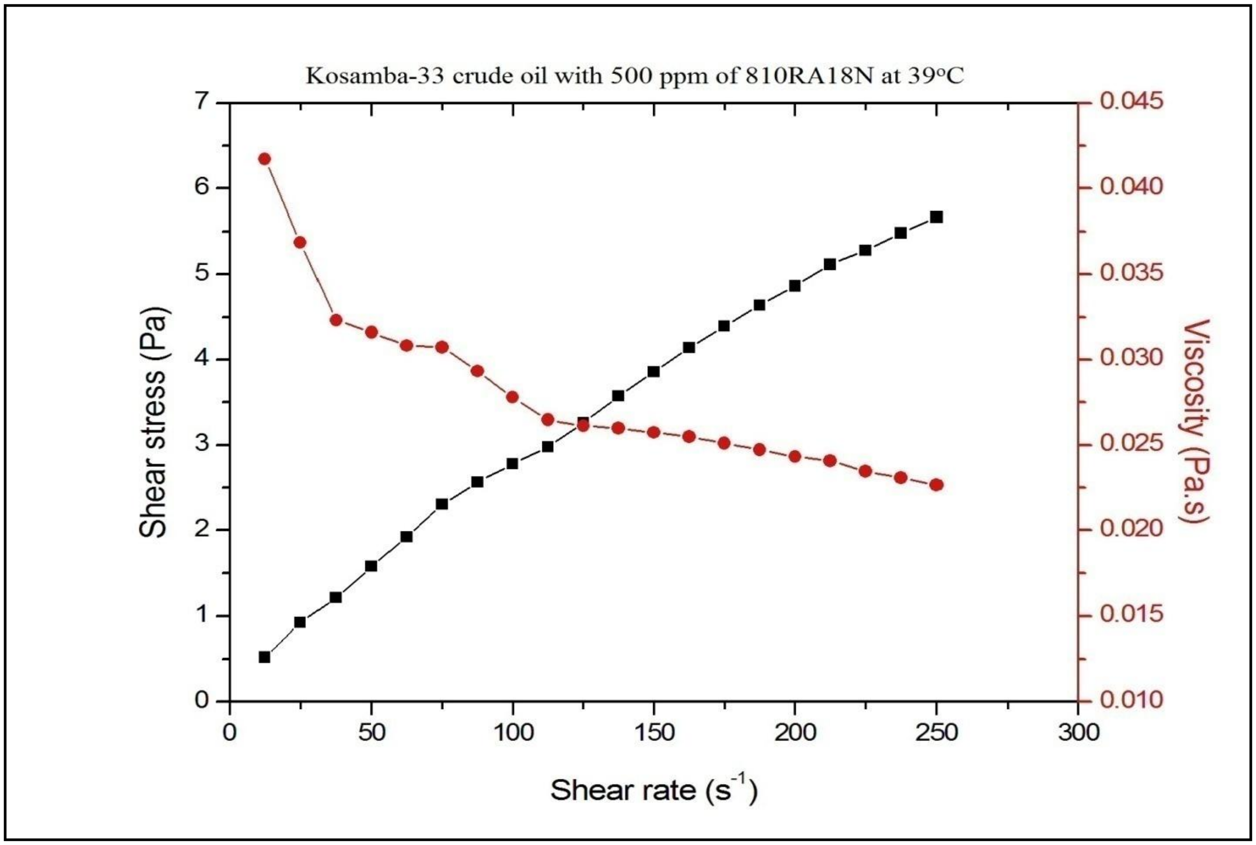

Fig 3.98 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10RA18N at 39°C

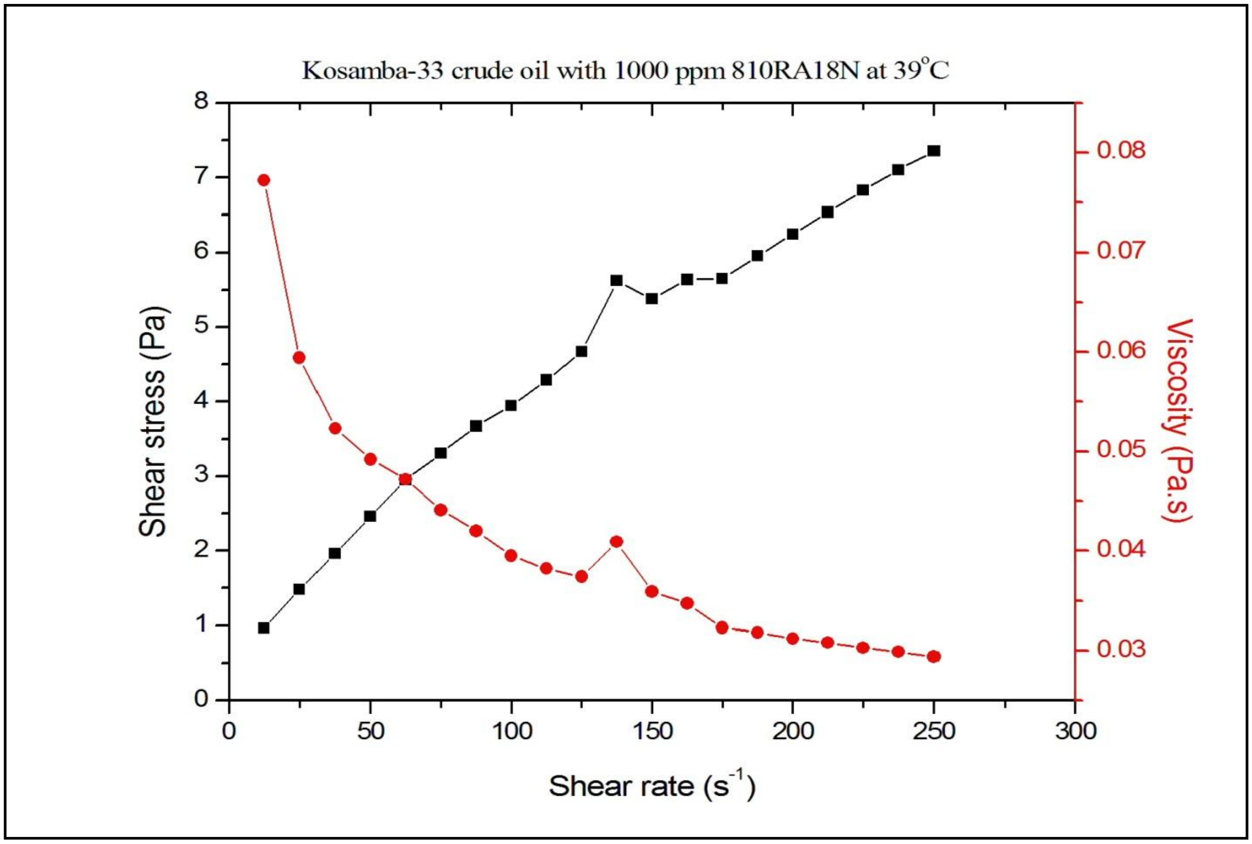

Fig 3.99 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10RA18N at 39°C

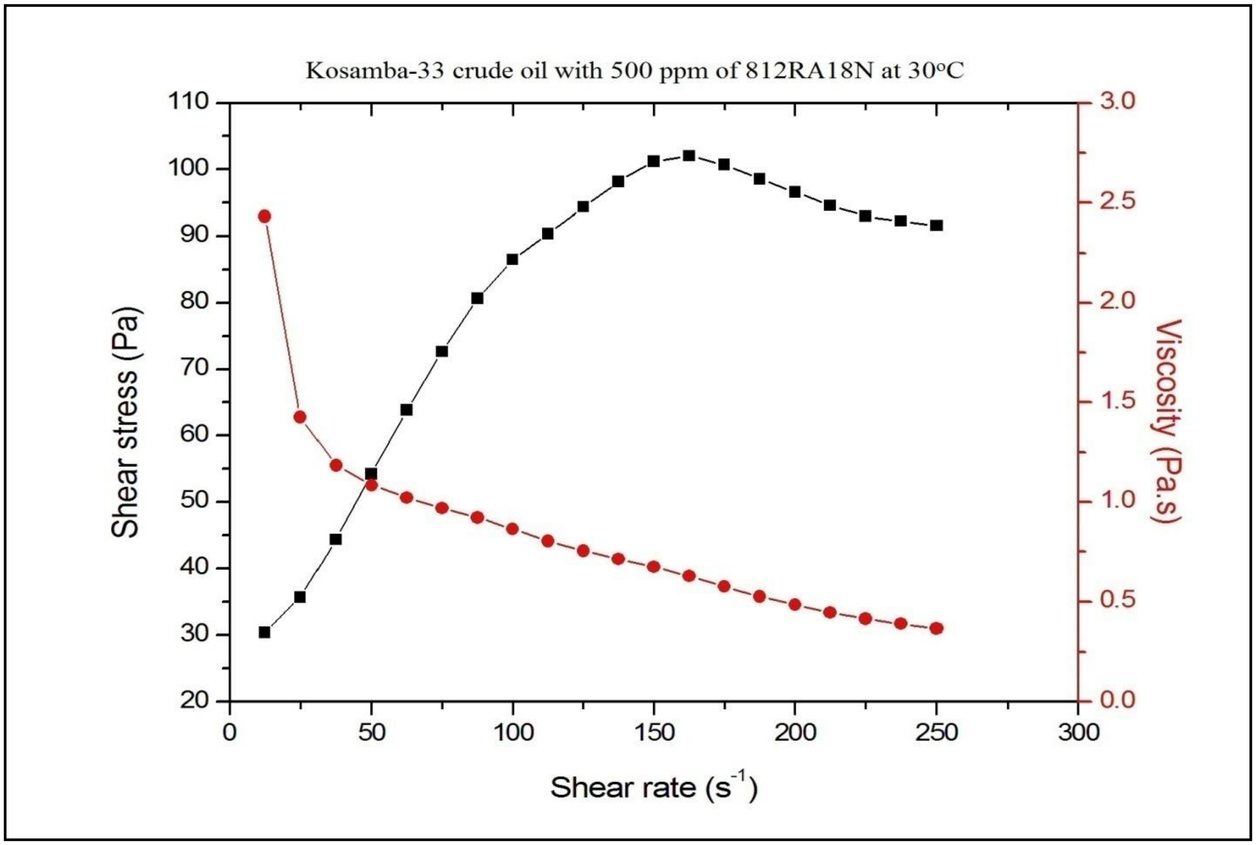

Fig 3.100 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-12RA18N at 30°C

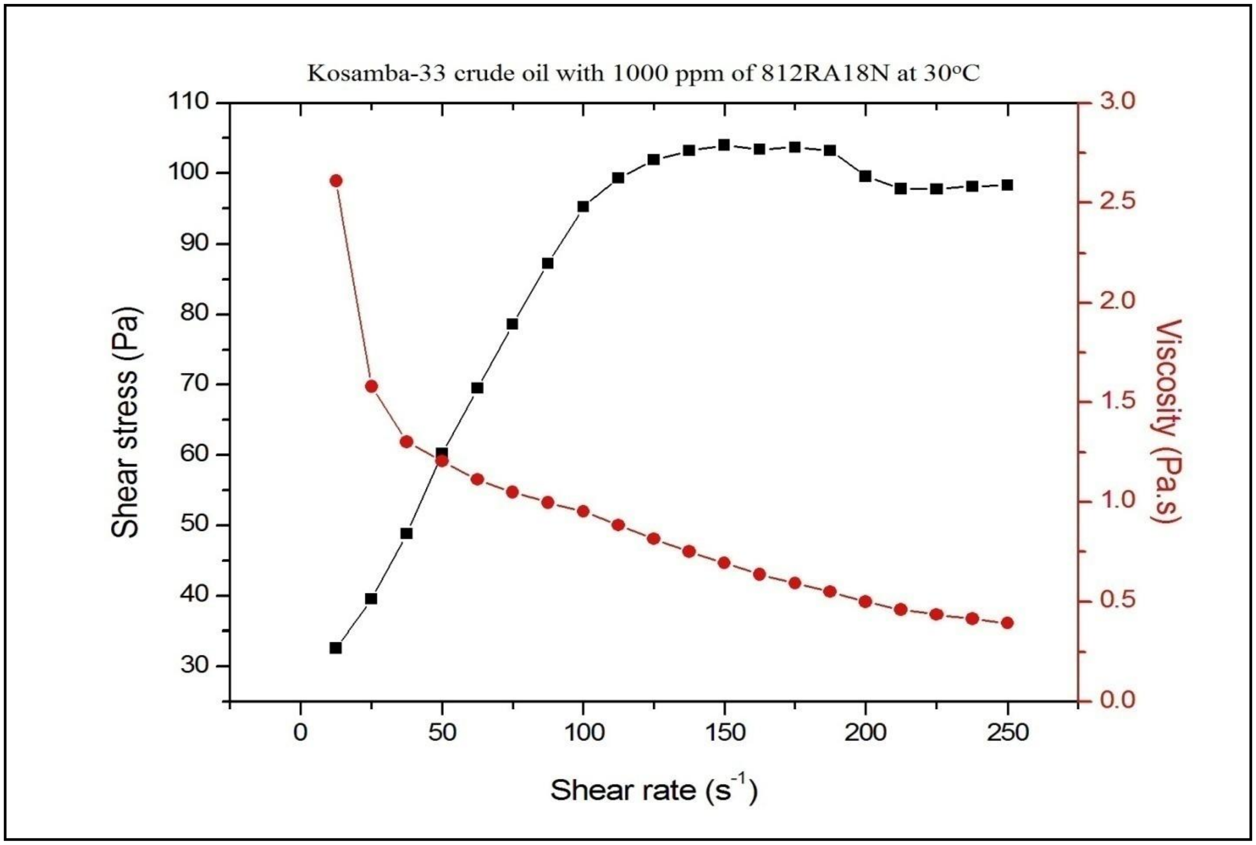

Fig 3.101 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-12RA18N at 30^{o}C

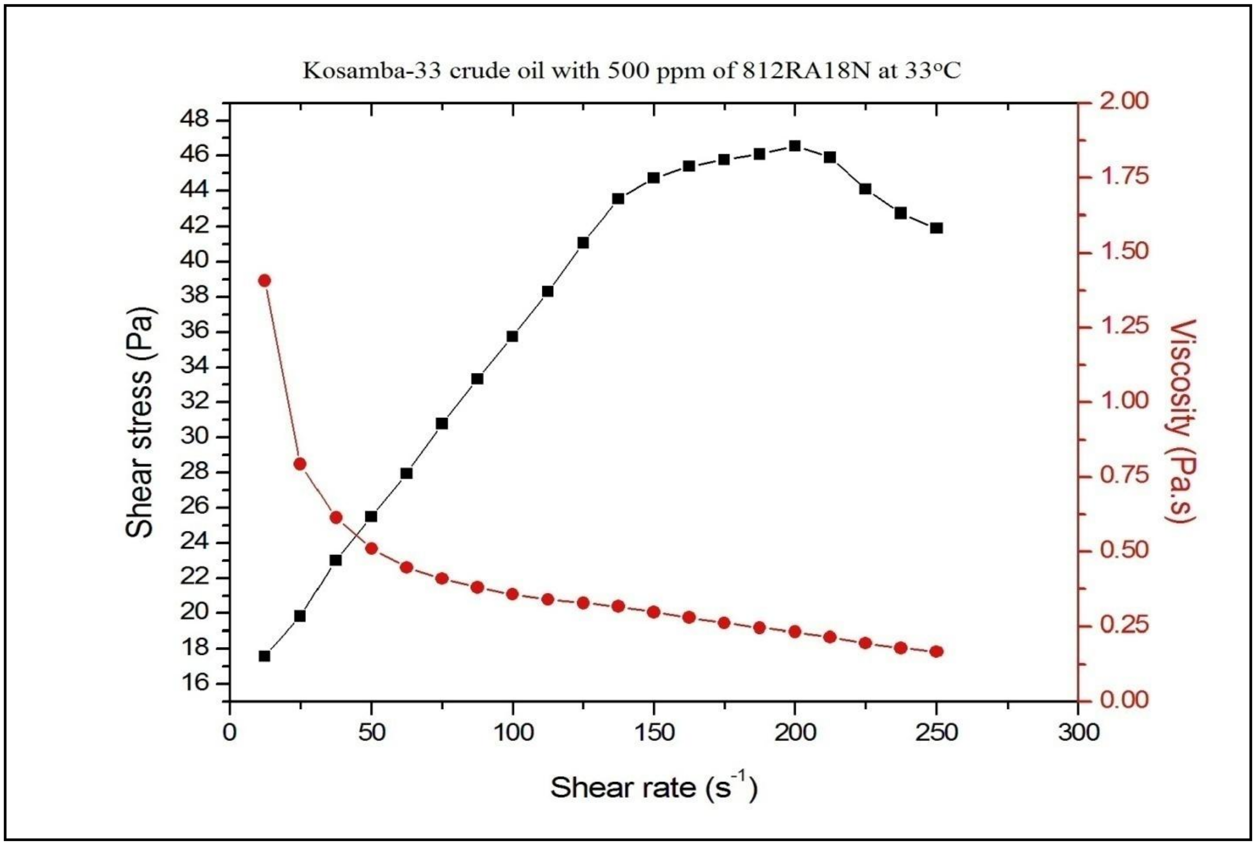

Fig 3.102 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-12RA18N at 33^{o}C

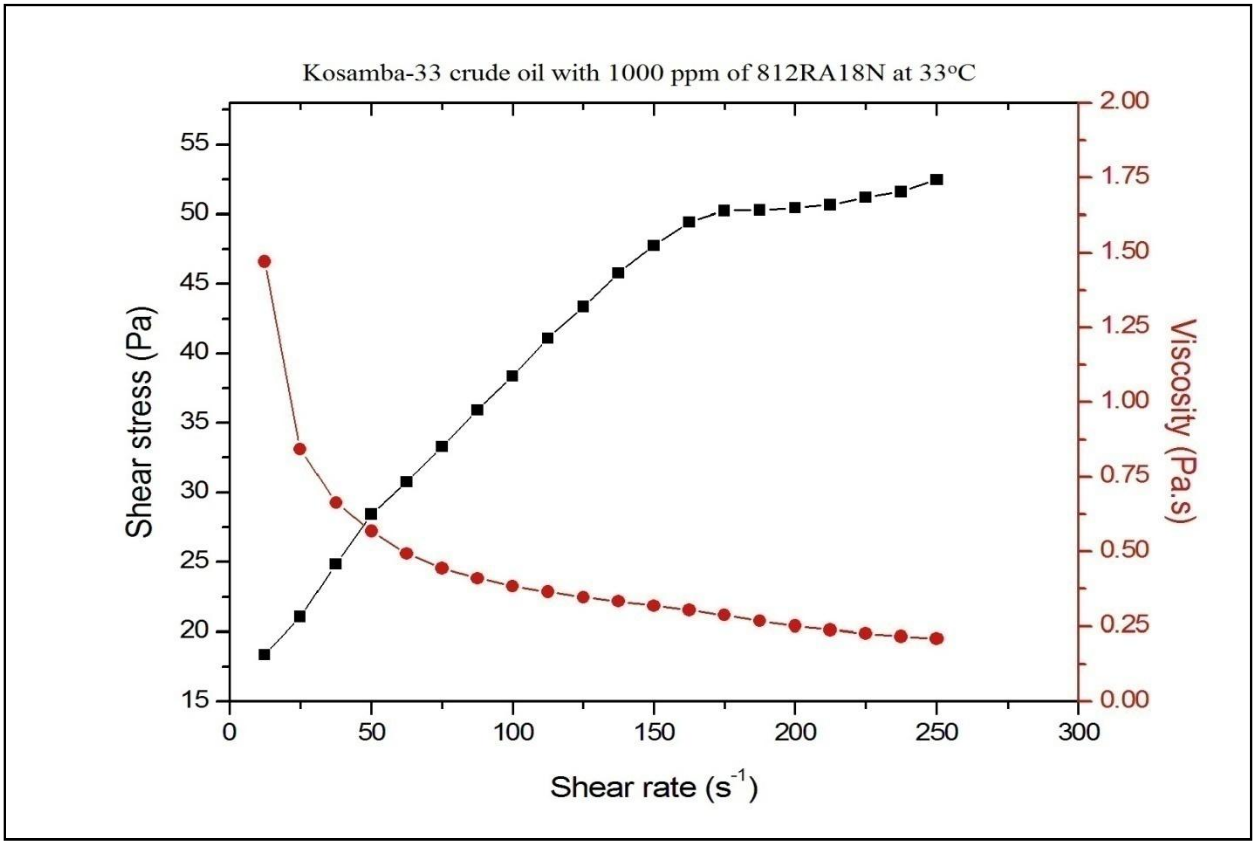

Fig 3.103 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-12RA18N at 33°C

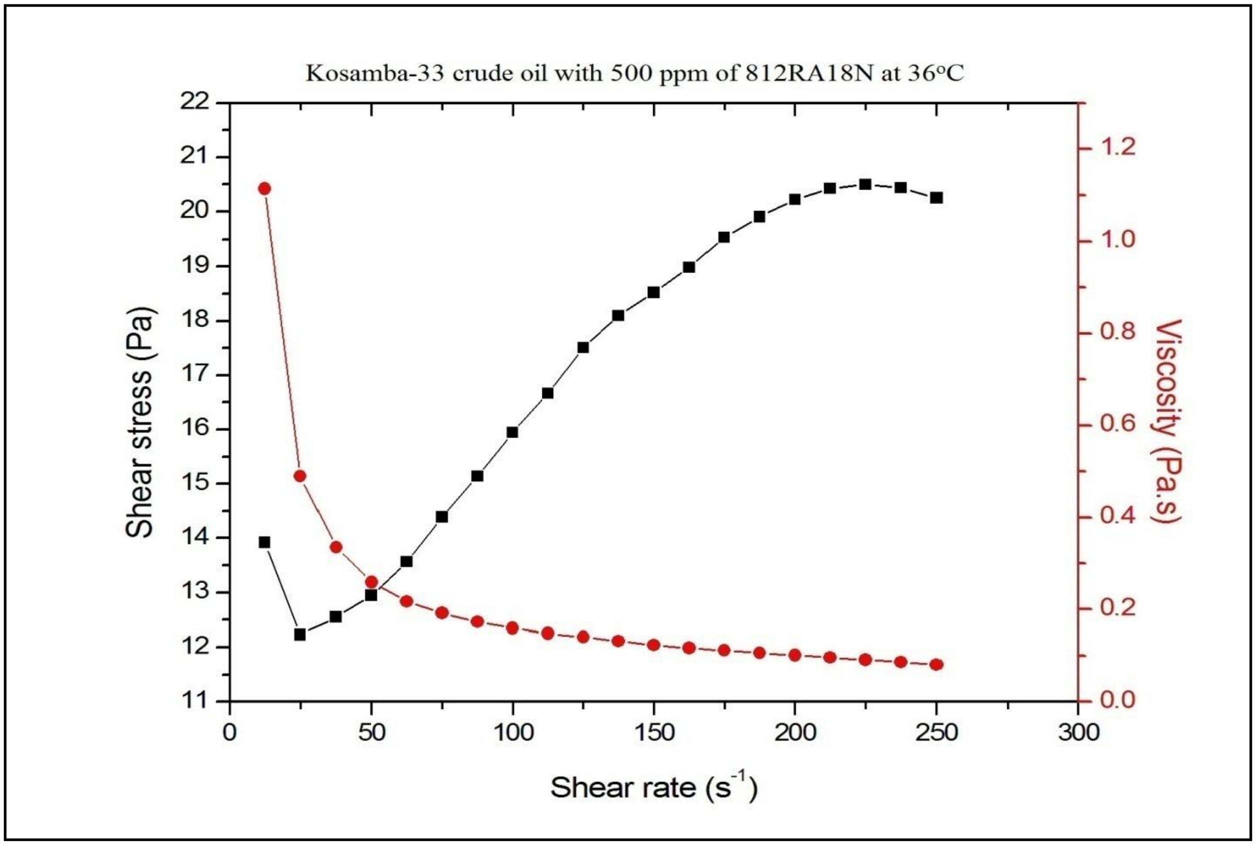

Fig 3.104 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-12RA18N at 36°C

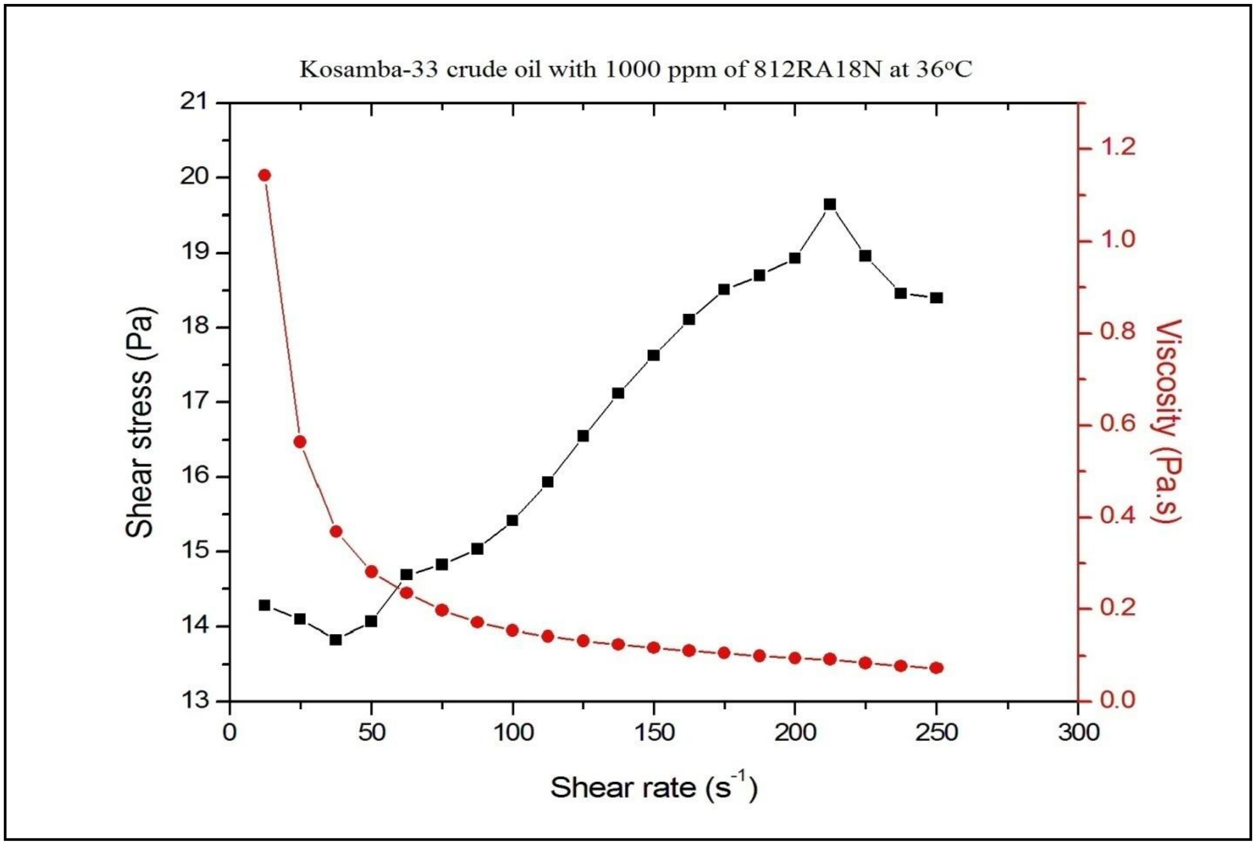

Fig 3.105 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-12RA18N at 36°C

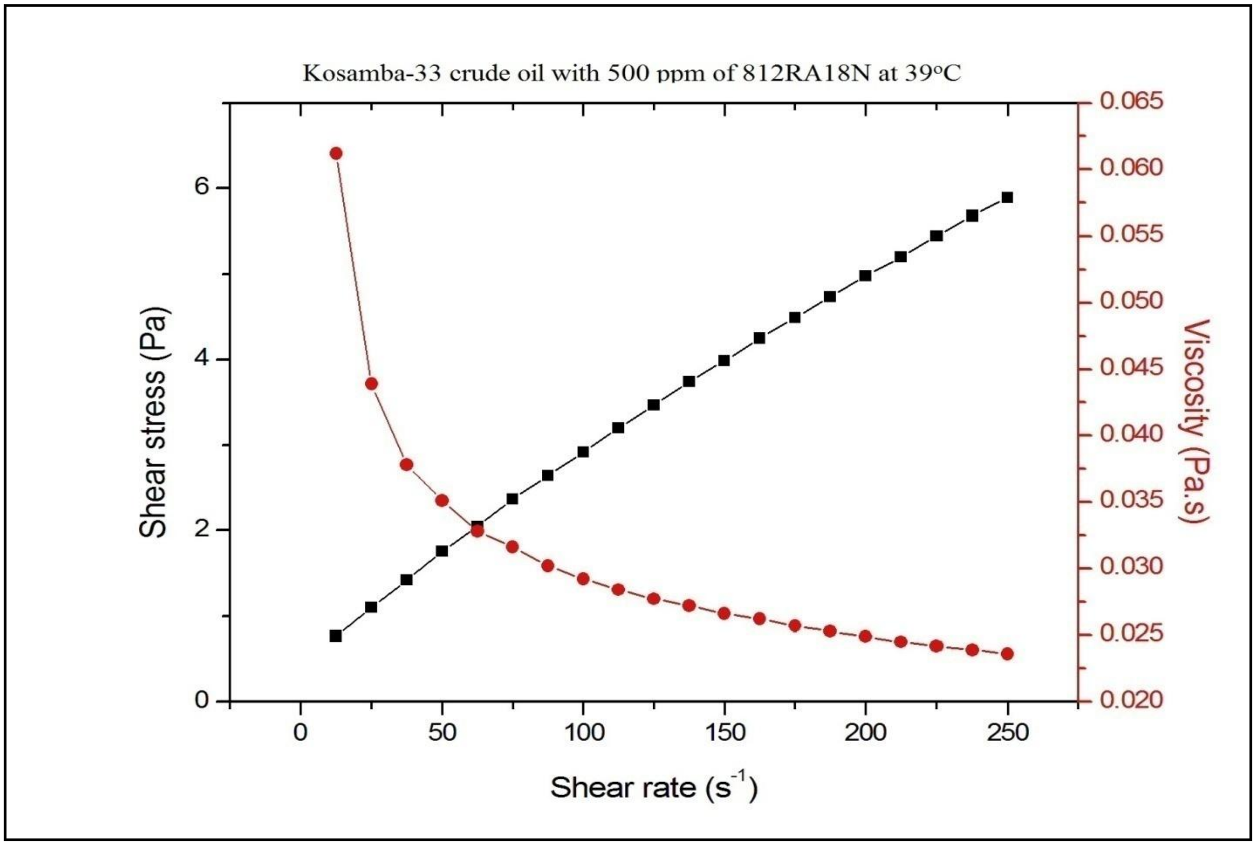

Fig 3.106 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-12RA18N at 39°C

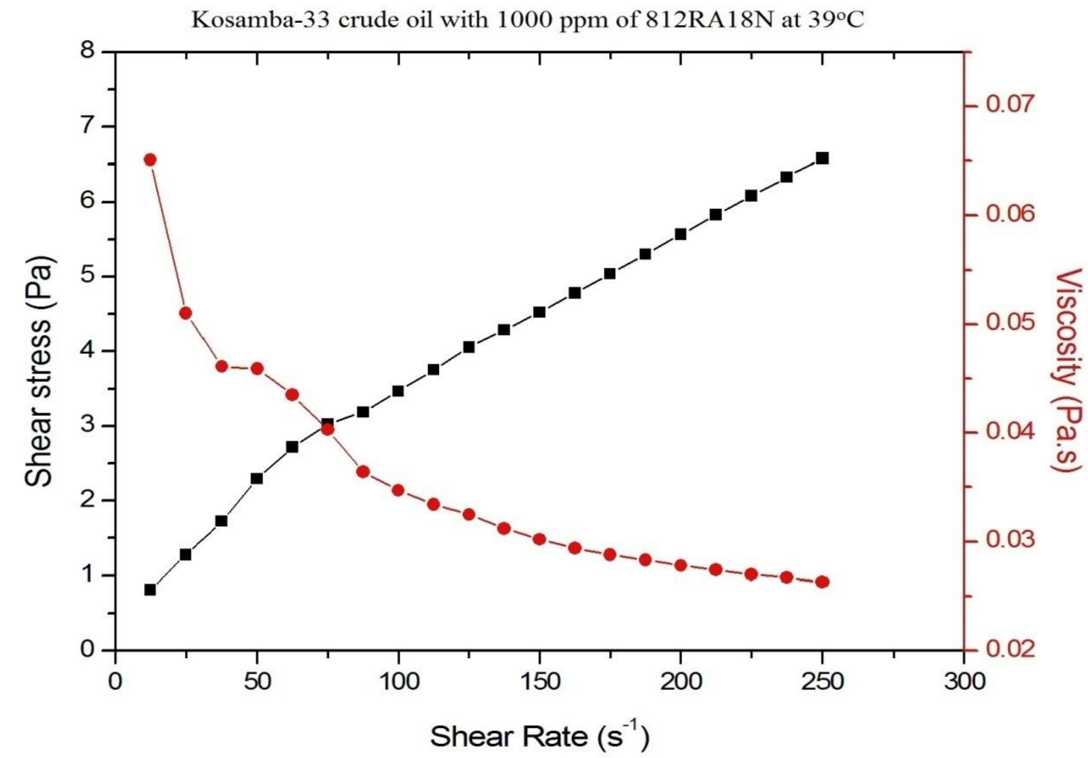

Fig 3.107 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-12RA18N at 39^{o}C

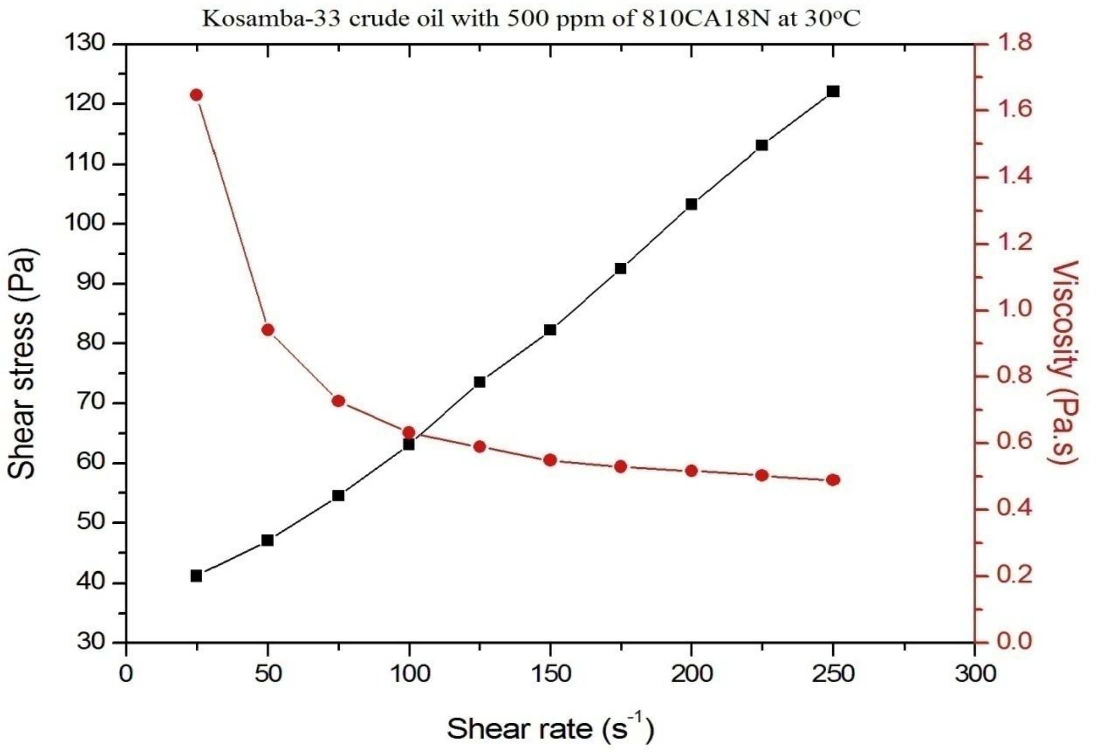

Fig 3.108 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10CA18N at 30^{o}C

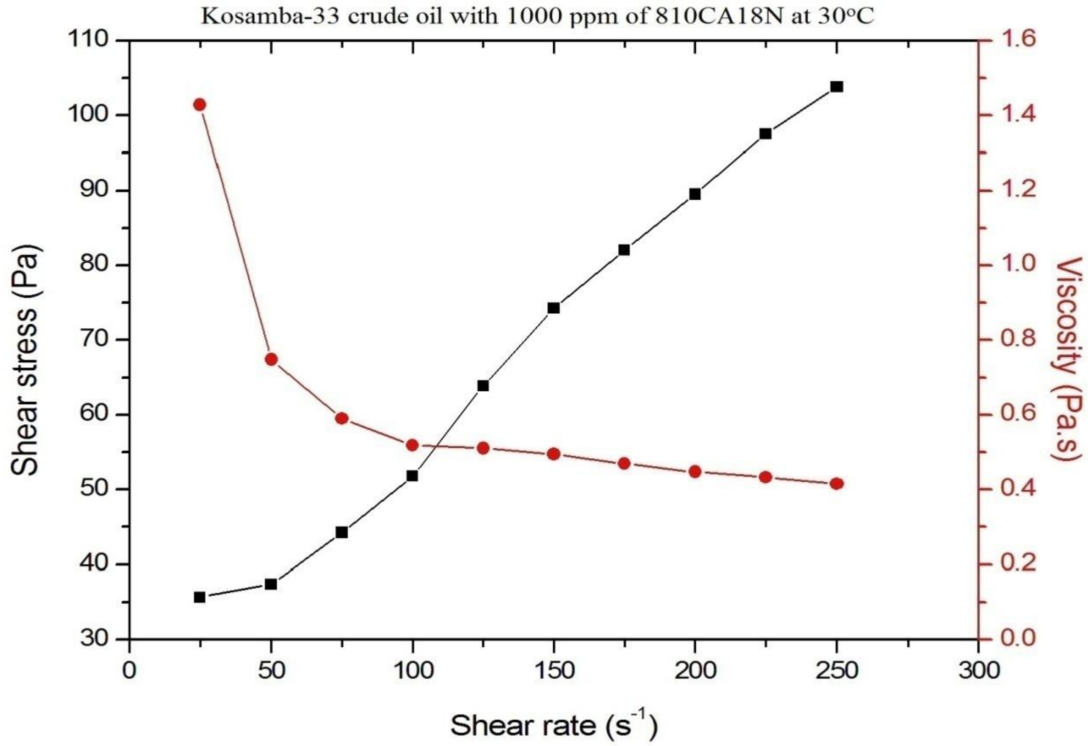

Fig 3.109 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10CA18N at 30^{o}C

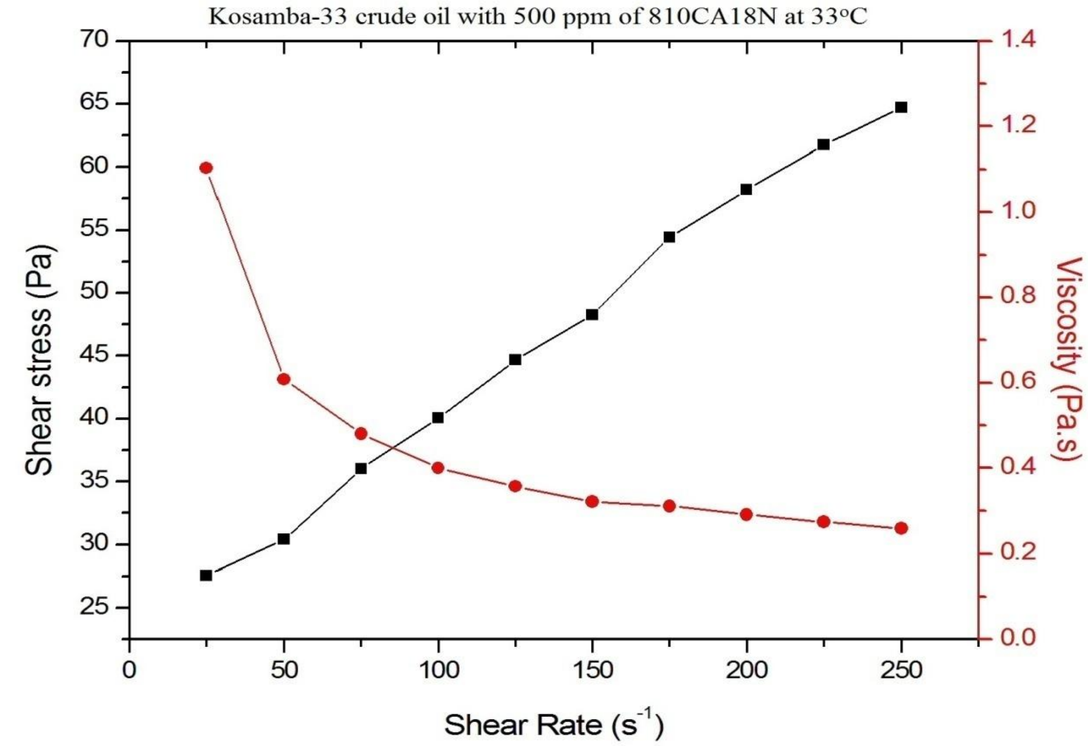

Fig 3.110 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10CA18N at 33^{o}C

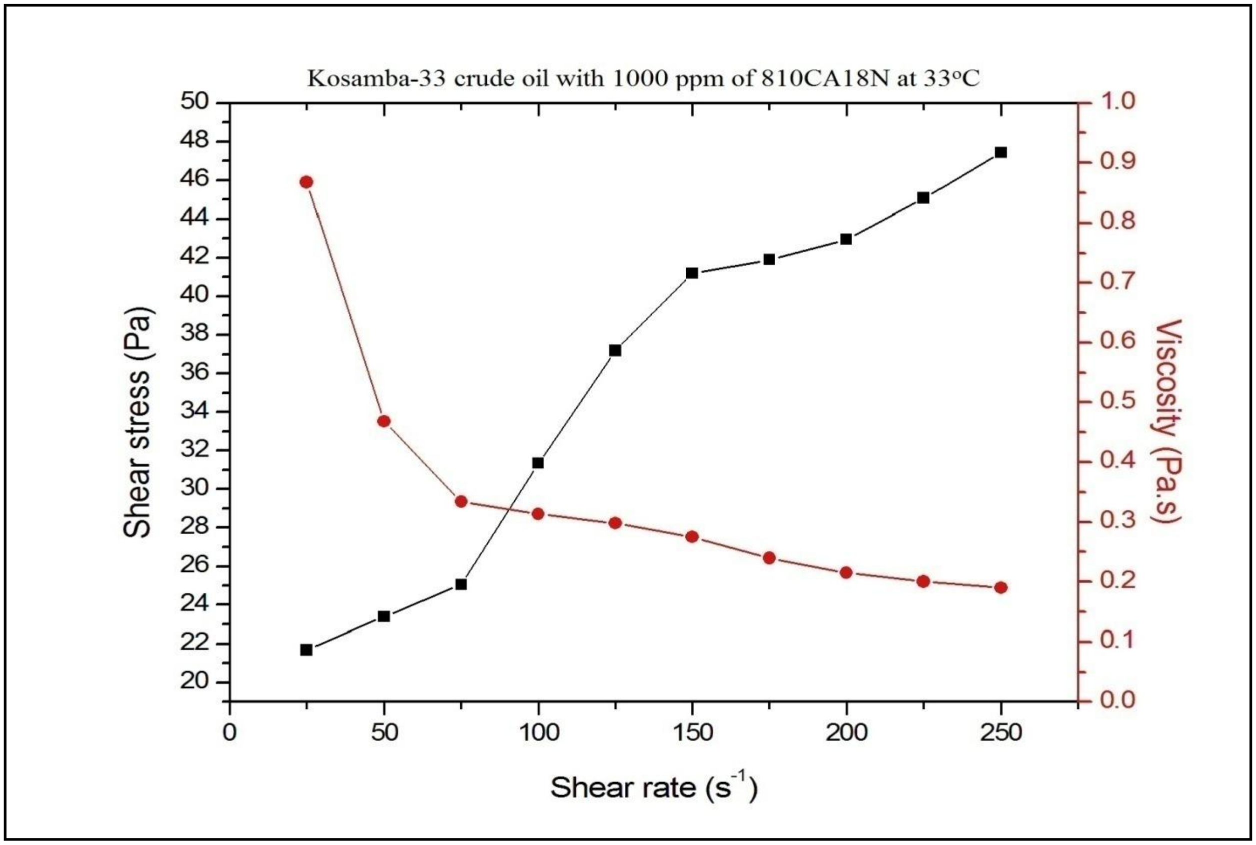

Fig 3.111 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10CA18N at 33°C

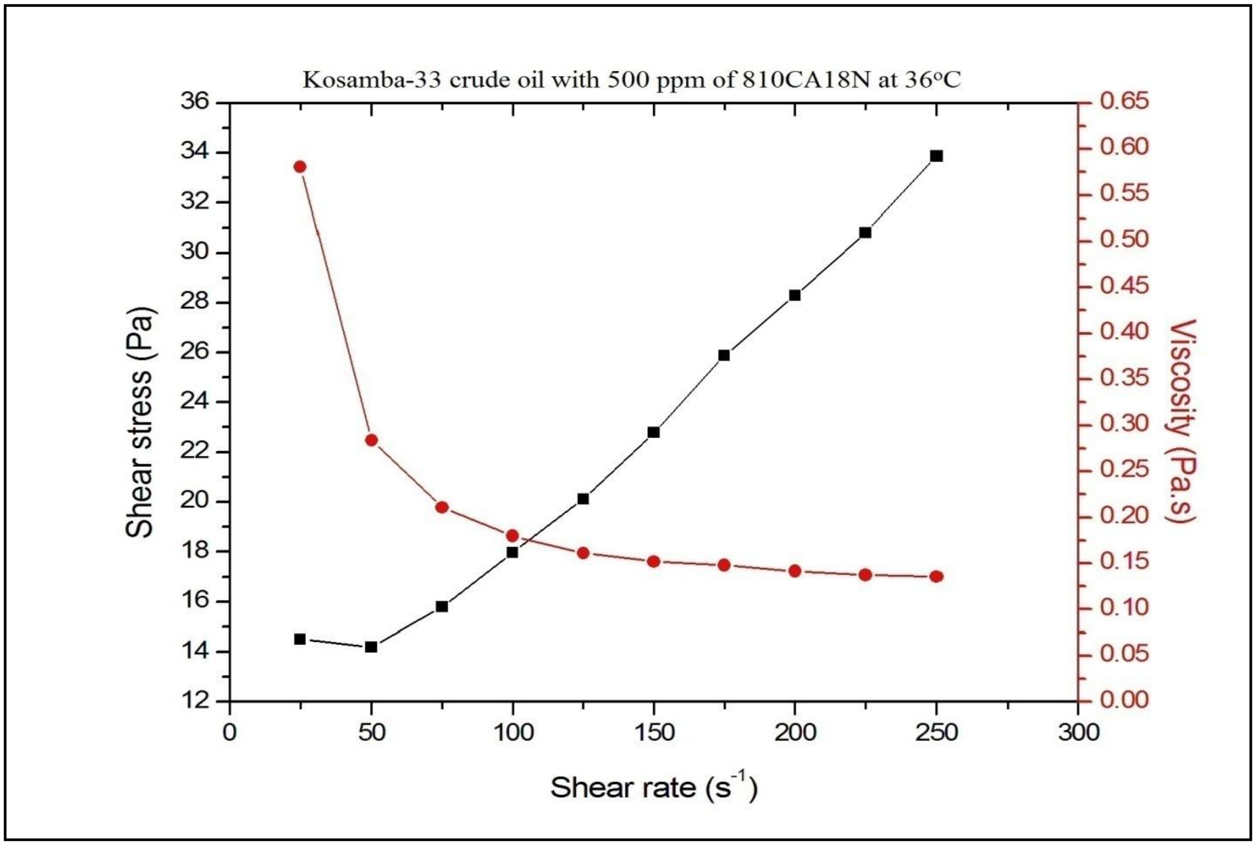

Fig 3.112 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10CA18N at 36°C

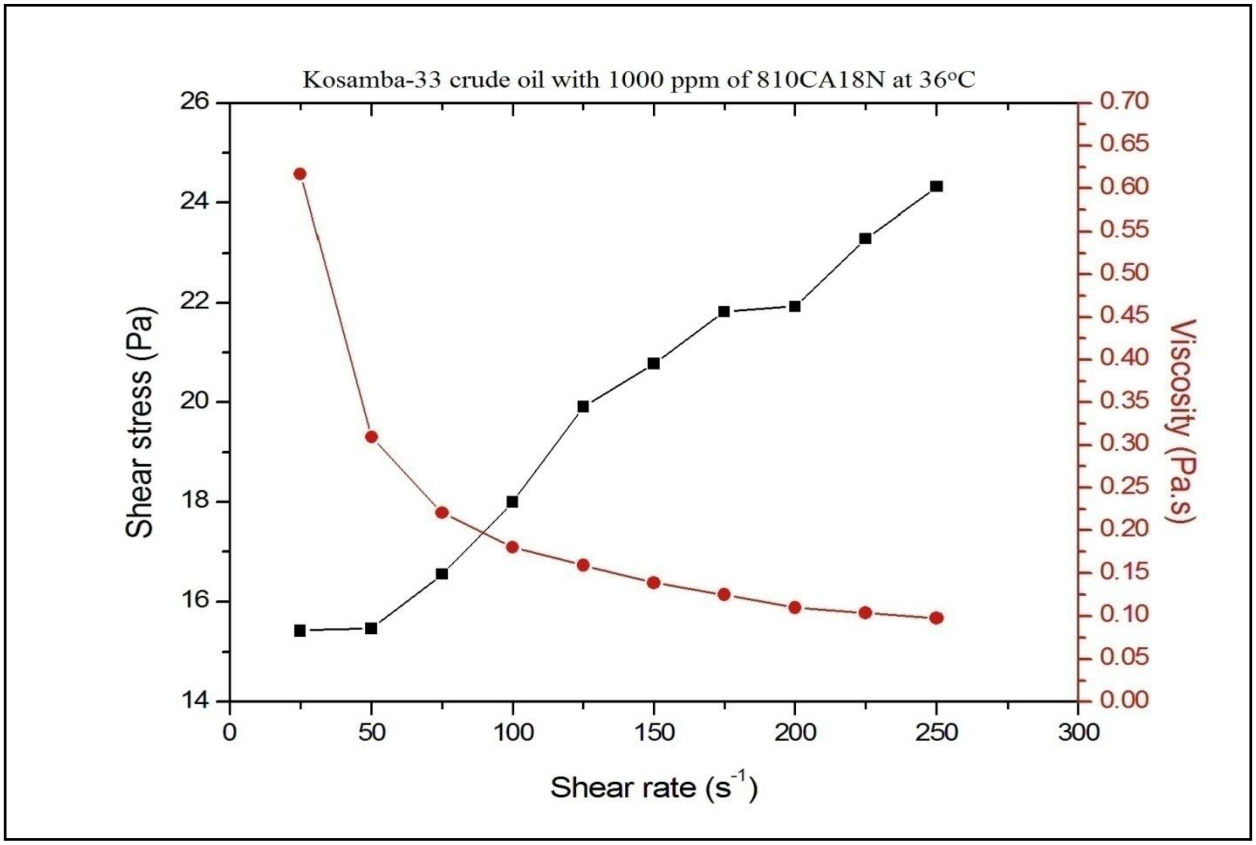

Fig 3.113 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10CA18N at 36^{o}C

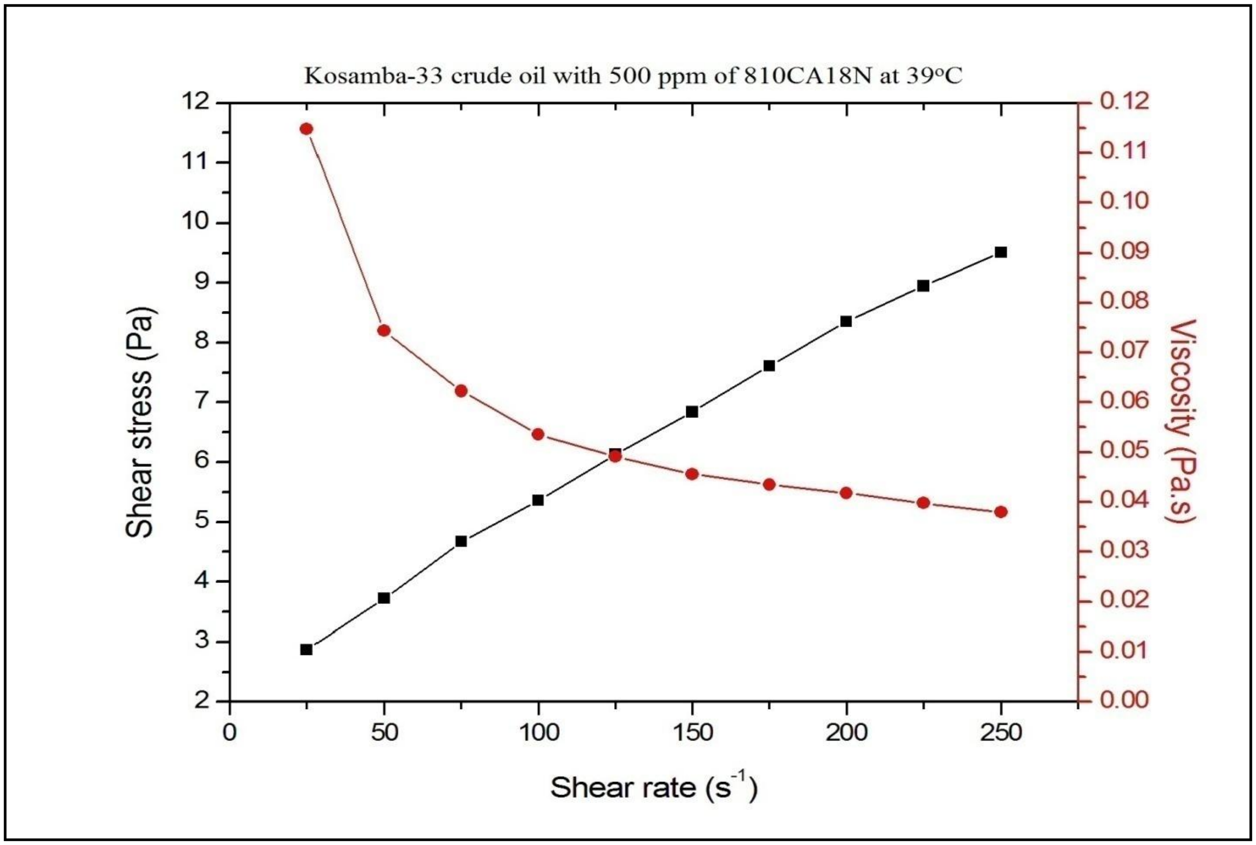

Fig 3.114 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-10CA18N at 39^{o}C

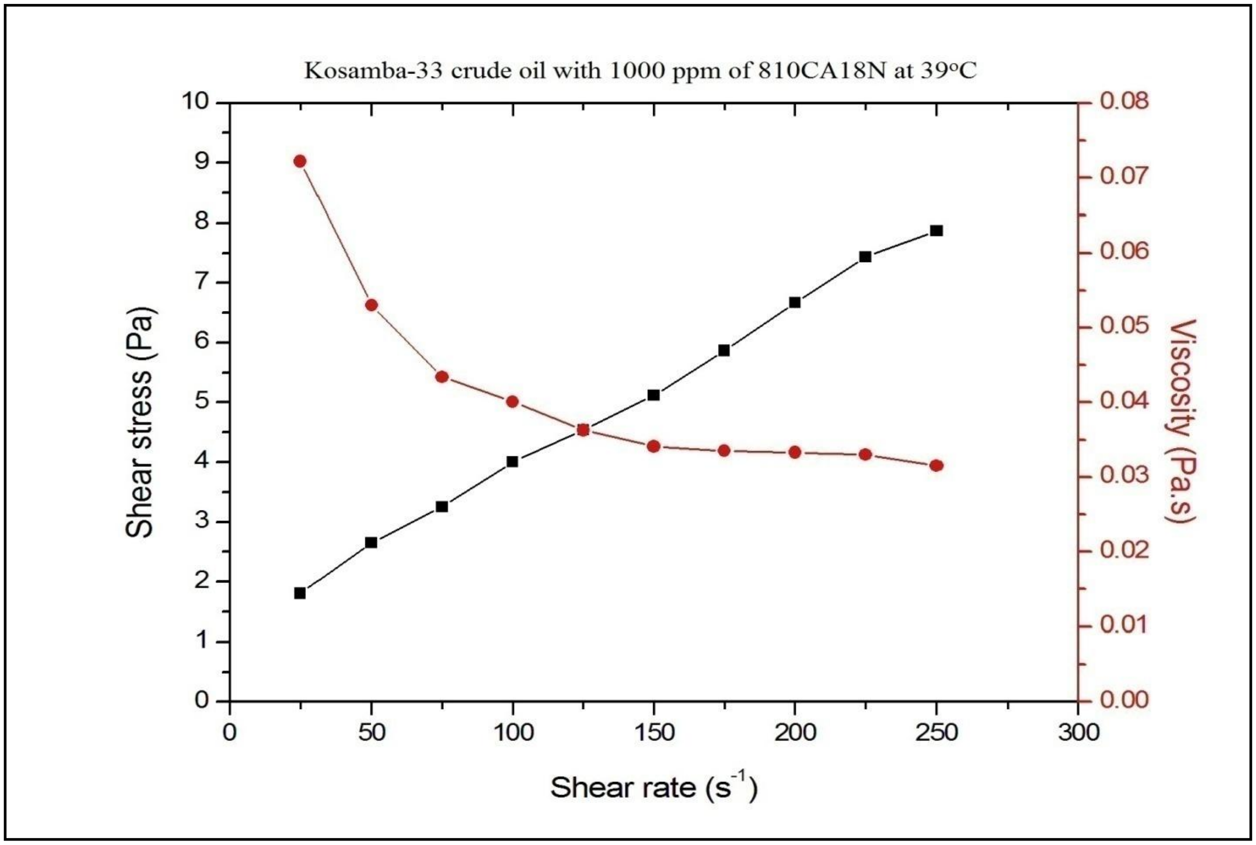

Fig 3.115 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-10CA18N at 39°C

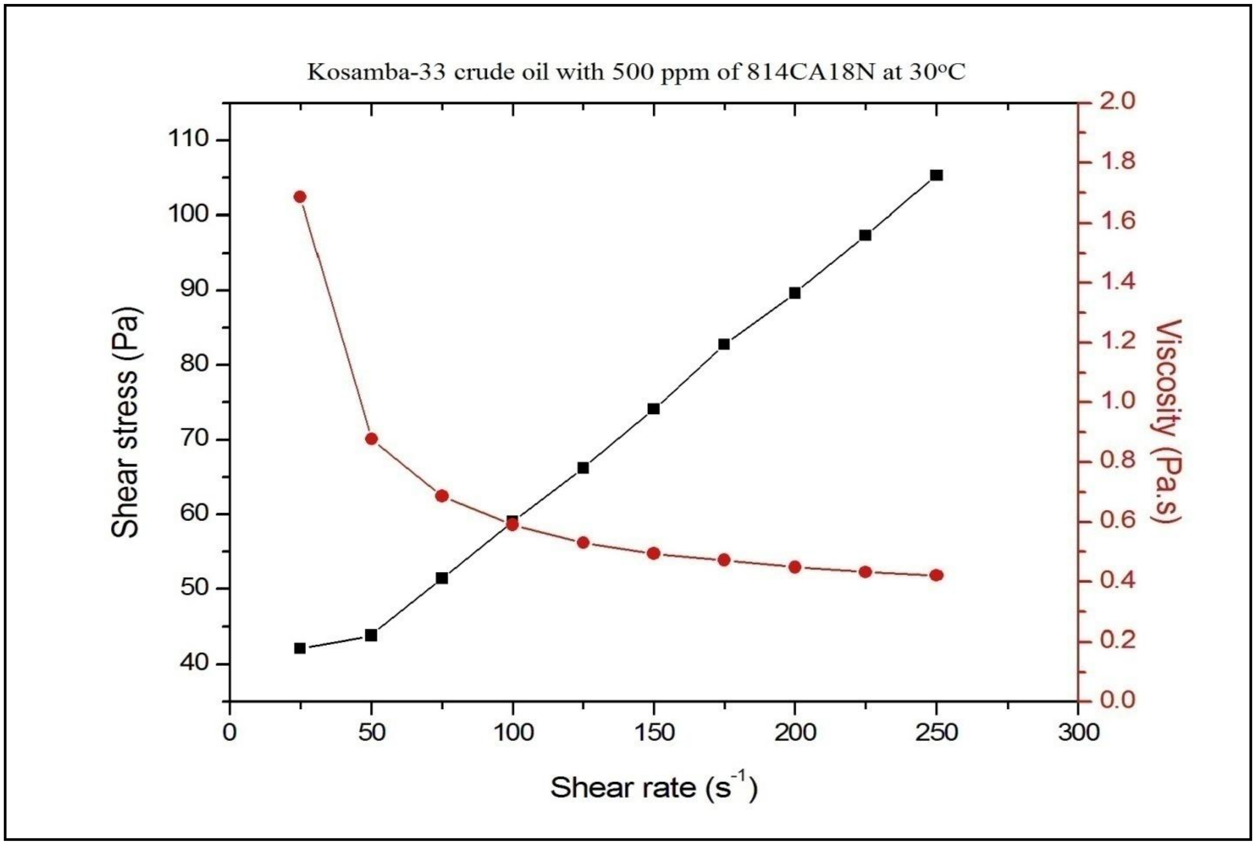

Fig 3.116 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-14CA18N at 30°C

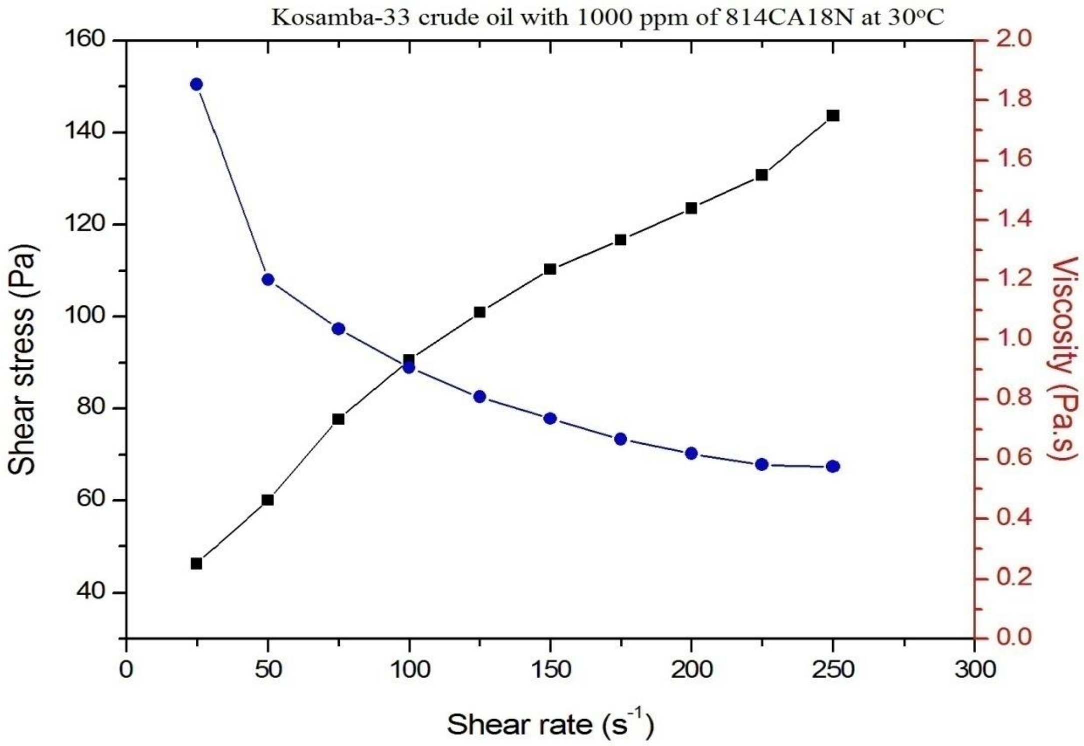

Fig 3.117 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-14CA18N at 30^{o}C

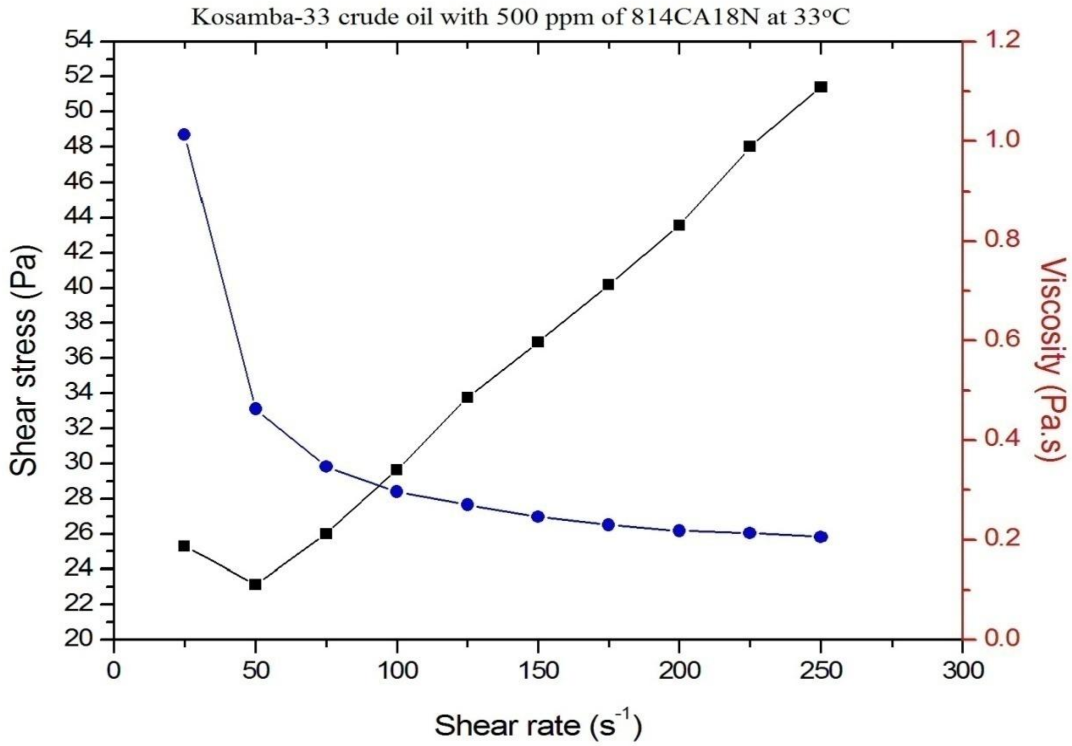

Fig 3.118 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-14CA18N at 33^{o}C

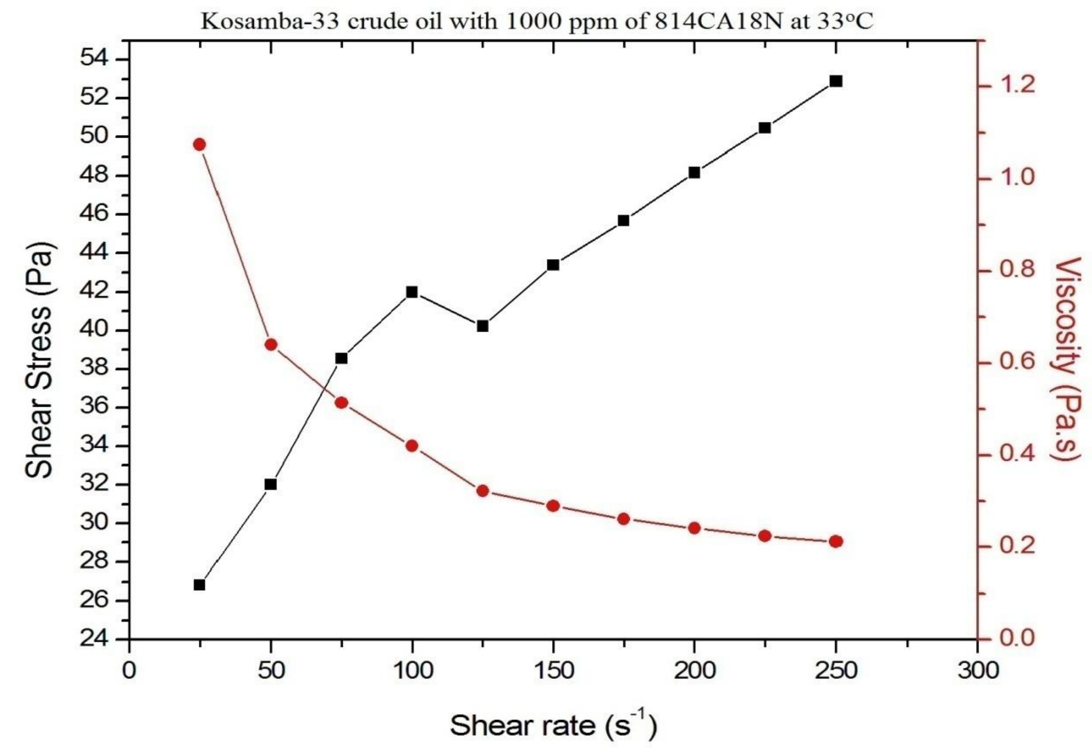

Fig 3.119 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-14CA18N at 33°C

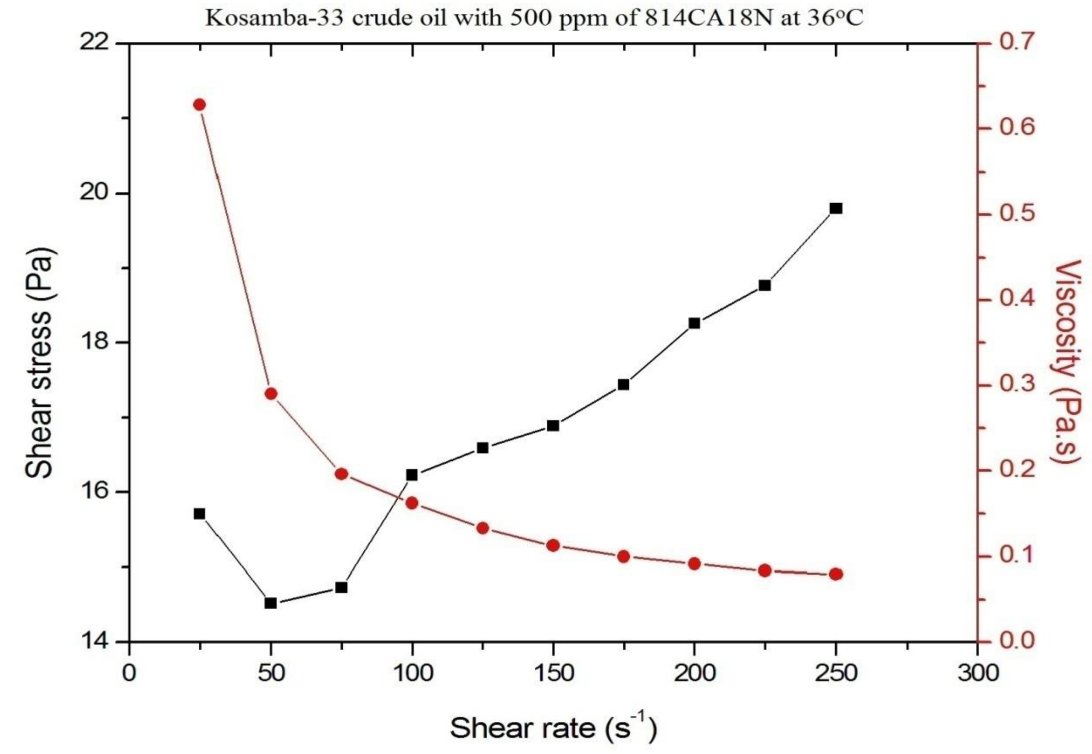

Fig 3.120 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-14CA18N at 36°C

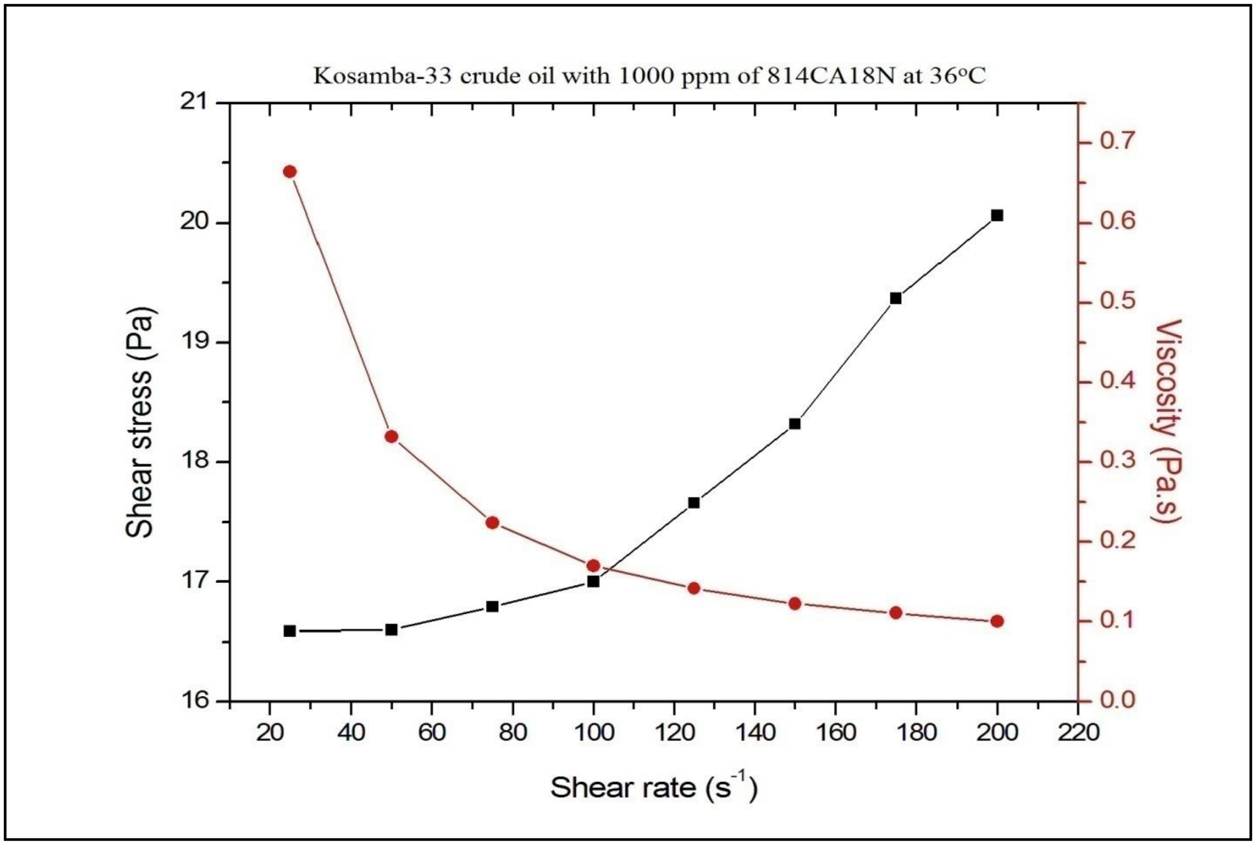

Fig 3.121 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-14CA18N at 36°C

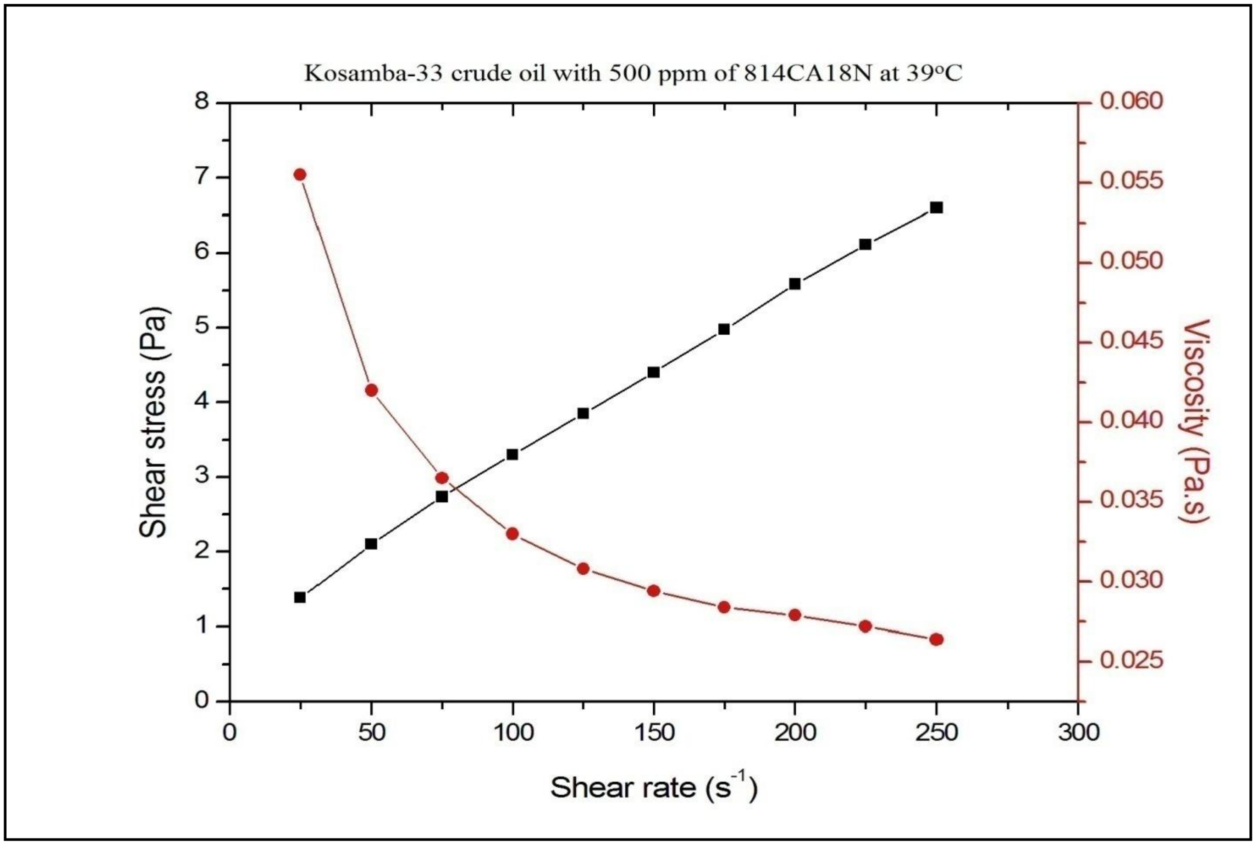

Fig 3.122 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-14CA18N at 39°C

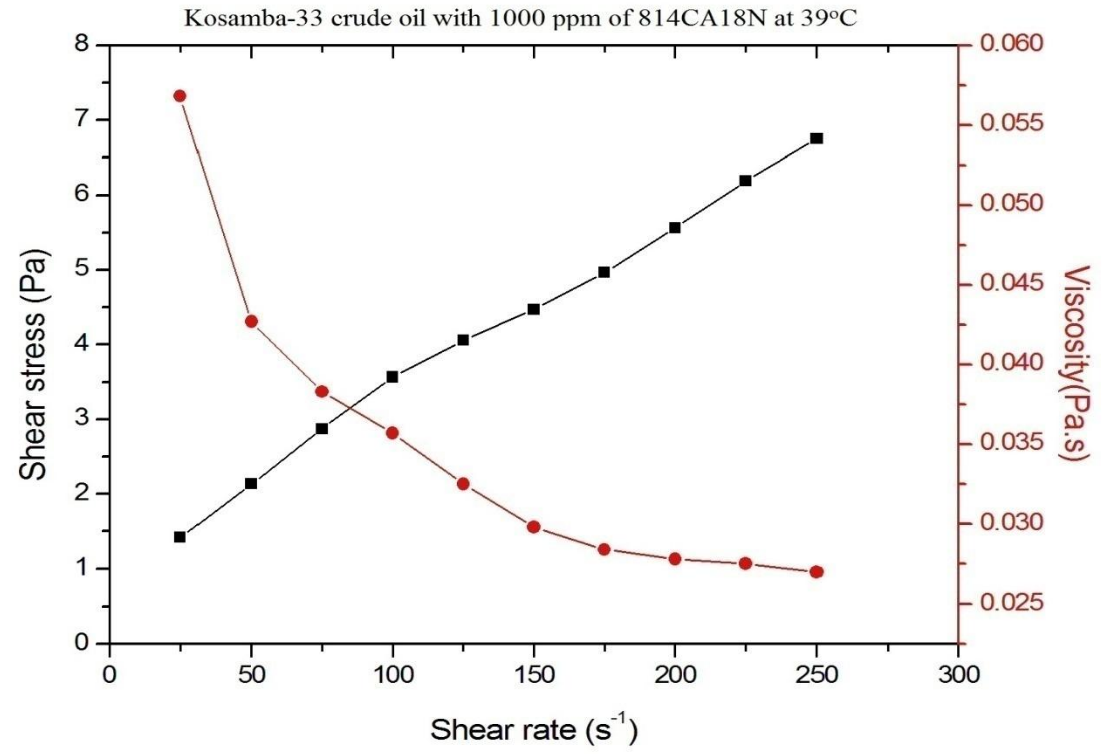

Fig 3.123 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-14CA18N at 39°C

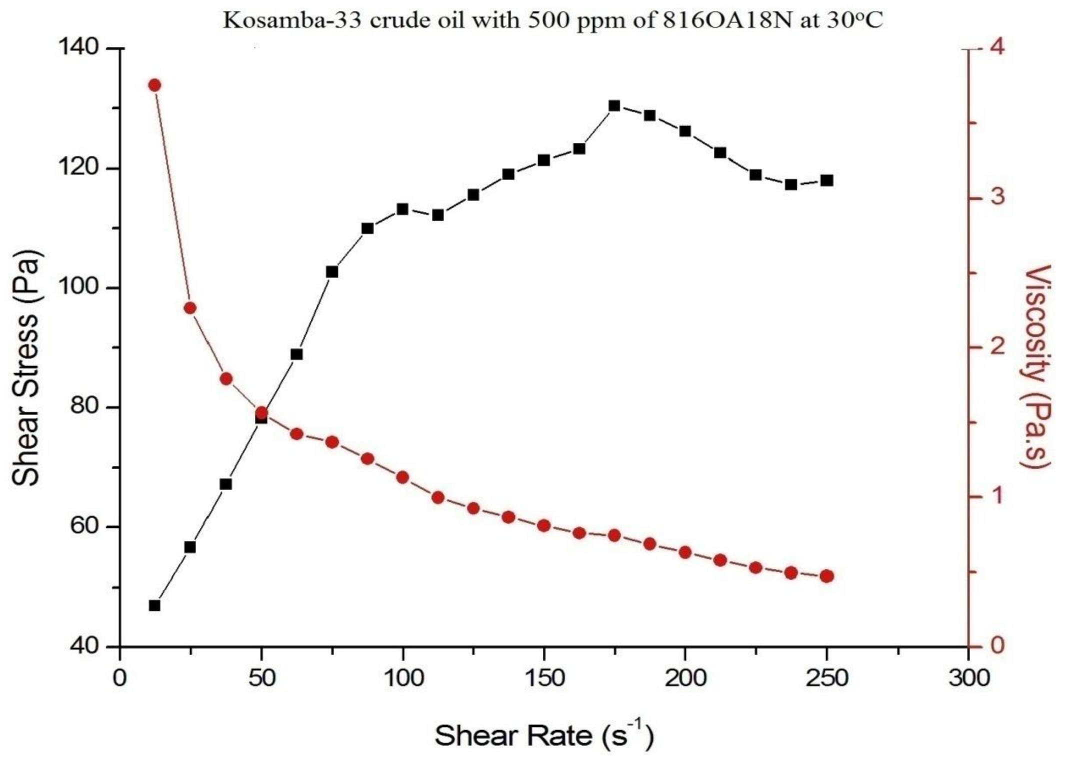

Fig 3.124 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-16OA18N at 30°C

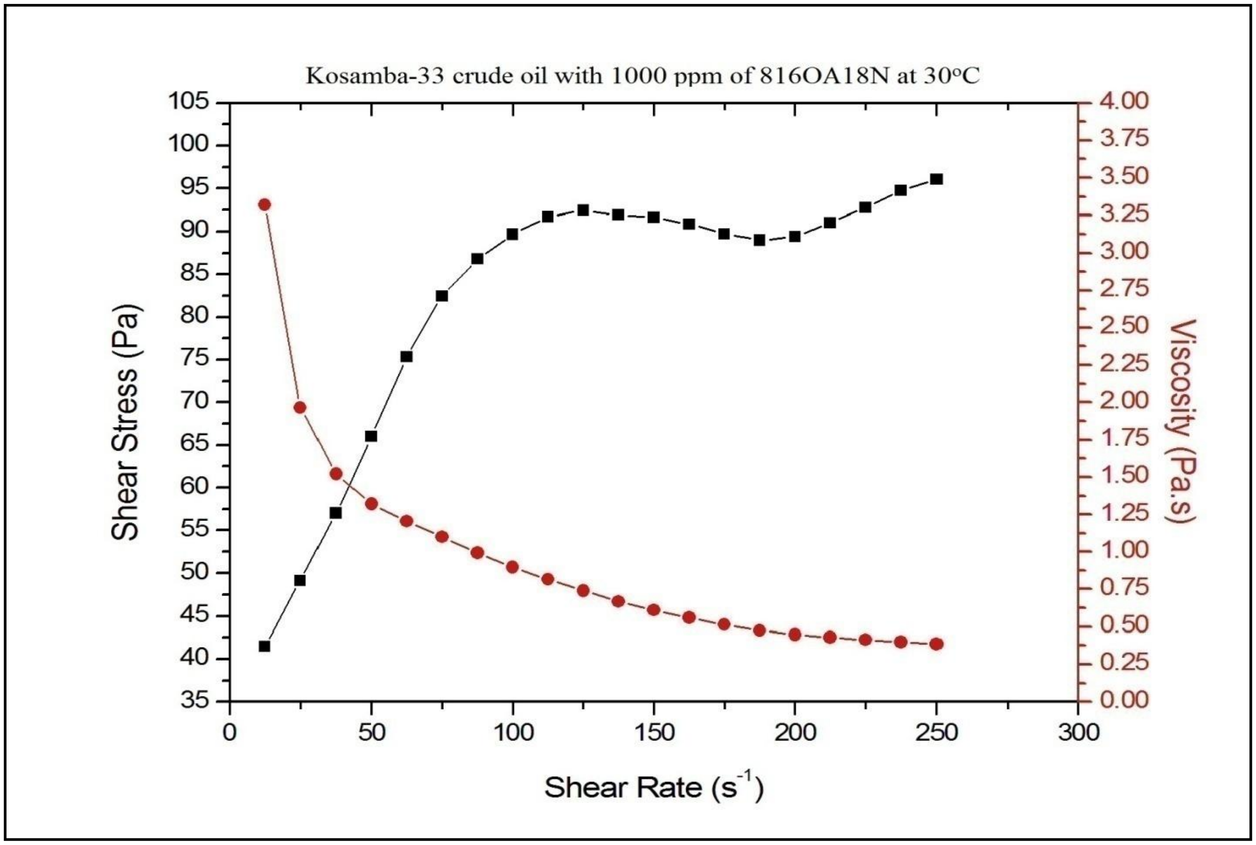

Fig 3.125 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-16OA18N at 30°C

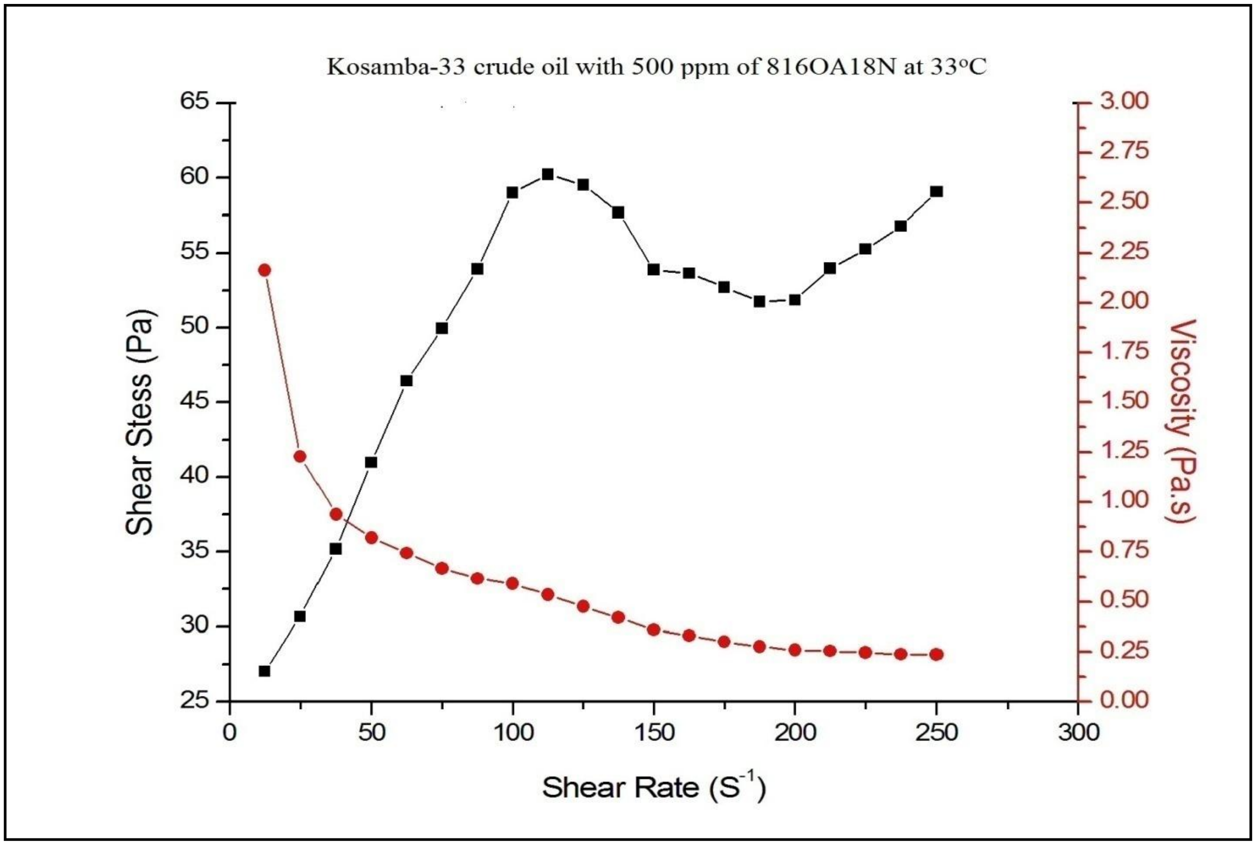

Fig 3.126 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-16OA18N at 33°C

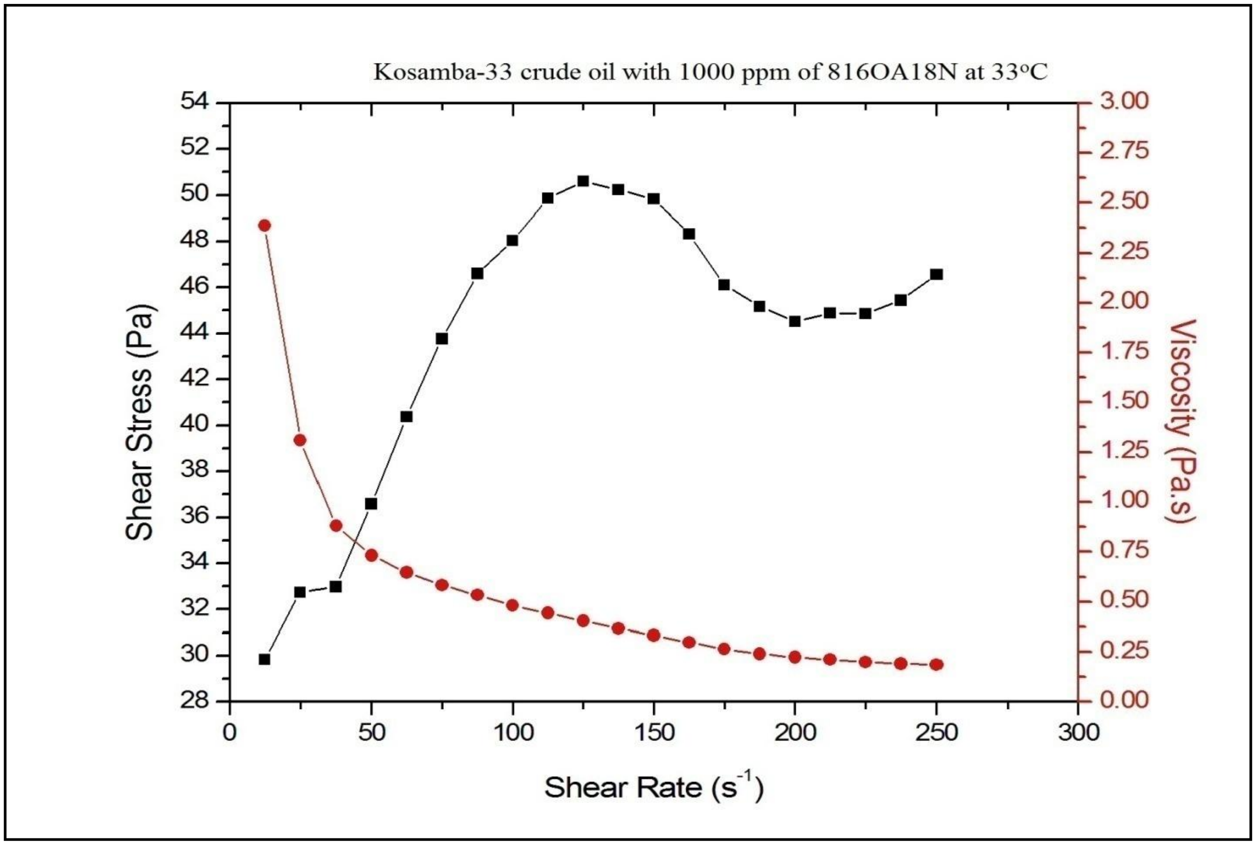

Fig 3.127 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-16OA18N at 33^{o}C

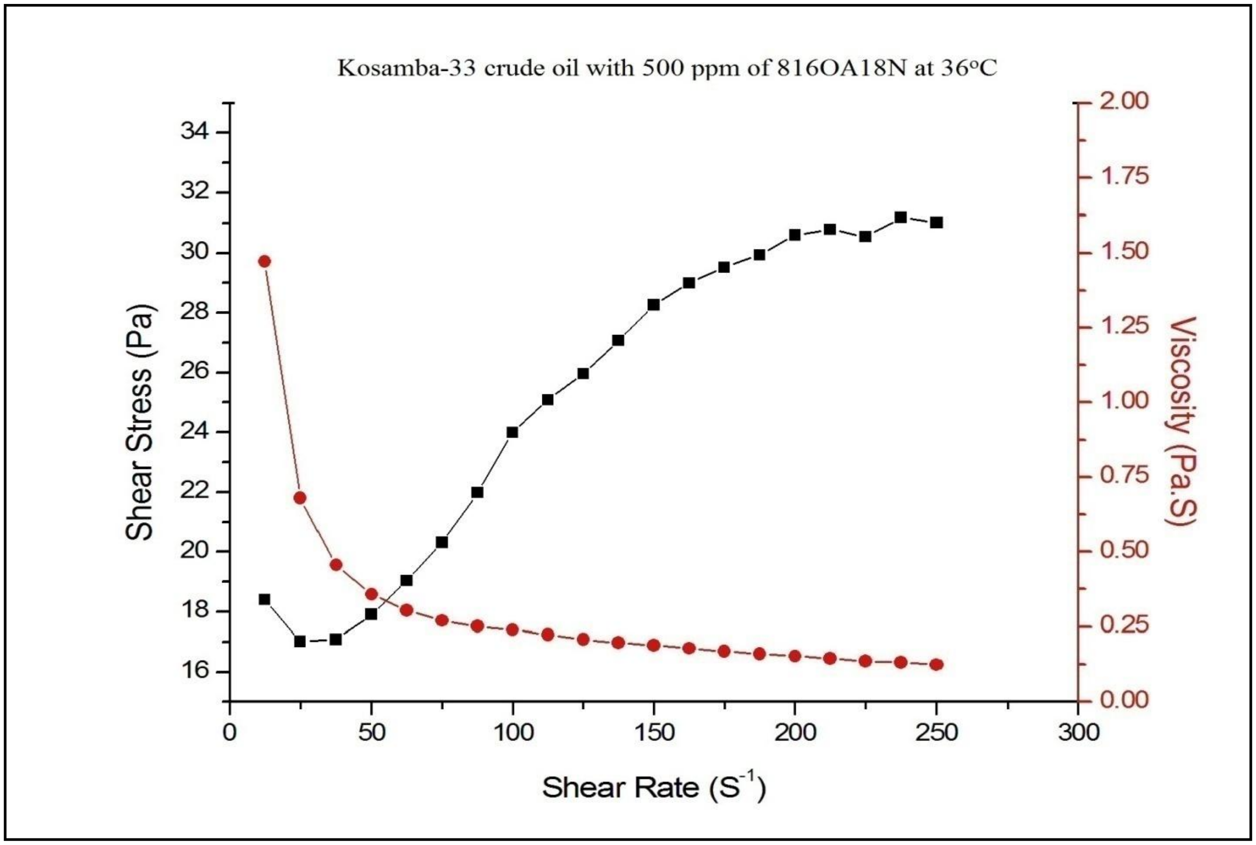

Fig 3.128 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-16OA18N at 36^{o}C

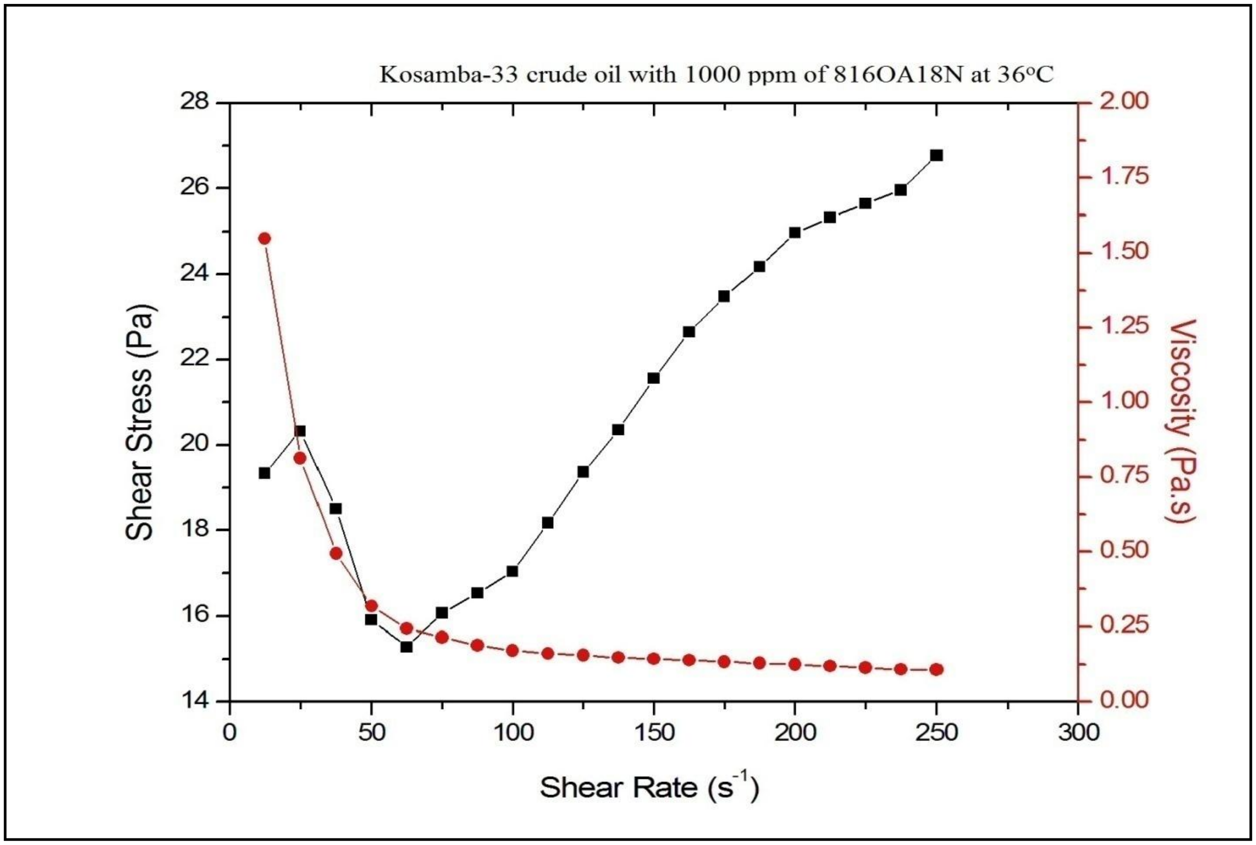

Fig 3.129 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-16OA18N at 36°C

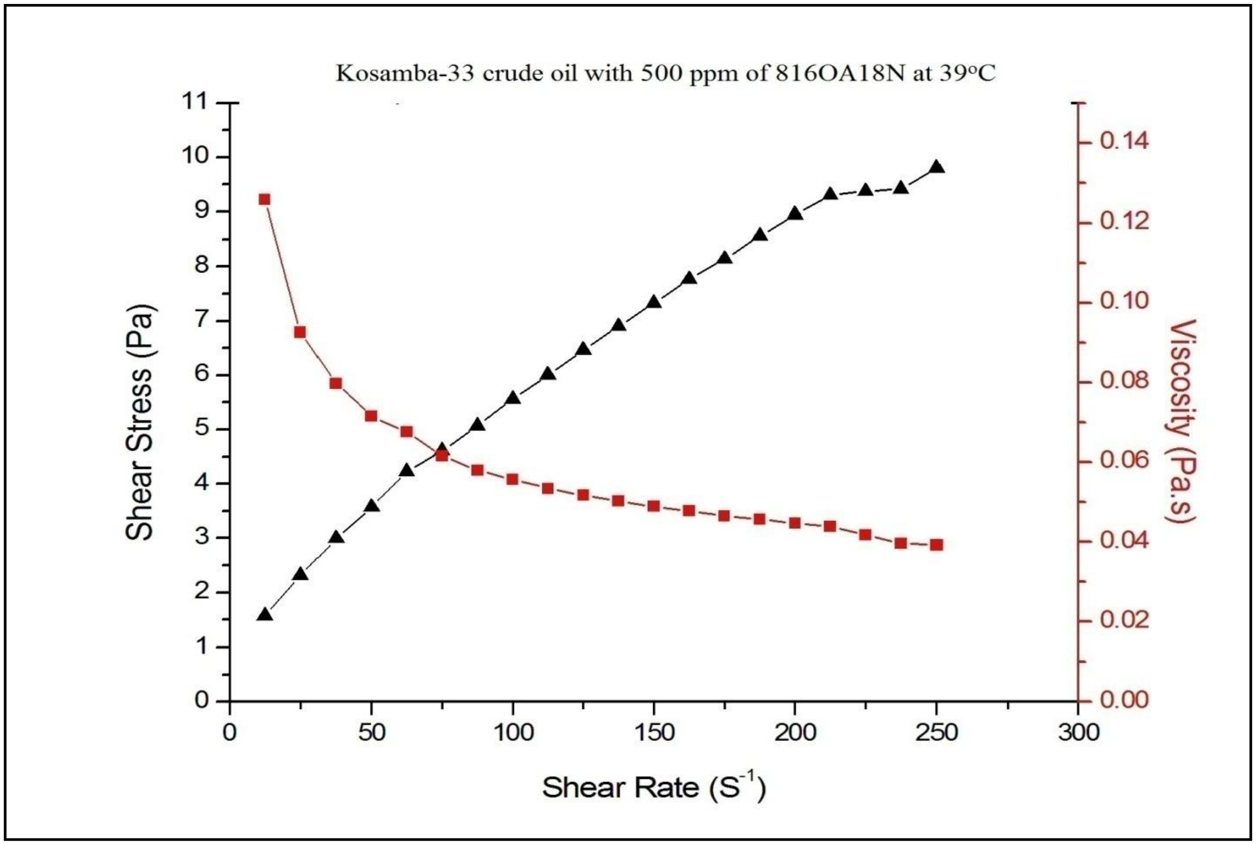

Fig 3.130 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-16OA18N at 39°C

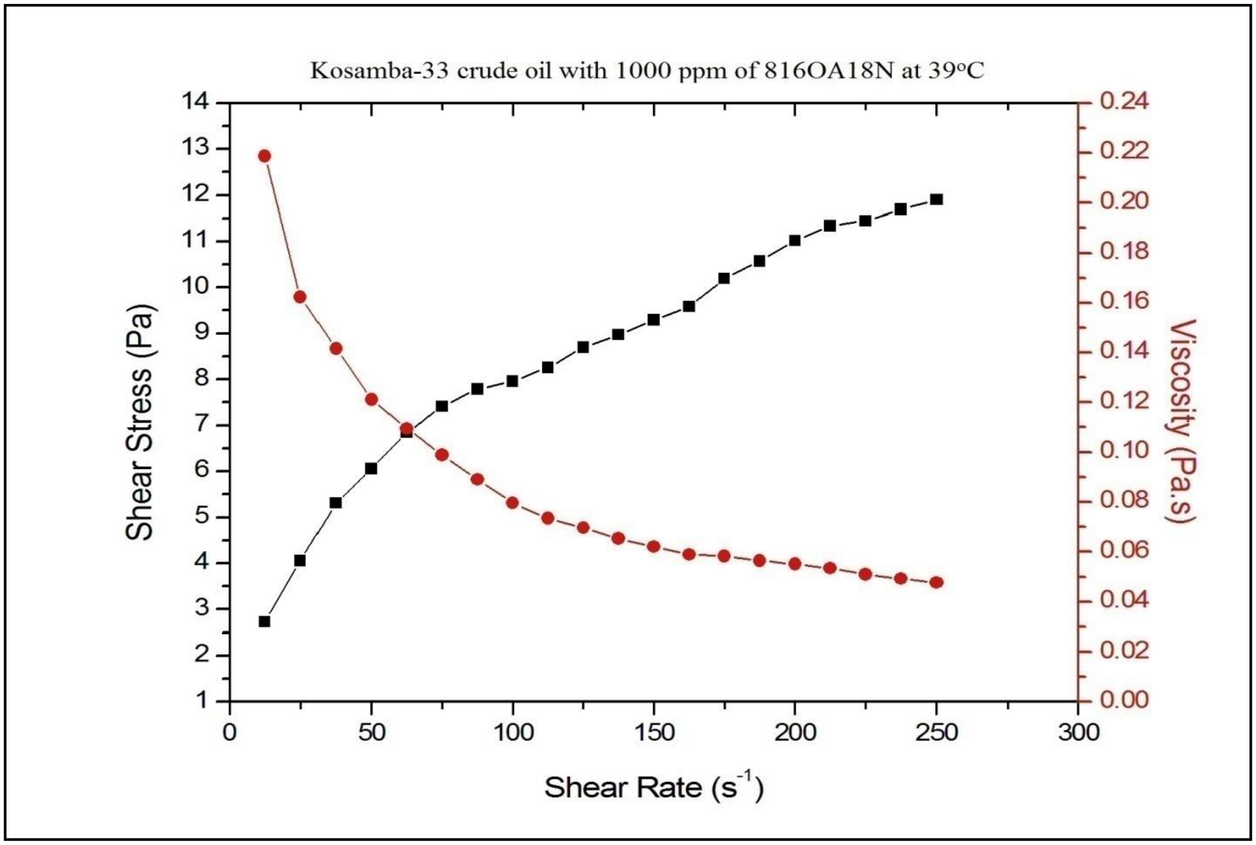

Fig 3.131 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-16OA18N at 39^{o}C

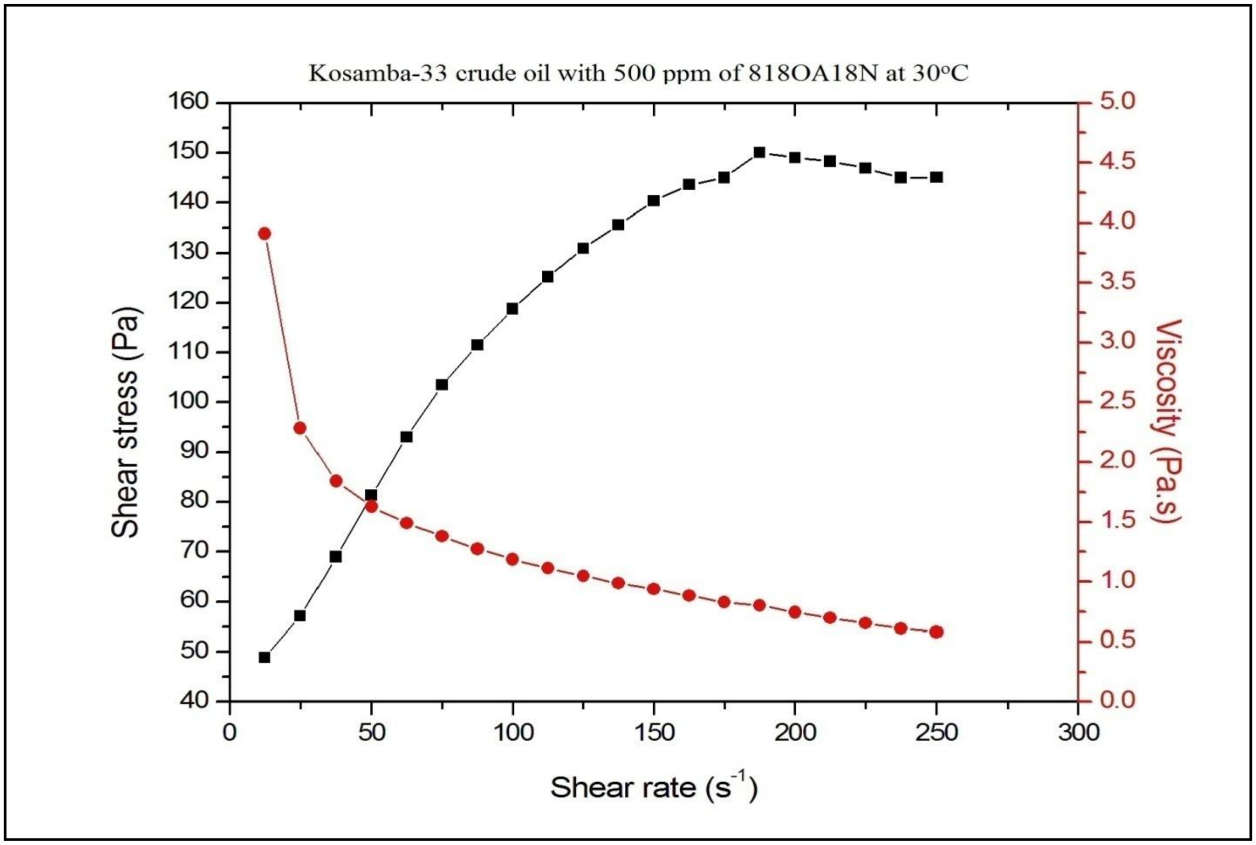

Fig 3.132 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-18OA18N at 30^{o}C

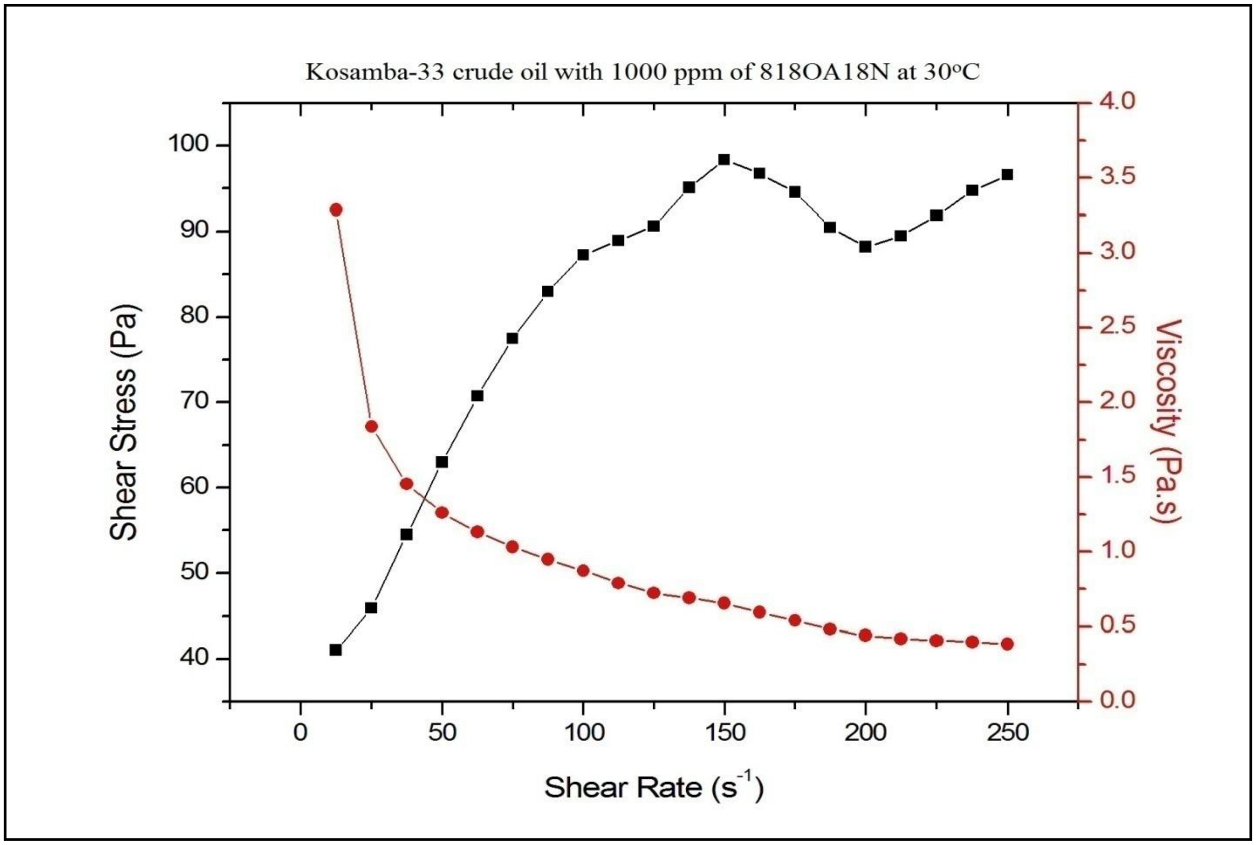

Fig 3.133 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-18OA18N at 30°C

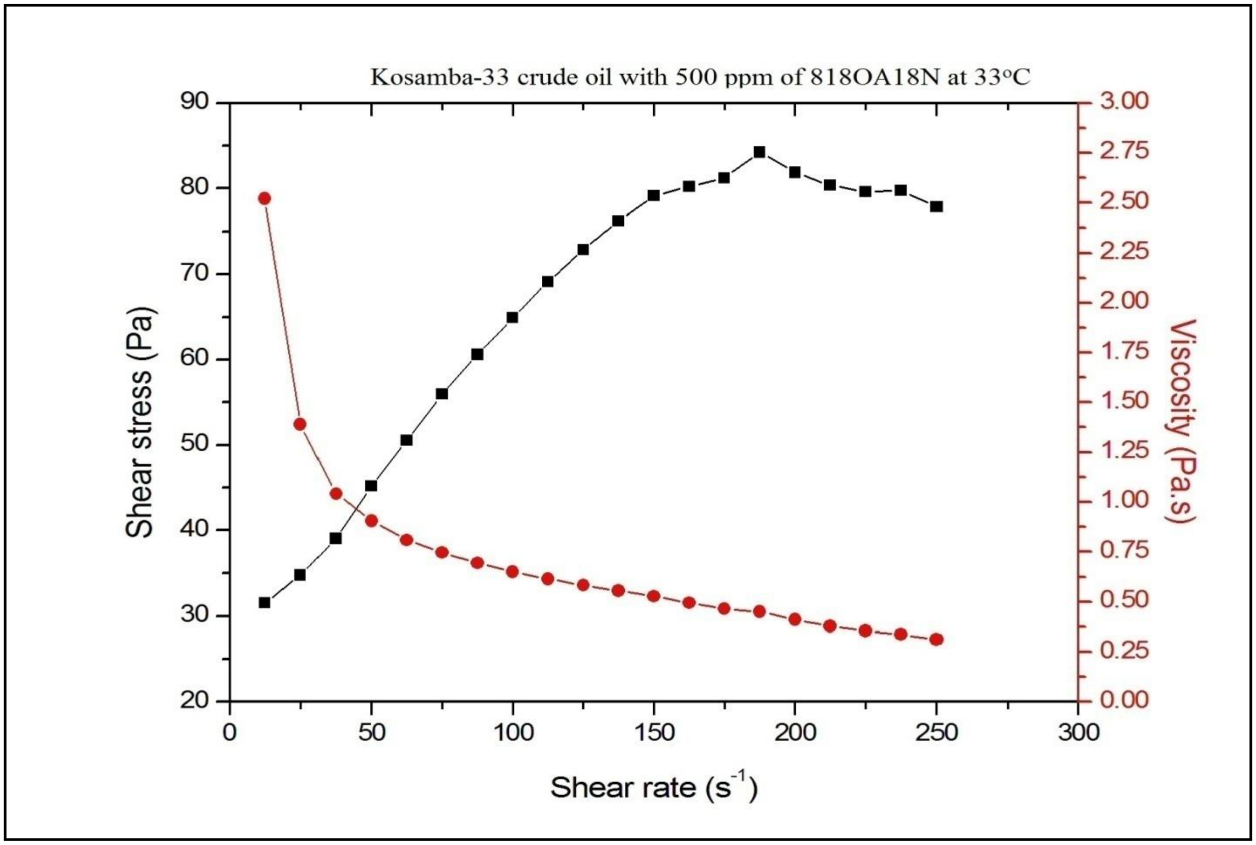

Fig 3.134 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-18OA18N at 33°C

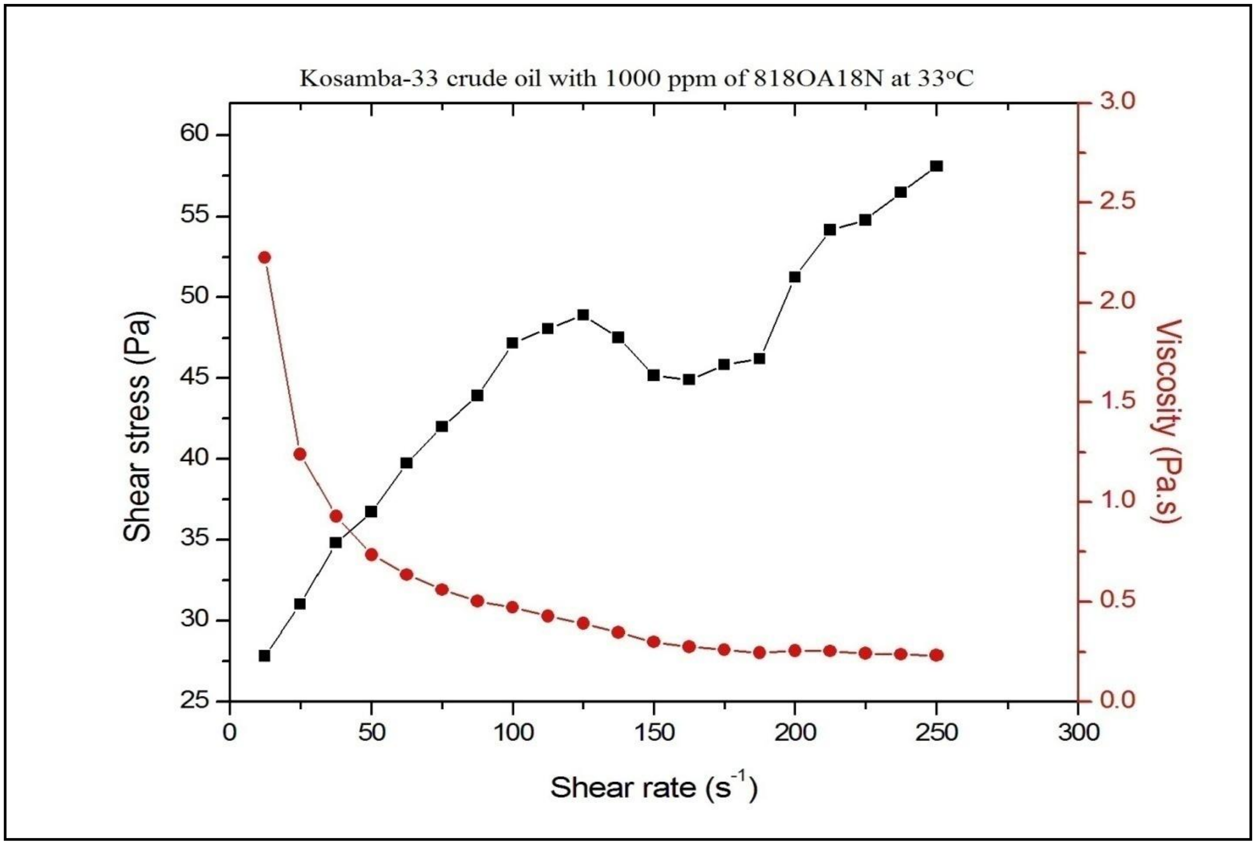

Fig 3.135 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-18OA18N at 33°C

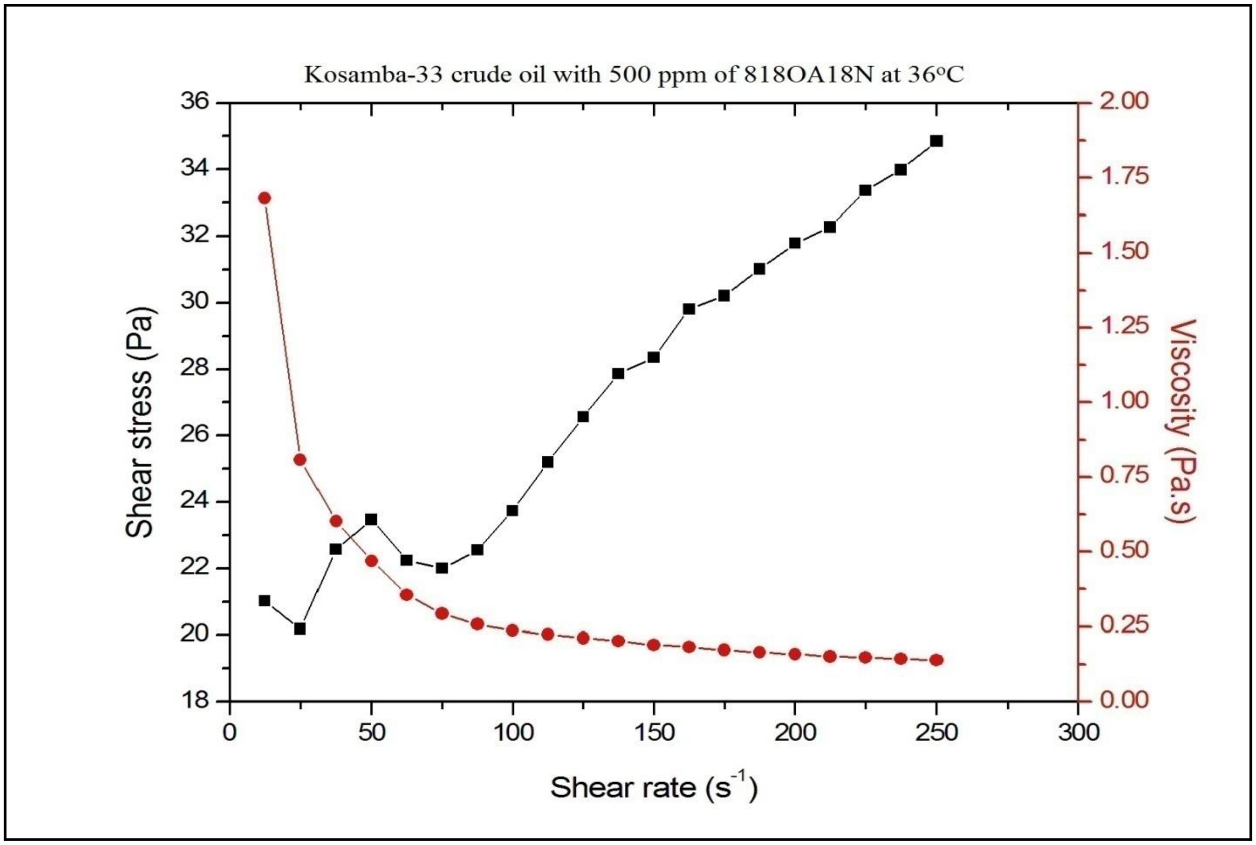

Fig 3.136 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-18OA18N at 36°C

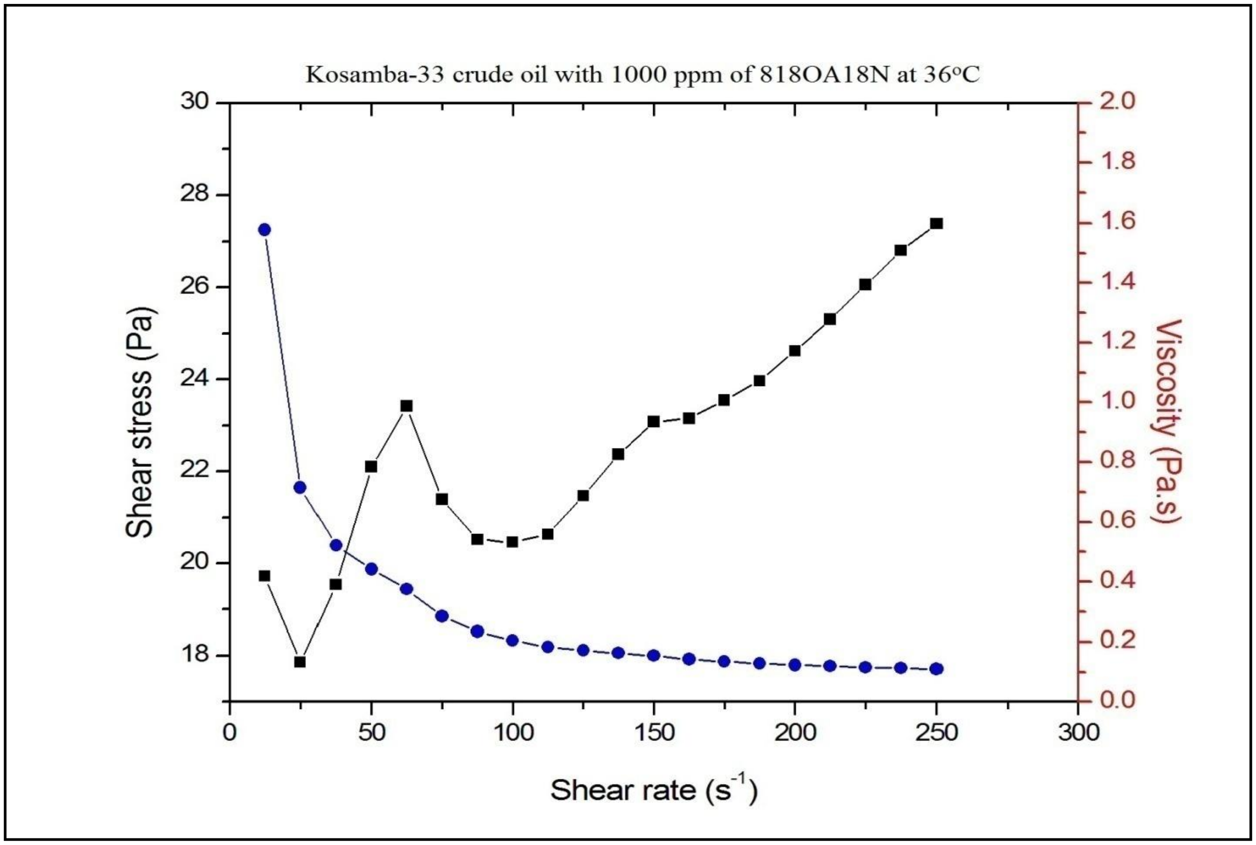

Fig 3.137 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-18OA18N at 36^{o}C

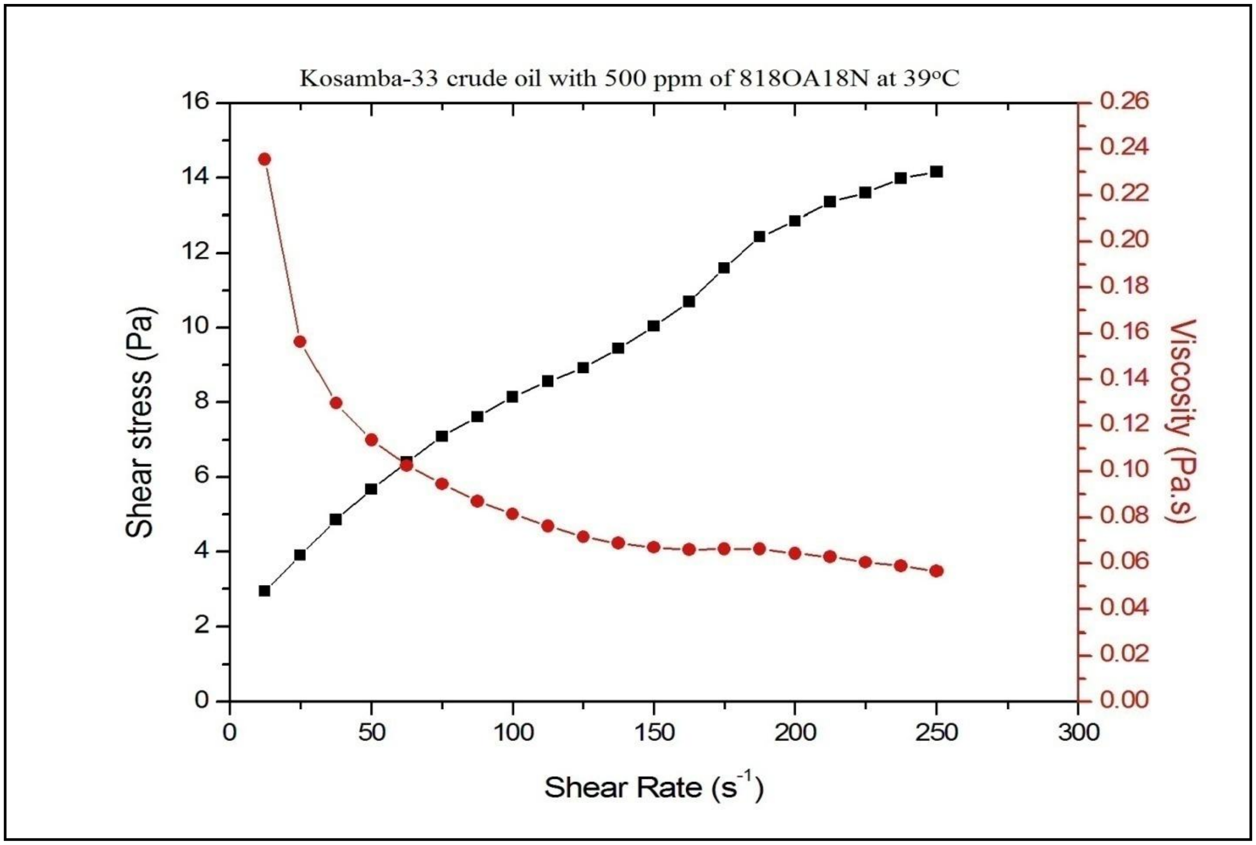

Fig 3.138 Rheogram of Kosamba-33 crude oil with 500 ppm of 8-18OA18N at 39^{o}C

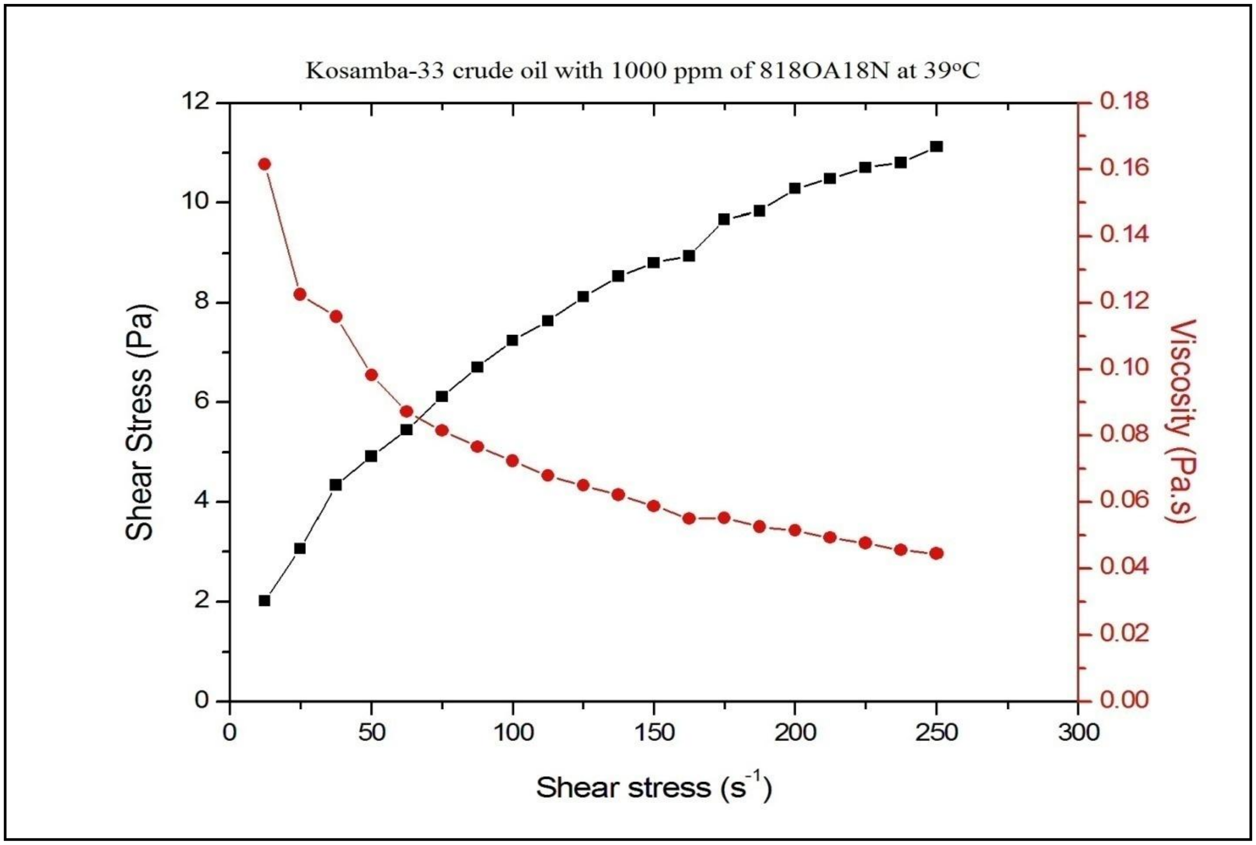

Fig 3.139 Rheogram of Kosamba-33 crude oil with 1000 ppm of 8-18OA18N at 39°C

Yield stress and viscosity values of virgin Kosamba-33 crude oil are as shown in Table 3.6. From the shown values, it is clear that at 39°C i.e. pour point of Kosamba-33 crude oil viscosity is 0.0710 Pa-s which increases to 1.40 Pa-s at 30°C. This clearly reveals that as temperature decreases, viscosity increases and vice-versa. Same is the case with yield stress also. It is seen that at 39°C, yield stress value is 2.540 Pa which increases to 60.44 Pa at 30°C. So viscosity and yield stress follows same trend in neat condition.

Rheogram of virgin and additive treated crude oil depicts zigzag nature for plot of shear stress v/s shear rate having constant slope overall. Wax crystals present in crude oil stays in the fluid state and shows Newtonian behavior at higher shear stress but as shear stress reduces, wax crystallize to impart zigzag nature to curve. Figure 3.71 to 3.73 show Rheograms of virgin Kosamba-33 crude oil at 33°C, 36°C and 39°C. Fig. 3.73 shows Newtonian behavior of crude oil at 39°C and beyond it, as shear rate v/s shear stress curve passes through origin and viscosity reduces with rise in shear rate and after shear rate 100 s^{-1} it become almost constant. The figure 3.71, 3.72 clearly shows high value of yield stress as 24.10 Pa and 11.75 Pa respectively. From such values, it can be concluded that at temperature below pour point of crude oil it shows non-

Newtonian behavior as increase in shear stress is not proportional to shear rate and curve does not pass through origin.

Above mentioned behavior can be explained as follows; at temperatures near pour point and at low shear rates the energy imparted by shear and dispersed energy in crude matrix tends to break down the wax crystals partially. Secondary bonds form among the flocculated wax structure, thus bringing partial decrease of yield stress and drop in viscosity (thinning effect)
without any tendency to flow. By increasing the shear rate, the dispersed energy is high enough to overcome yield stress and start flow, which is evident by increasing the shear stress of flow curve. At lower temperature, the dispersed energy is mostly directed to the decrease of progressive yield stress and thus less amount of energy is given to the decrease of viscosity, hence thinning effect is lowered.

On increasing the shear rate, the size of aggregates decreases and this process releases some of the continuous phase originally immobilized within the aggregates. As a result, the effective dispersed phase concentration decreases and brings decrease of viscosity. The viscosity decreases with increasing the shear rate until the aggregates are completely broken down into the basic particles. So the waxy crude oil system shows non-Newtonian characteristic. [32]

The selection of additives from each series of polymers for further rheological studies was done based on its efficiency to reduce pour point at different concentration ranging from 100 to 1000 ppm. The additive which showed best performance at all concentrations (i.e. from 100 to 1000ppm) was selected which is as shown by circles in table 3.5.

The selected additives are 8-12UA18N, 8-16UA18N, 8-10CA18N, 8-14CA18N, 8-12RA18N, 8-14RA18N, 8-10OA18N and 8-16OA18N were taken at 39°C, 36°C, 33 °C and 30°C at 500 ppm and 1000 ppm concentration and their Rheograms are shown from Figure 3.74 to Figure 3.139. From all the above additives employed, 8-16UA18N and 8-14RA18N were capable of reducing rheological parameters of viscosity and yield value to great extent as compared to virgin crude oil at 500 ppm and 1000 ppm concentration respectively.

However, the other additives 8-12UA18N, 8-10CA18N, 8-14CA18N, 8-12RA18N, 8-10OA18N and 8-16OA18N showed reverse behavior by increasing viscosity as well as yield value of Kosamba-33 crude oil to some extent.

3.2.5 Conclusion

3.2.5.1 Pour Point of Kosamba-33 crude oil

From Table 3.5 shows pour point data for Kosamba-33 crude oil, it can be concluded that additives 8-12UA18N, 8-16UA18N, 8-10CA18N, 8-14CA18N, 8-12RA18N, 8-14RA18N, 8-10OA18N and 8-16OA18N showed good efficiency as pour point depressants. Probable reason for good efficiency of these additives can be matching of carbon number of the wax present in Kosamba-33 crude oil with pendant chain. These additives successfully adsorbed and co-crystallized on wax surface inhibiting wax crystal growth. Additives having effective PPD behavior were found to have C_{13} to C_{20} pendant alkyl chain length. Also, the presence of aromatic ring made molecule more bulky which helped in improving its pour point depressing tendency. Hence, it can be concluded that the matching of carbon number, presence of aromatic ring and polar ester, nitrogen group together acted effectively to depress pour point of Kosamba-33 crude oil.

3.2.5.2 Rheological Studies

Rheogram for all additives clearly indicate that the curve of shear stress v/s shear rate is not straight line but is zigzag and have constant slope overall. Rheogram of virgin crude oil shows Newtonian characteristics of crude oil above its pour point in which shear stress v/s shear rate plot passes through origin and viscosity is reducing with increase in shear rate and after certain shear rate it is constant. Non-Newtonian behavior is seen when temperature is decreased and it requires yield stress to start its flow.

The result obtained clearly indicates that additives like 8-16UA18N, 8-14RA18N brought reasonably good reduction in viscosity of Kosamba-33 crude oil. As viscosity of crude oil decreased, the yield stress also decreased. 8-16UA18N at 500 ppm reduced viscosity to 0.0410, 0.0979, 0.1260 and 0.2010 Pa-s at 39^{o}C, 36^{o}C, 33^{o}C and 30^{o}C respectively. At 1000 ppm, the viscosity values obtained are 0.0499, 0.1199, 0.1885 and 0.3768 Pa-s at 39^{o}C, 36^{o}C, 33^{o}C and 30^{o}C respectively. The yield stress values observed in range of 1.995 to 10.65 Pa at 500 ppm and 2.630 to 8.50 Pa at 1000 ppm.

Now for 8-14RA18N at 500 ppm, the viscosity values reported are 0.0305, 0.2136, 0.3992 and 0.8338 Pa-s at 39^{o}C, 36^{o}C, 33^{o}C and 30^{o}C respectively. When concentration was increased to 1000 ppm, the viscosity values noted were 0.0356, 0.2186, 0.4323 & 0.8963 Pa-s at 39^{o}C, 36^{o}C, 33^{o}C and 30^{o}C respectively. The yield stress values observed in range of 0.6907 to 47.72 Pa at 500 ppm and 1.027 to 21.86 Pa at 1000 ppm.

The rheological parameters of viscosity and yield stress for above additives are clearly lower as compared to that of virgin crude oil. Hence, these additives can be successfully employed for Kosamba-33 crude oil. The possible mechanism for decrease in viscosity is that additive molecules reduce the cohesive forces between resin and asphaltene molecules by reducing the formation of hydrogen bond. The mutual overlapping of condensed ring of asphaltene and resins is inhibited. The additive molecule itself combines with asphaltene and resin molecules via H-bonds and reduced the interaction level of asphaltene and resins. Hence, viscosity decreases and flowing state of oil is retained.

Now, the remaining additives coded 8-12UA18N, 8-10CA18N, 8-14CA18N, 8-12RA18N, 8-10OA18N and 8-16OA18N showed reverse results of increasing viscosity of Kosamaba-33 crude oil. It can be observed from Table 3.6 with increase in concentration of additive viscosity and yield stress increases. Flow behavior is affected. Hence these additives are not suitable for Kosamba-33 crude oil.

Rise in viscosity can be attributed to reduction in solubility of additive in crude oil at decreased temperature. Hence, morphology of wax crystals remains unaffected and precipitation of additive takes place. Due to longer pendant chains, polymers interlock like zipper making immovable structures. Sliding of polymer molecules does not take place leading to rise in viscosity and yield stress.

CHAPTER-3 (III)

EVALUATION OF POLYMERIC FLOW IMPROVERS OR POUR POINT DEPRESSANTS ON BOMBAY HIGH (MUMBAI, MAHARASHTRA, INDIA) CRUDE OIL

3.3.1 Pour Point Determination

The pour point determination was done by the standard method ASTM D-97/IP-15 as described in section-3.1.2 (Chapter-3, Part-1). The pour point results of virgin Bombay High crude oil and additive doped crude oil is as shown in Table 3.8.

3.3.2 Rheological Studies

The rheological studies were performed by the method described in section 3.1.3 (Chapter-3, Part-1). The rheological data is as shown in Table 3.9.

3.3.3 Results and Discussions

3.3.3.1 Evaluation of Polymeric Additives as Pour Point Depressants

Table 3.7 Pour Point Data of Neat and Treated Bombay High Crude oil

Kosamba-47	Temperature (°C)							
Sample Code	Virgin Crude	100 ppm	200 ppm	400 ppm	500 ppm	1000 ppm	Maximum depression in pour point	Extent of pour point depression
8-6UA18N	22	5	10	7	7	7	5	17
8-10UA18N	22	19	19	19	19	19	19	3
8-12UA18N	22	19	19	19	19	19	19	3
8-14UA18N	22	19	13	19	19	19	13	9
8-16UA18N	22	19	19	19	19	19	19	3
8-18UA18N	22	19	19	19	19	19	19	3
8-22UA18N	22	19	19	19	19	19	19	3
8-6CA18N	22	16	19	19	19	19	16	6
8-10CA18N	22	19	19	19	19	19	19	3
8-12CA18N	22	19	19	19	19	19	19	3
8-14CA18N	22	19	19	16	16	19	16	6
8-16CA18N	22	16	19	16	16	19	16	6
8-18CA18N	22	19	19	19	19	19	19	3
8-22CA18N	22	19	19	19	19	16	16	6
8-6RA18N	22	16	19	19	19	19	16	6
8-10RA18N	22	19	19	19	19	19	19	3
8-12RA18N	22	19	19	19	19	19	19	3
8-14RA18N	22	19	19	19	16	16	16	6
8-16RA18N	22	19	19	16	16	16	16	6
8-18RA18N	22	19	19	19	19	16	16	6
8-22RA18N	22	19	19	19	19	19	19	2
8-6OA18N	22	19	19	19	19	19	19	3
8-10OA18N	22	19	19	19	19	19	19	3
8-12OA18N	22	19	19	19	19	19	19	3
8-14OA18N	22	19	19	19	16	16	16	6
8-16OA18N	22	19	19	16	16	16	16	6
8-18OA18N	22	19	19	19	19	19	19	3
8-22OA18N	22	19	19	19	19	19	19	3

3.3.3.2 Evaluation of Polymeric Additives on Rheological Parameters

Table 3.8 Effect of Additive Concentration on Rheological Parameters of Bombay High Crude Oil

Code	Additive Concentration (ppm)	Temperature (°C)	Viscosity (Pa-s)	Yield Stress (Pa)
Blank	0	22	0.1249	05.00
		19	0.2012	10.43
		16	0.2472	11.03
		13	0.2765	12.15
		10	0.3041	13.36
8-6UA18N	500	22	0.1090	4.11
		19	0.1749	8.25
		16	0.2124	9.96
		13	0.1802	9.05
		10	0.1666	7.63
8-6UA18N	1000	22	0.3664	25.73
		19	0.2148	13.56
		16	0.2248	12.42
		13	0.2311	12.03
		10	0.2315	11.14
8-14UA18N	500	22	0.1762	14.78
		19	0.1362	7.02
		16	0.1557	7.29
		13	0.1610	7.43
		10	0.1594	7.11
8-14UA18N	1000	22	0.2563	18.55
		19	0.1473	9.31
		16	0.1230	7.52
		13	0.0474	2.8-6
		10	0.0441	2.37
8-14CA18N	500	22	0.0208	0.43
		19	0.0263	1.00
		16	0.0274	1.23
		13	0.0264	1.18
		10	0.0231	1.05
8-14CA18N	1000	22	0.0198	0.45
		19	0.0266	0.90
		16	0.0333	1.56
		13	0.0305	1.45
		10	0.0270	1.42
8-16CA18N	500	22	0.0095	0.19
		19	0.0111	0.37
		16	0.0113	0.54
		13	0.0101	0.44
		10	0.0096	0.42

Code	Additive Concentration (ppm)	Temperature (^{o}C)	Viscosity (Pa-s)	Yield Stress (Pa)
8-16CA18N	1000	22	0.0026	0.045
		19	0.0027	0.056
		16	0.0027	0.056
		13	0.0025	0.079
		10	0.0023	0.045
8-14RA18N	500	22	0.2981	23.34
		19	0.2336	12.34
		16	0.2619	12.35
		13	0.2872	13.11
		10	0.2937	12.35
8-14RA18N	1000	22	0.1545	09.55
		19	0.1714	9.15
		16	0.1800	9.84
		13	0.1720	7.34
		10	0.1734	7.78
8-16RA18N	500	22	0.0395	1.95
		19	0.0556	2.76
		16	0.0758	3.64
		13	0.1139	5.76
		10	0.1538	8.52
8-16RA18N	1000	22	0.1030	6.78
		19	0.1082	5.06
		16	0.1533	7.72
		13	0.0796	11.04
		10	0.0944	12.09
8-14OA18N	500	22	0.2176	11.86
		19	0.3085	16.06
		16	0.3863	19.09
		13	0.9125	73.16
		10	0.4557	25.73
8-14OA18N	1000	22	0.0018	0.047
		19	0.0015	0.027
		16	0.0016	0.036
		13	0.0014	0.037
		10	0.0013	0.032
8-16OA18N	500	22	0.0056	0.146
		19	0.0065	0.232
		16	0.0074	0.305
		13	0.0078	0.314
		10	0.0086	0.411
8-16OA18N	1000	22	0.0266	0.937
		19	0.0336	1.57
		16	0.0371	1.78
		13	0.0386	1.76
		10	0.0376	1.61

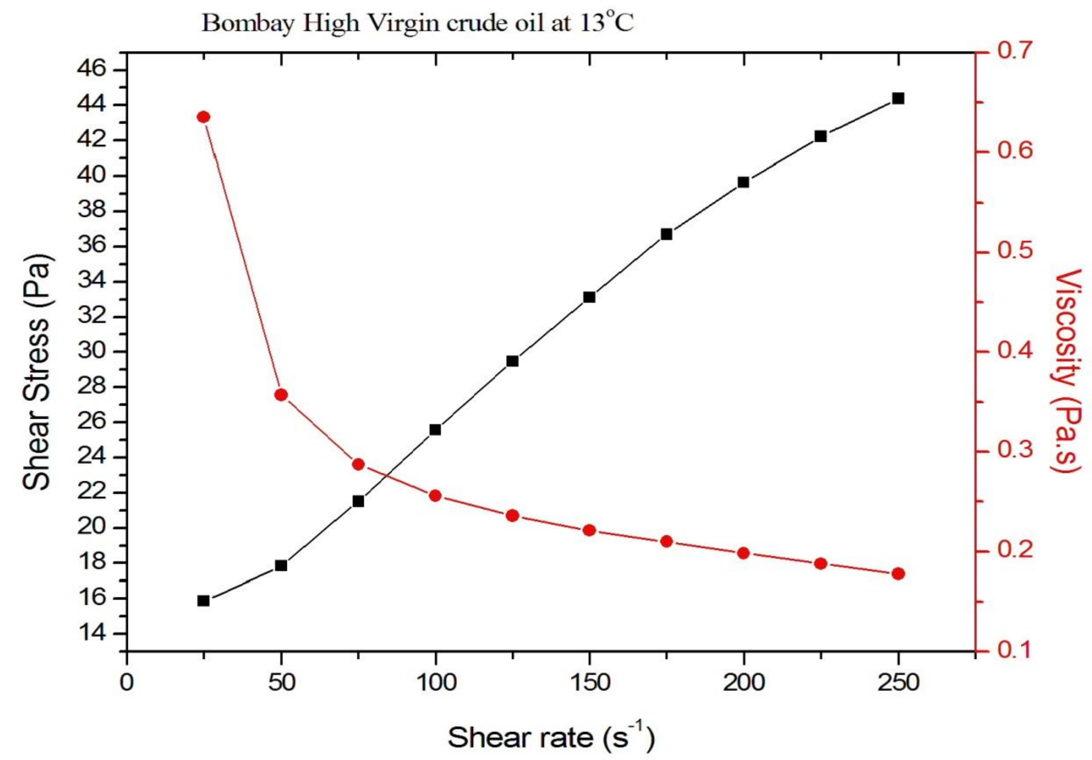

Fig. 3.140 Rheogram of Bombay High Virgin Crude oil at 13^{o}C

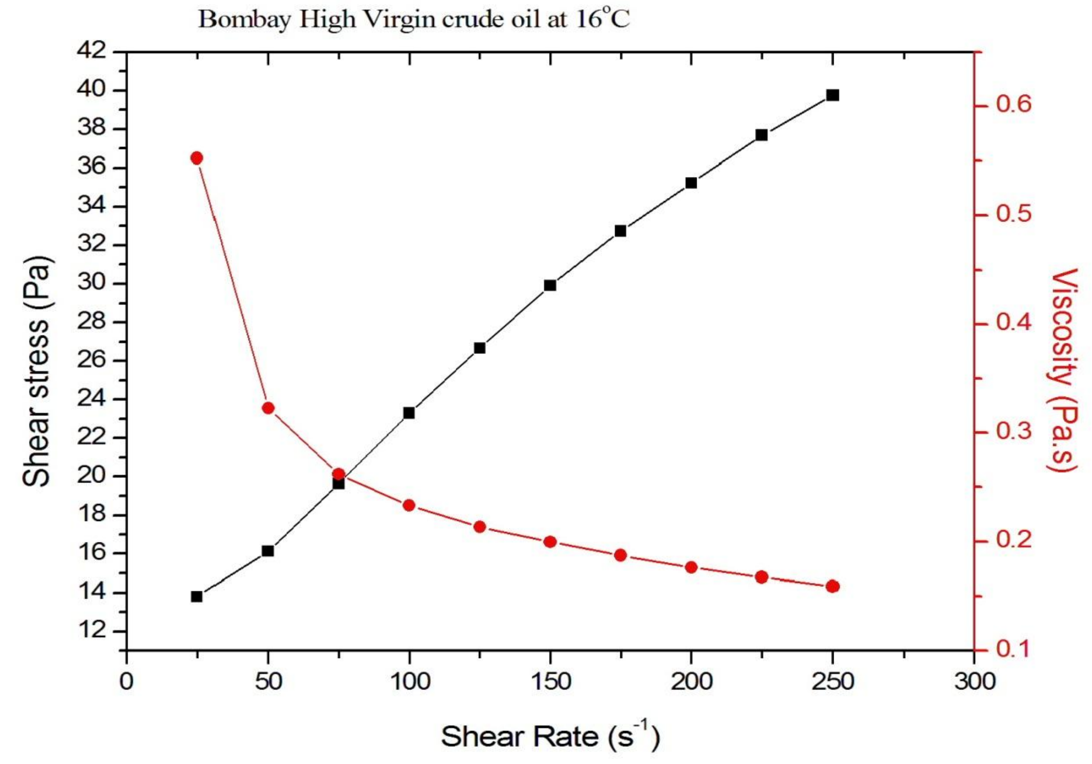

Fig. 3.141 Rheogram of Bombay High Virgin Crude oil at 16^{o}C

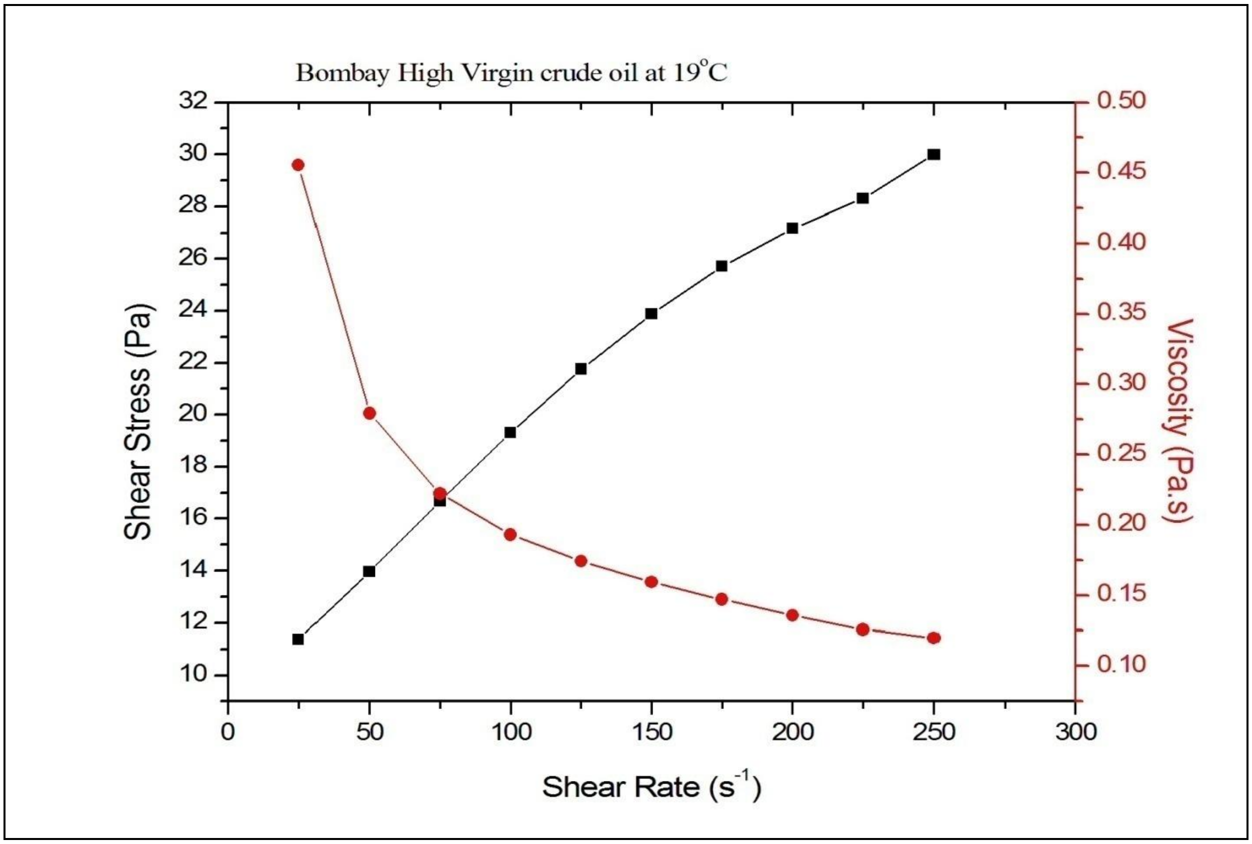

Fig. 3.142 Rheogram of Bombay High Virgin Crude oil at 19^{o}C

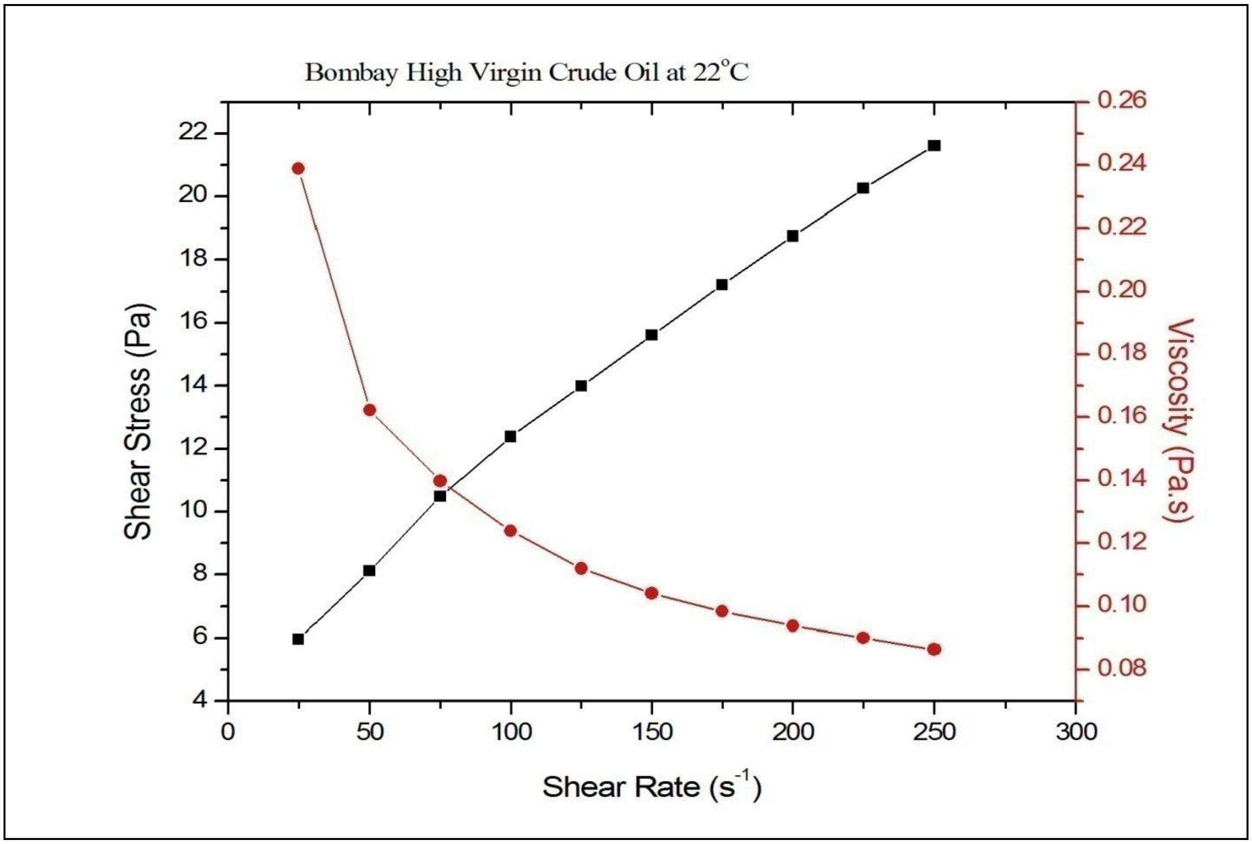

Fig. 3.143 Rheogram of Bombay High Virgin Crude oil at 22^{o}C

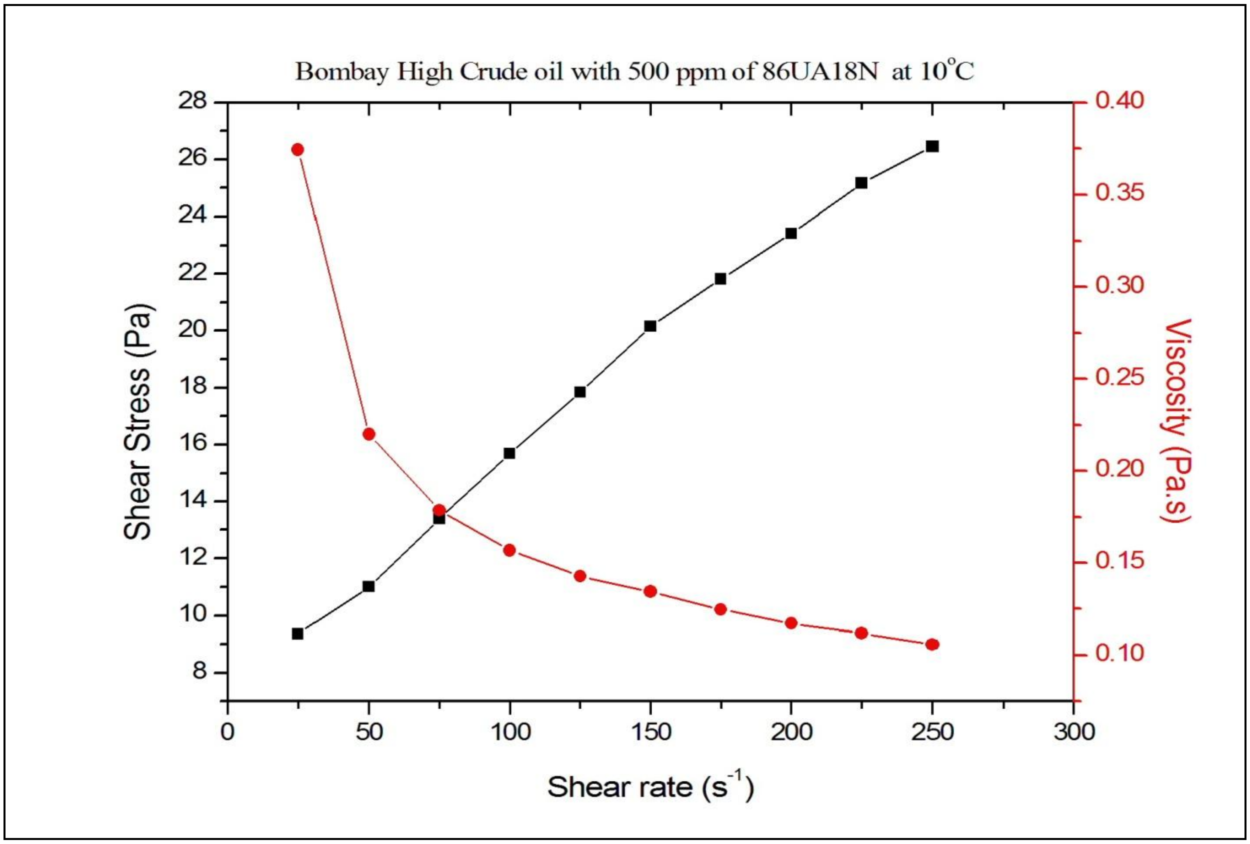

Fig. 3.144 Rheogram of Bombay High Crude oil with 500 ppm of 8-6UA18N at 10°C

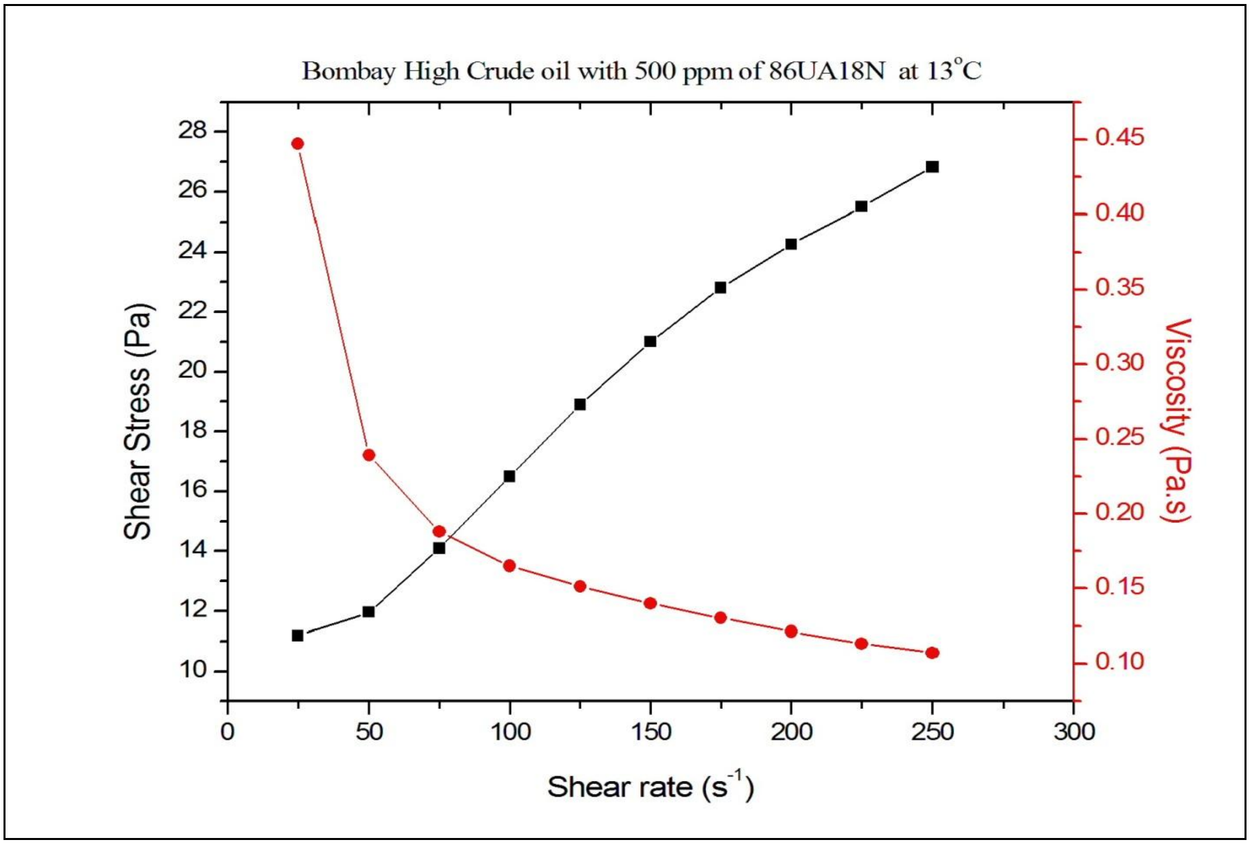

Fig. 3.145 Rheogram of Bombay High Crude oil with 500 ppm of 8-6UA18N at 13°C

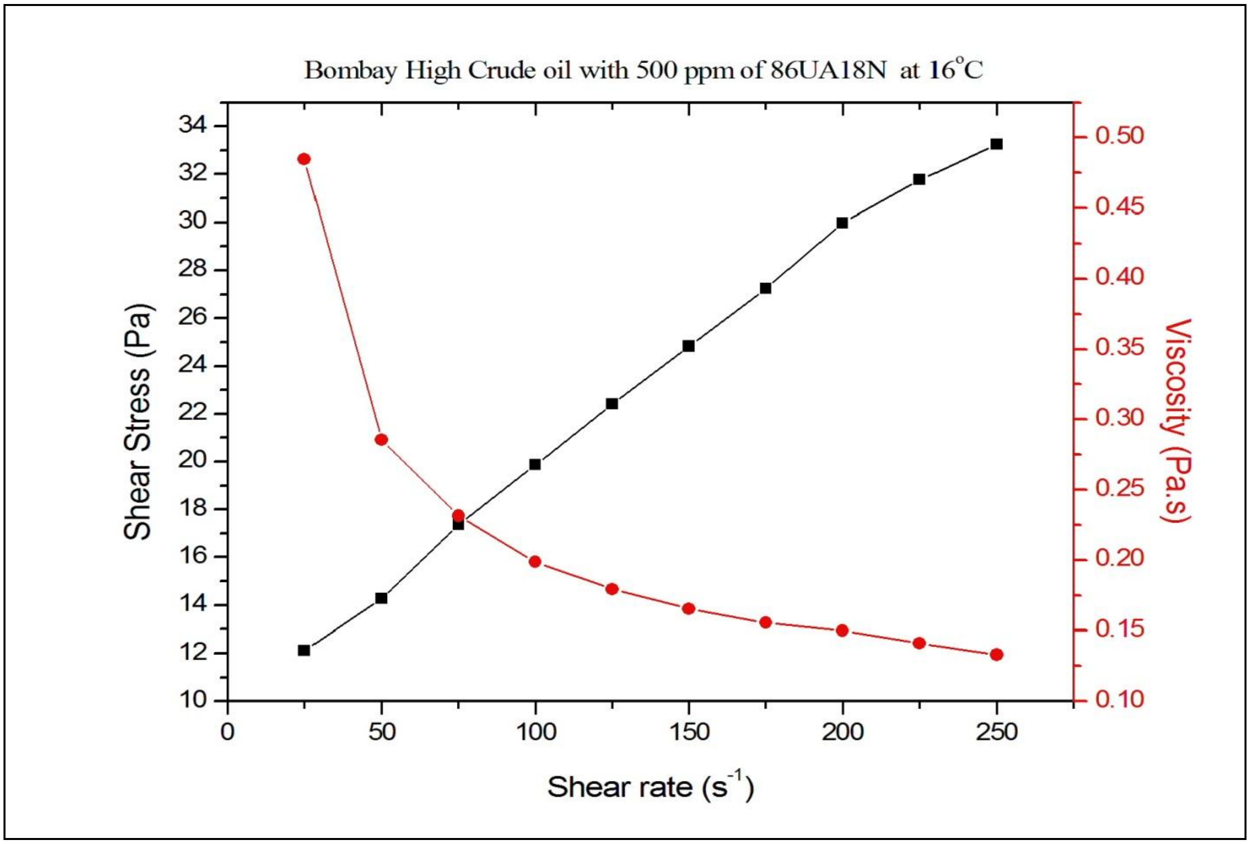

Fig. 3.146 Rheogram of Bombay High Crude oil with 500 ppm of 8-6UA18N at 16°C

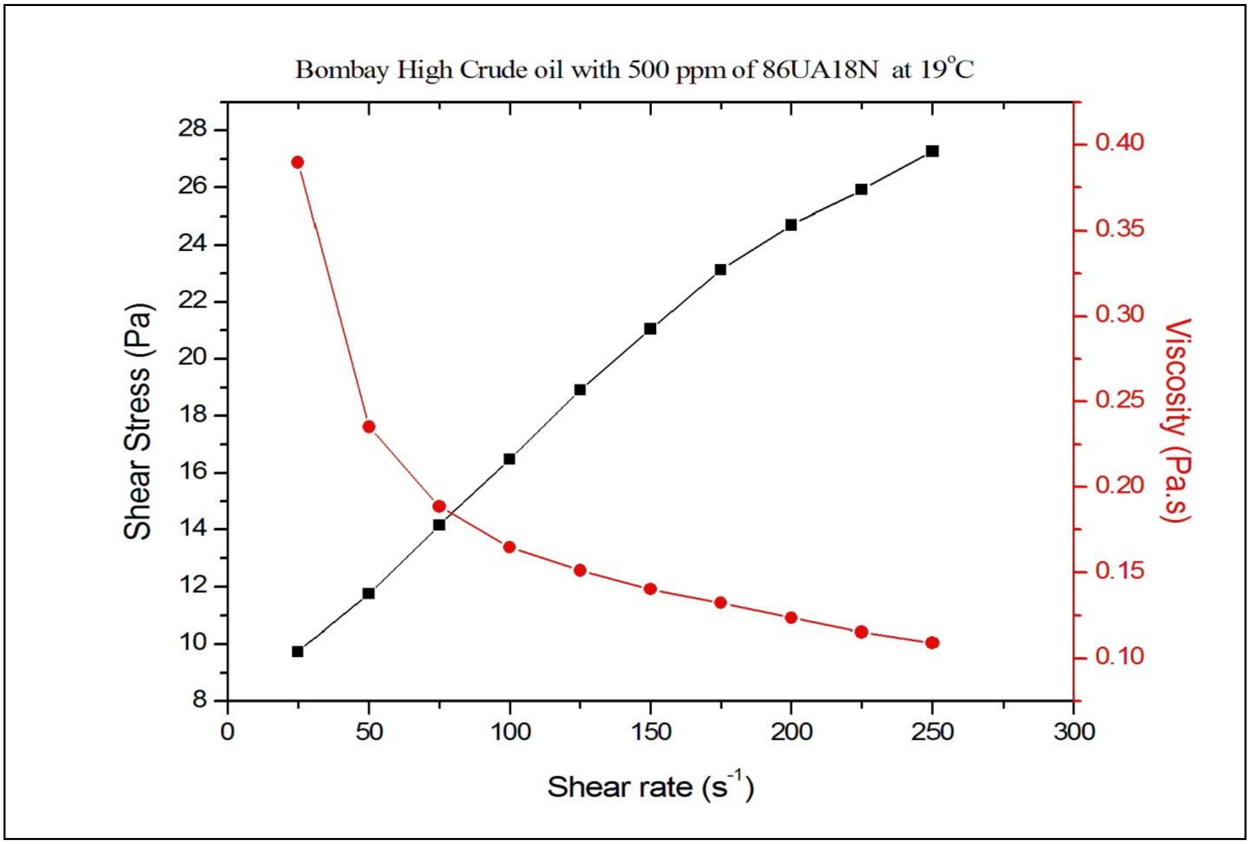

Fig. 3.147 Rheogram of Bombay High Crude oil with 500 ppm of 8-6UA18N at 19°C

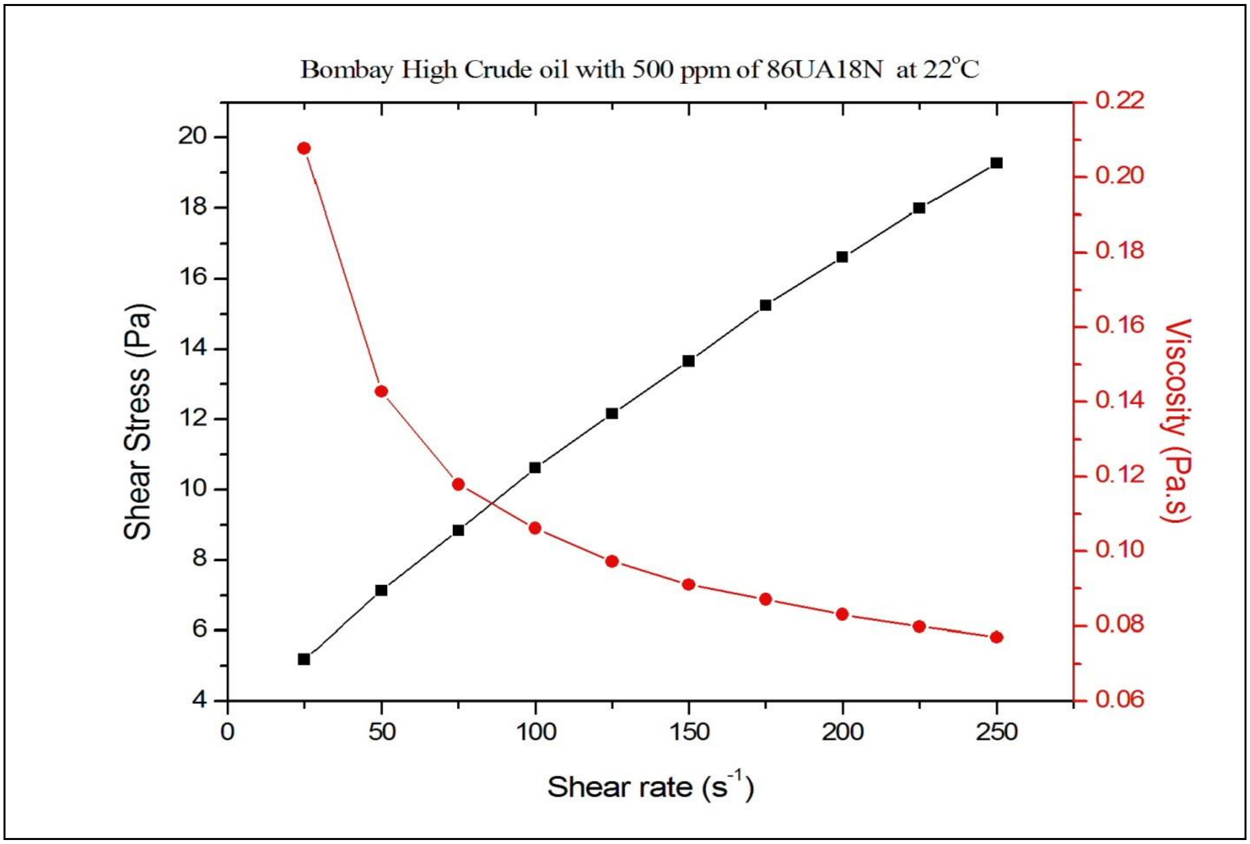

Fig. 3.148 Rheogram of Bombay High Crude oil with 500 ppm of 8-6UA18N at 22°C

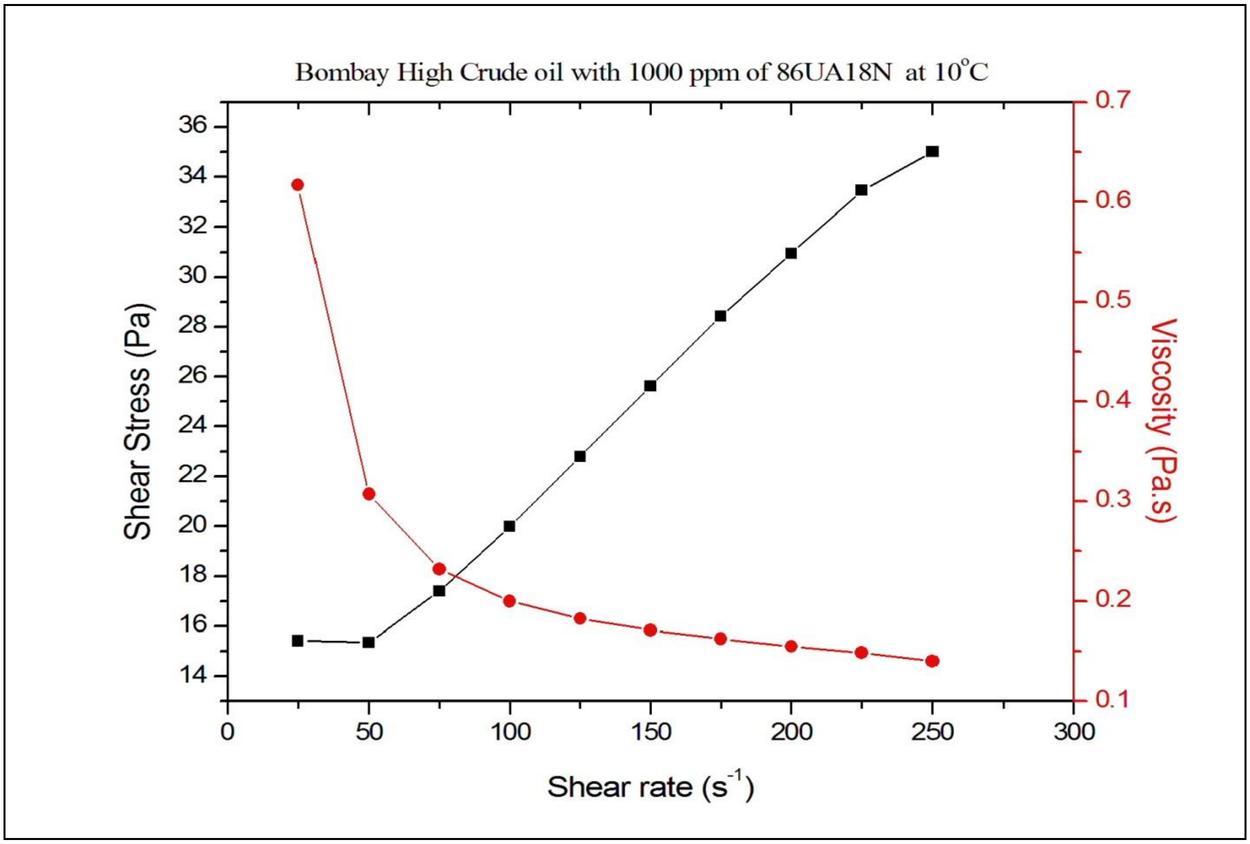

Fig. 3.149 Rheogram of Bombay High Crude oil with 1000 ppm of 8-6UA18N at 10°C

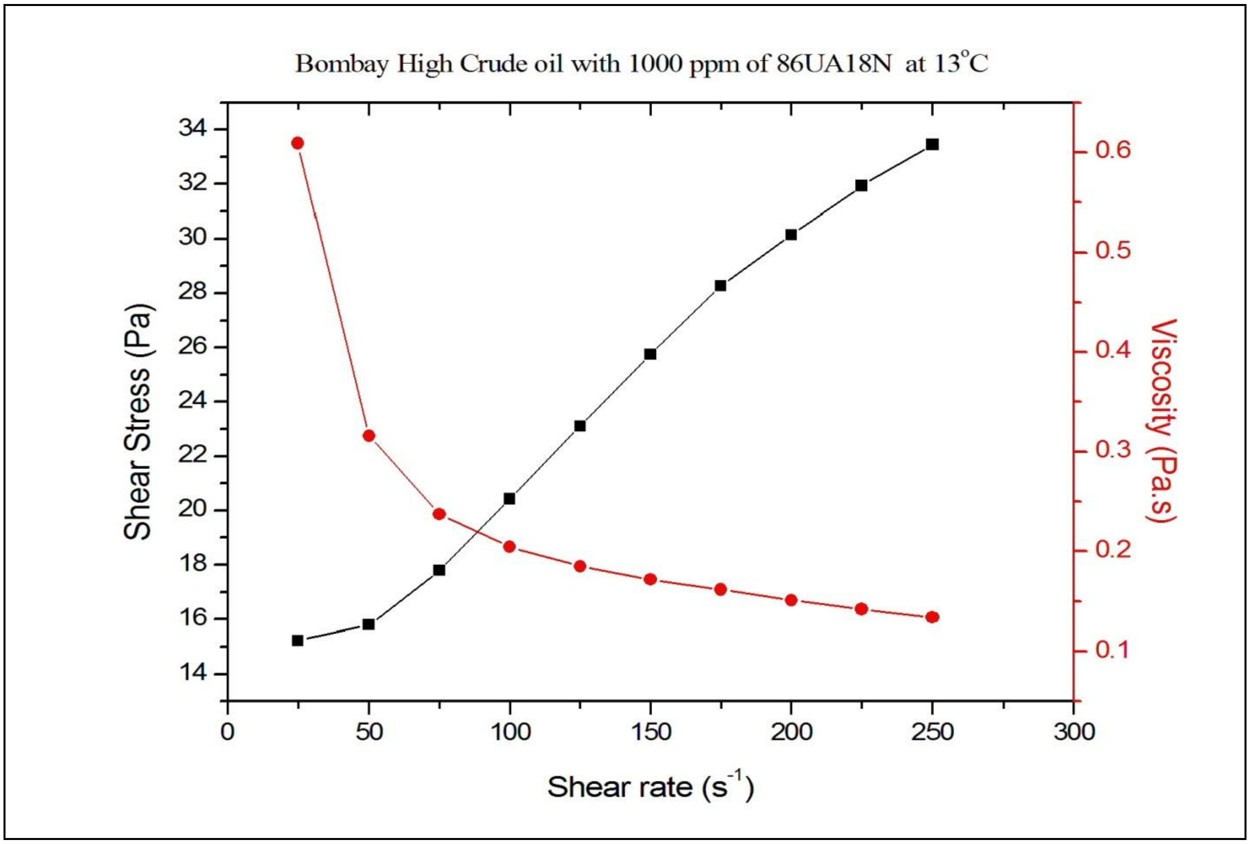

Fig. 3.150 Rheogram of Bombay High Crude oil with 1000 ppm of 8-6UA18N at 13°C

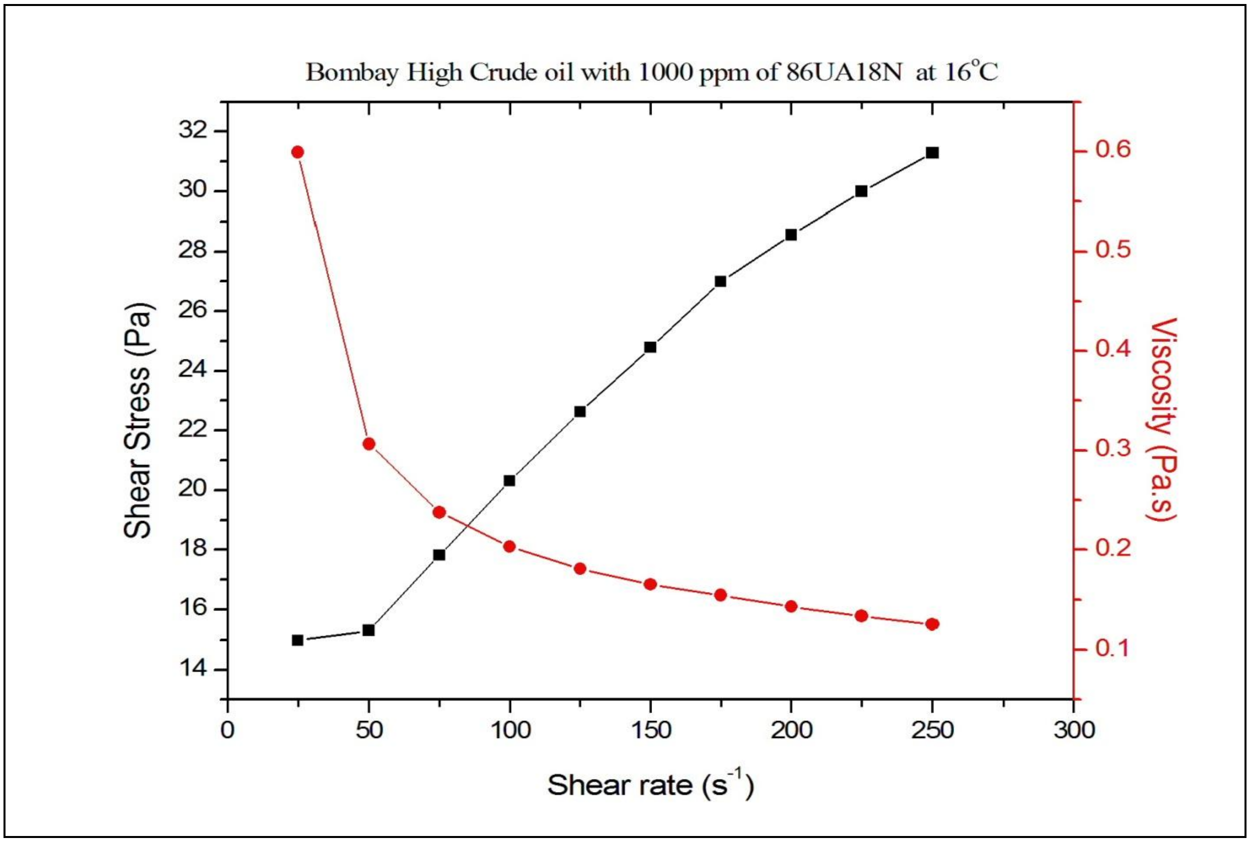

Fig. 3.151 Rheogram of Bombay High Crude oil with 1000 ppm of 8-6UA18N at 16°C

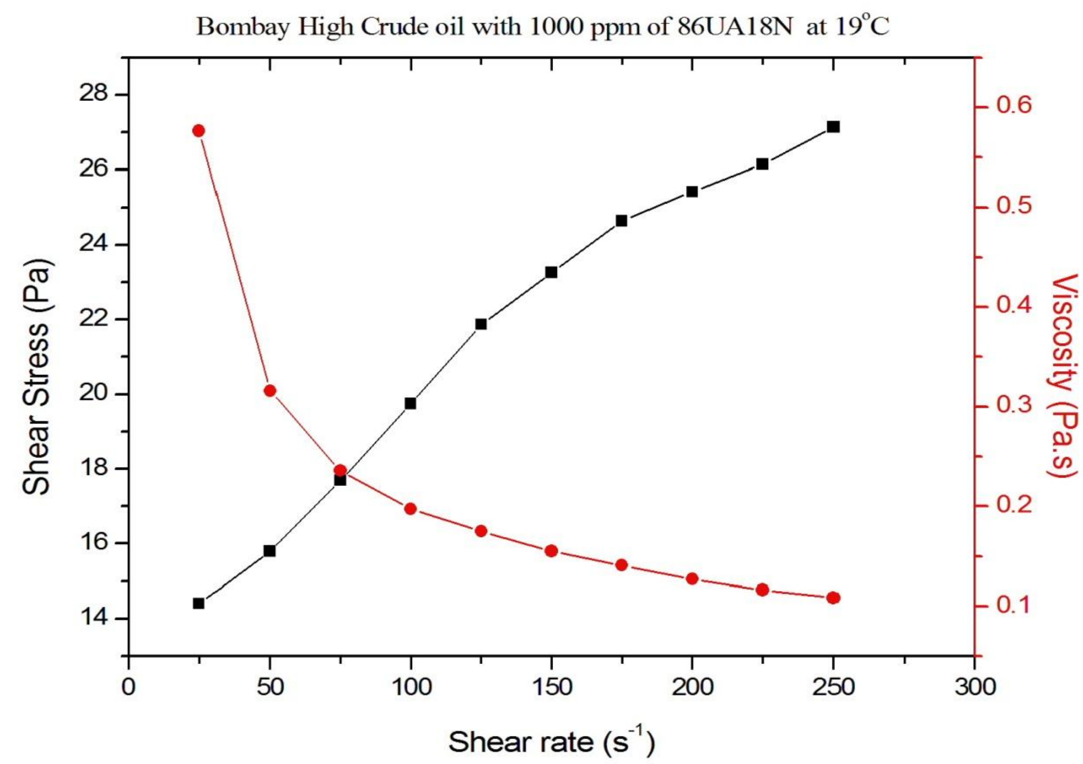

Fig. 3.152 Rheogram of Bombay High Crude oil with 1000 ppm of 8-6UA18N at 19°C

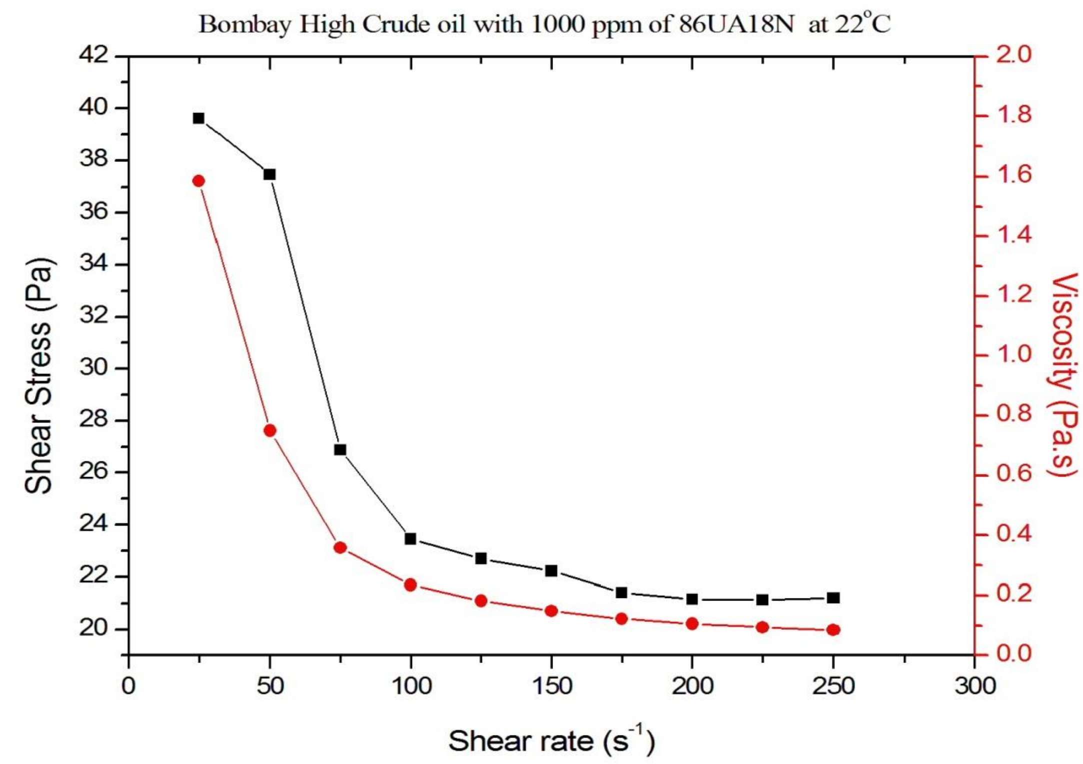

Fig. 3.153 Rheogram of Bombay High Crude oil with 1000 ppm of 8-6UA18N at 22°C

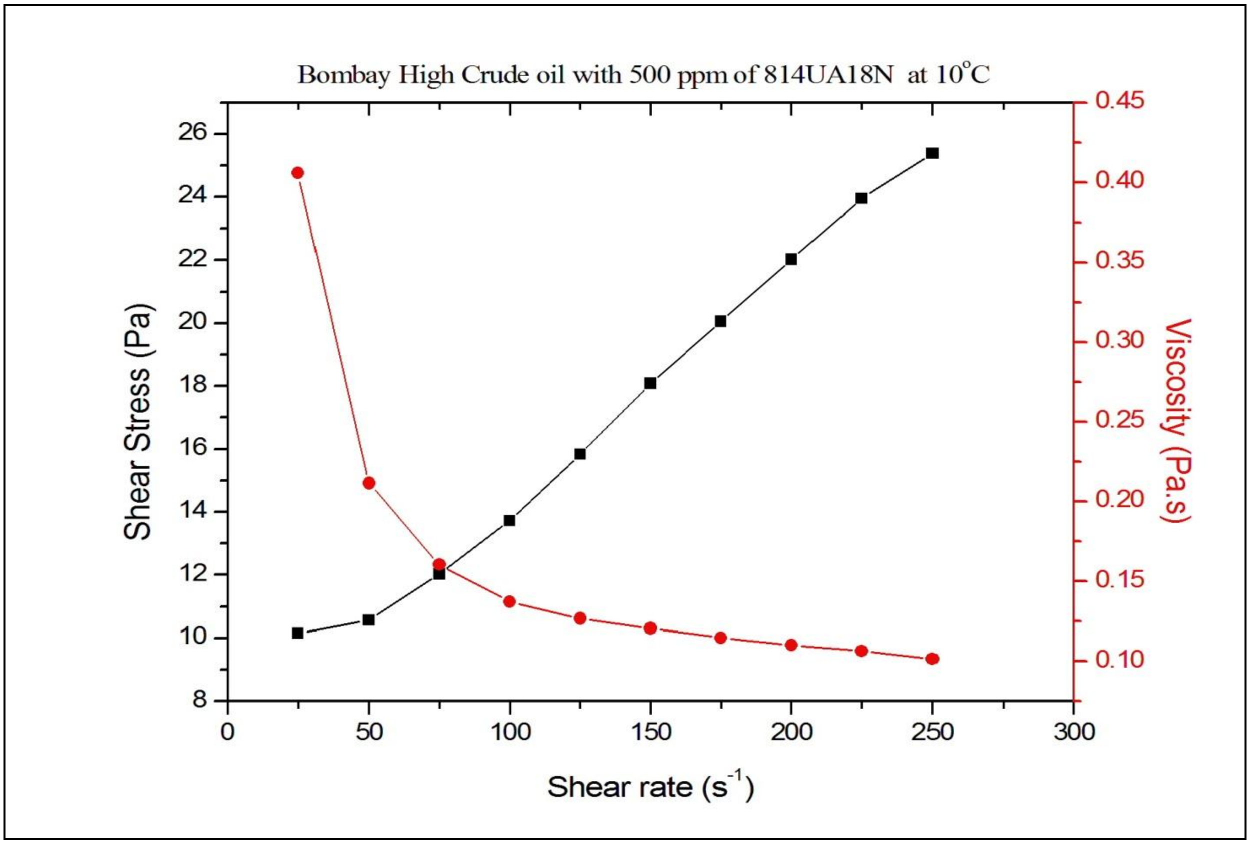

Fig. 3.154 Rheogram of Bombay High Crude oil with 500 ppm of 8-14UA18N at 10°C

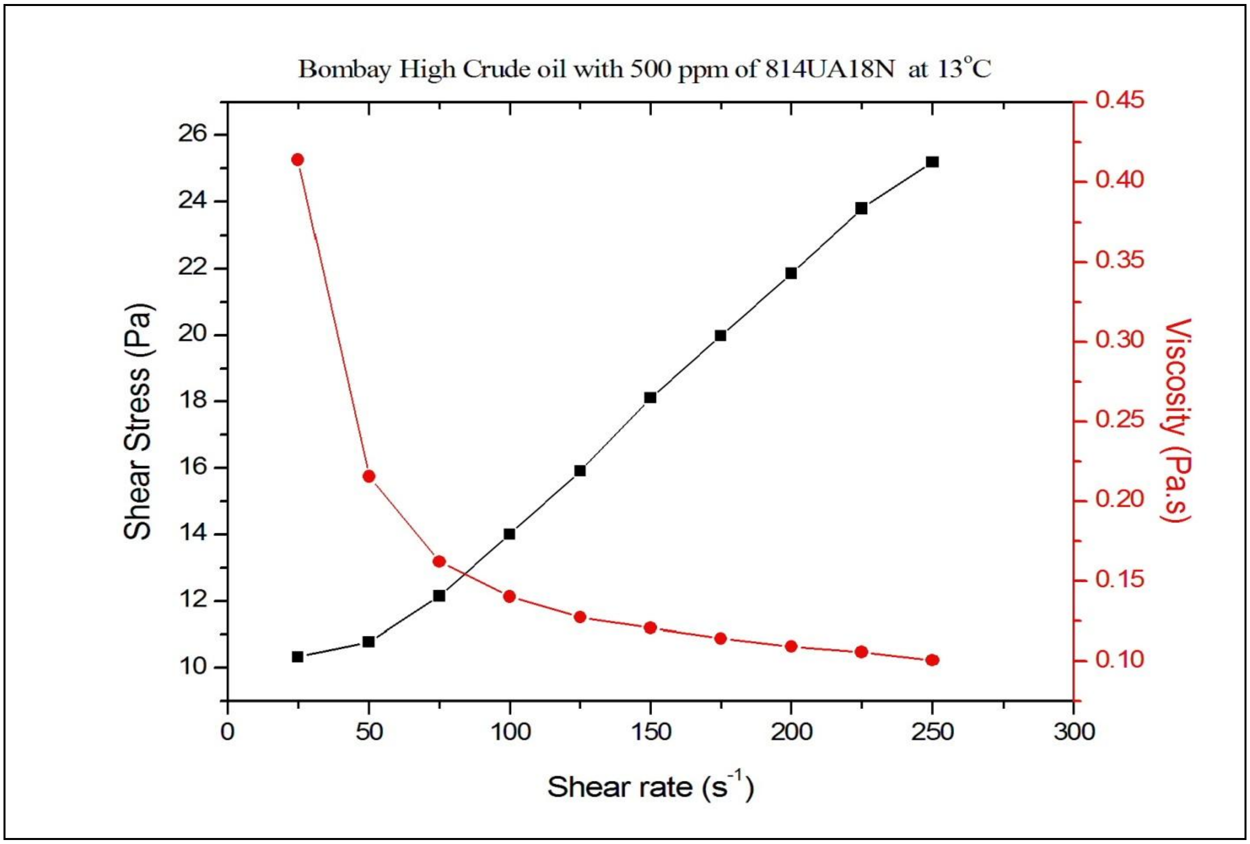

Fig. 3.155 Rheogram of Bombay High Crude oil with 500 ppm of 8-14UA18N at 13°C

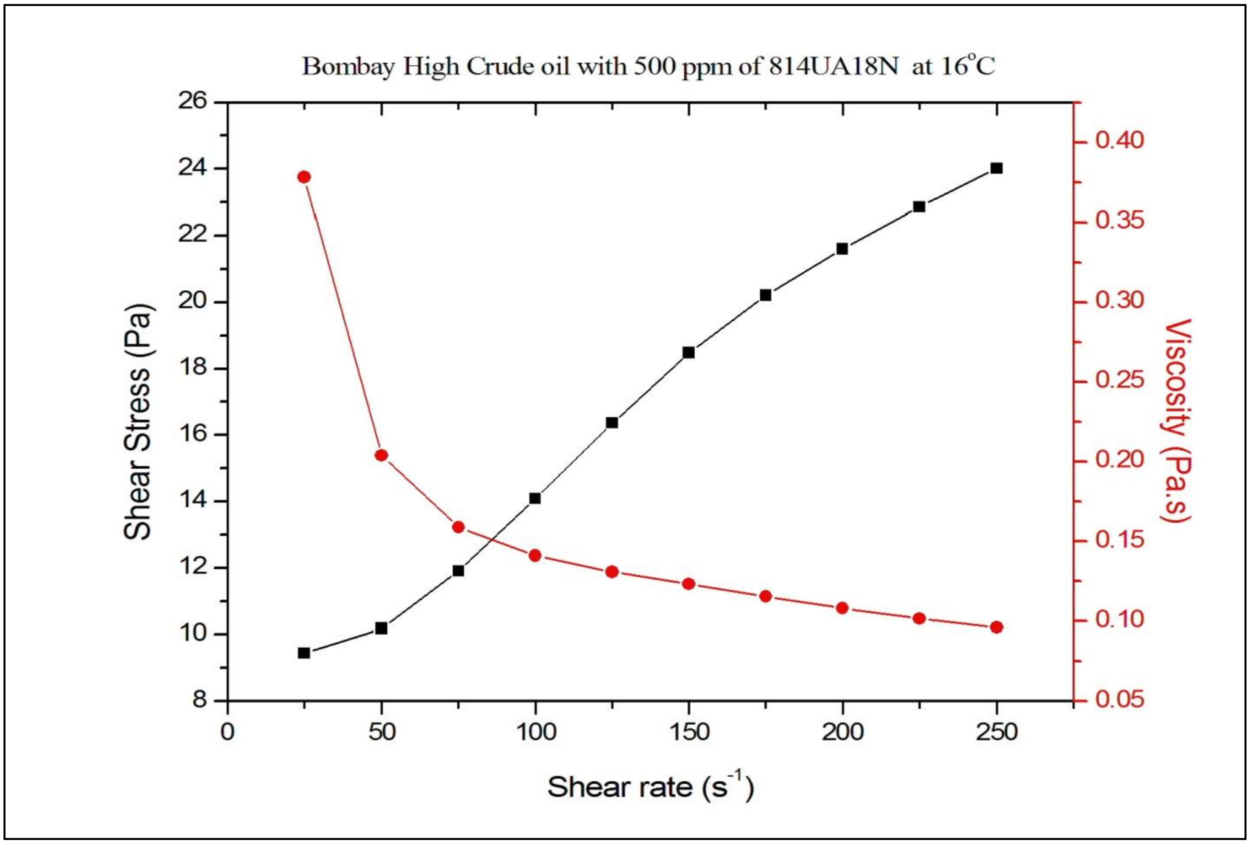

Fig. 3.156 Rheogram of Bombay High Crude oil with 500 ppm of 8-14UA18N at 16°C

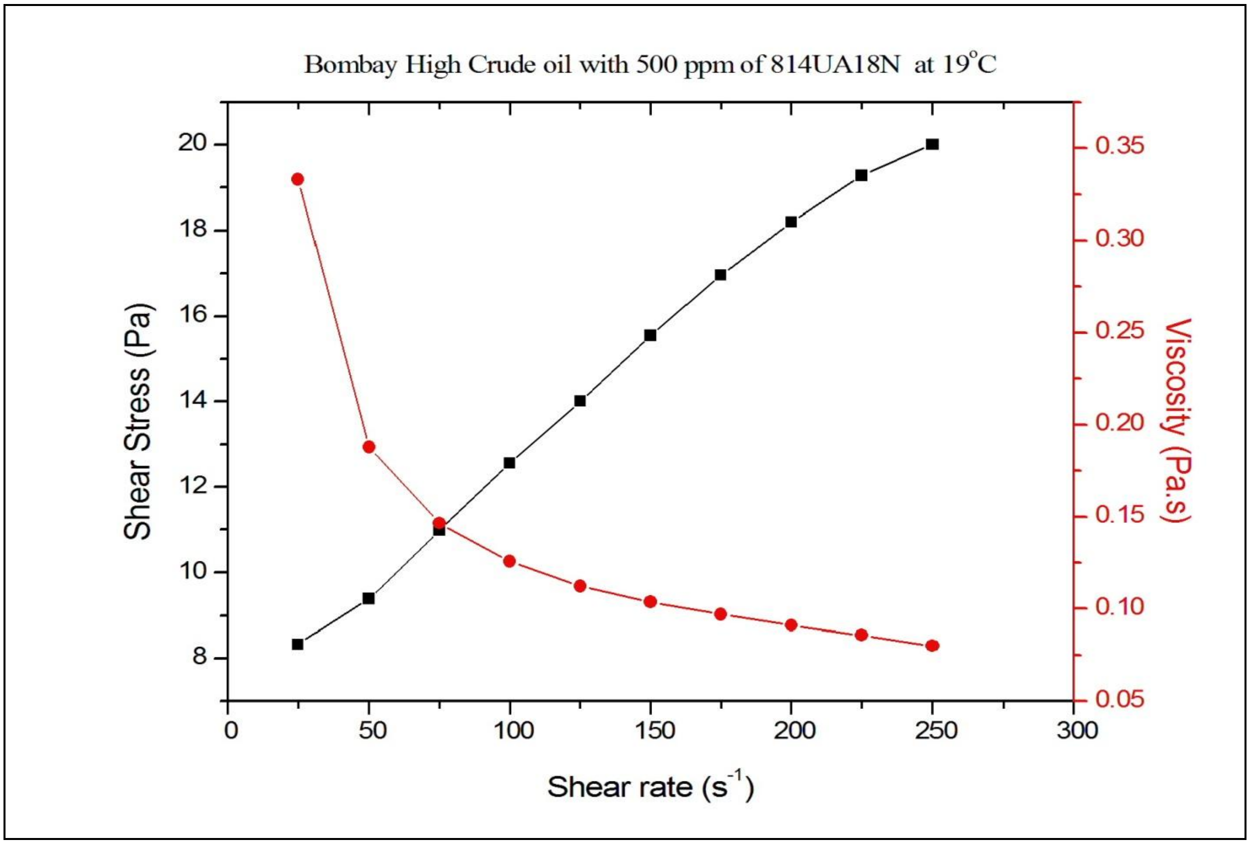

Fig. 3.157 Rheogram of Bombay High Crude oil with 500 ppm of 8-14UA18N at 19°C

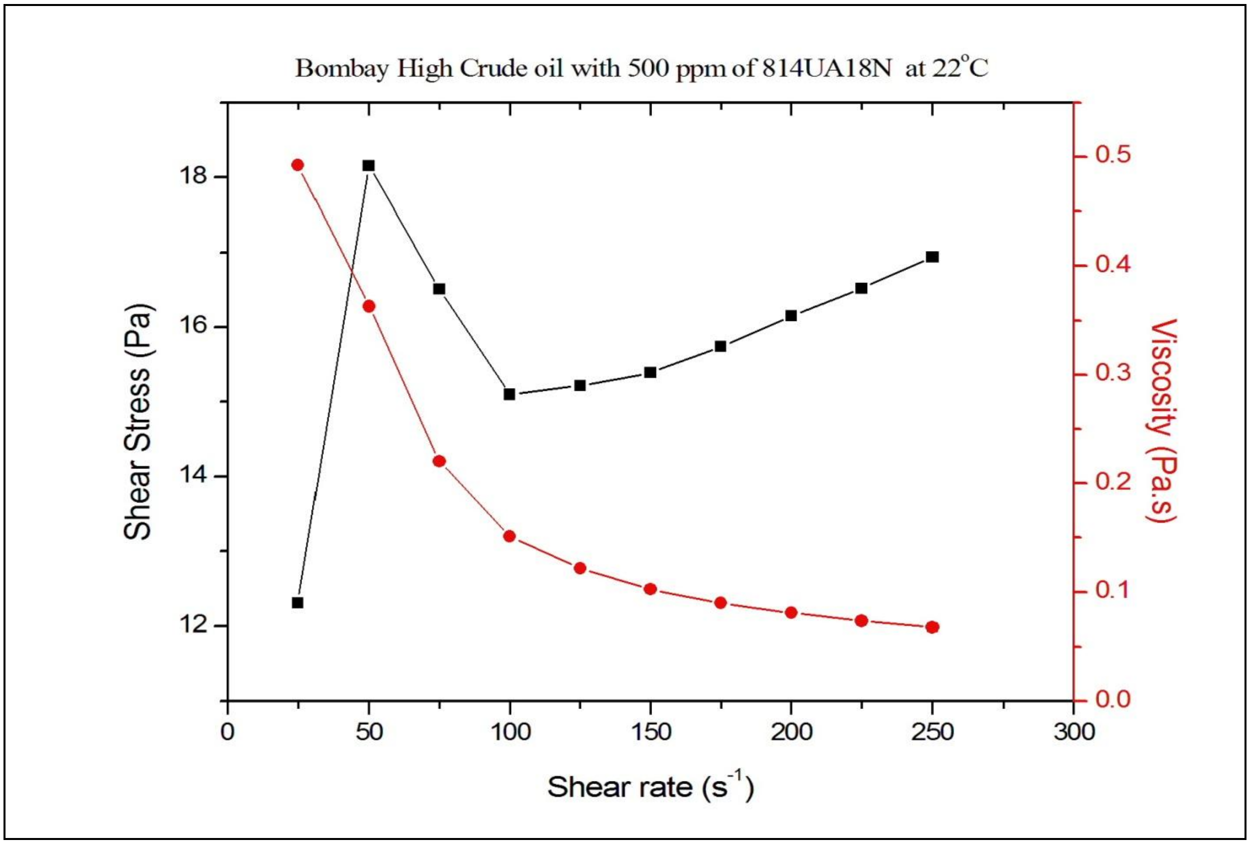

Fig. 3.158 Rheogram of Bombay High Crude oil with 500 ppm of 8-14UA18N at 22°C

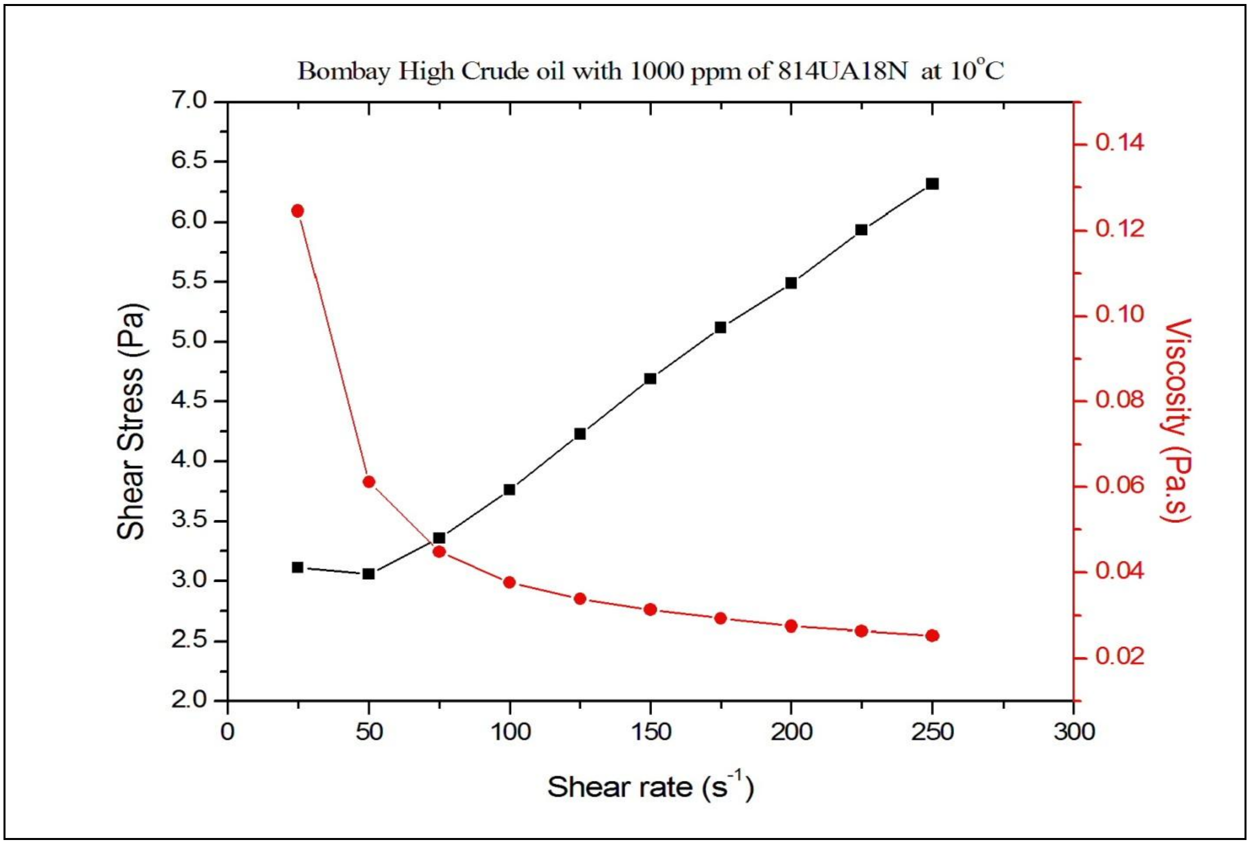

Fig. 3.159 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14UA18N at 10°C

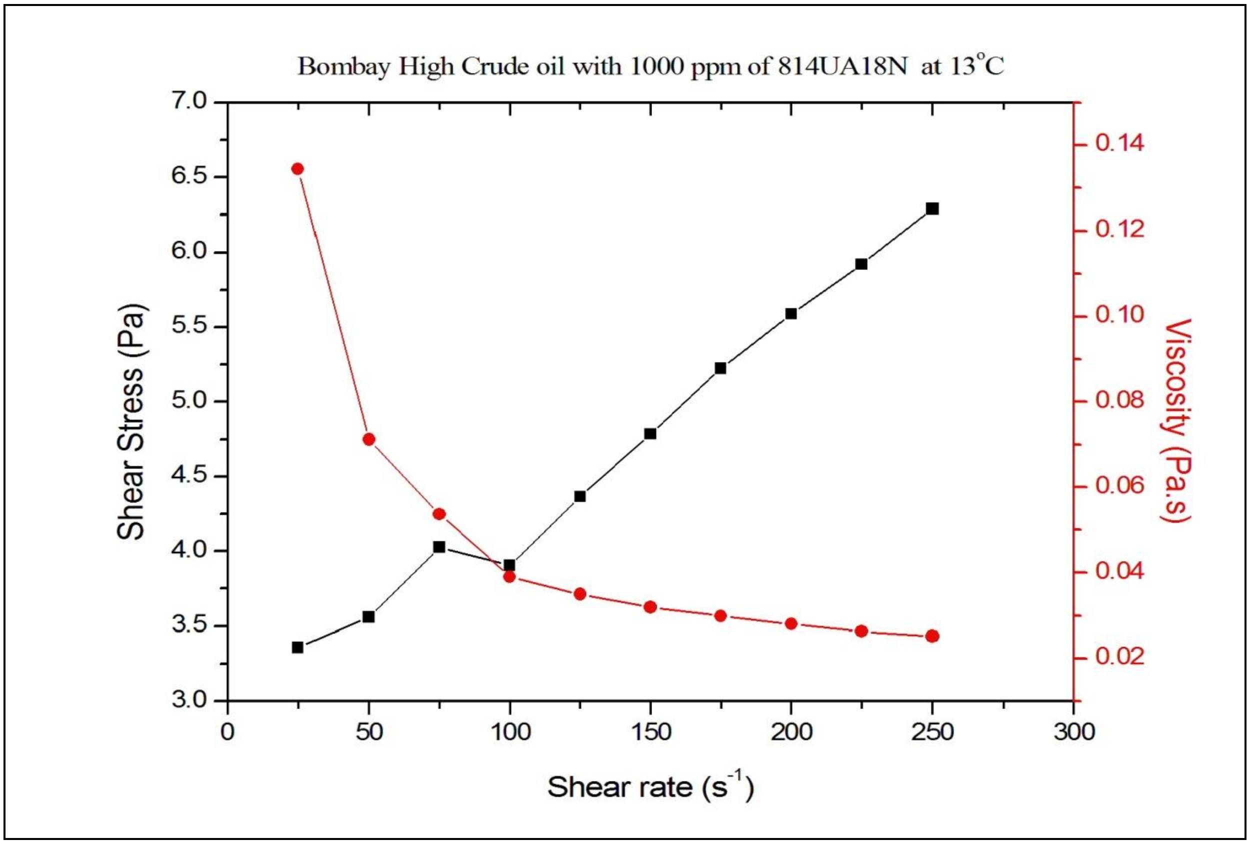

Fig. 3.160 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14UA18N at 13°C

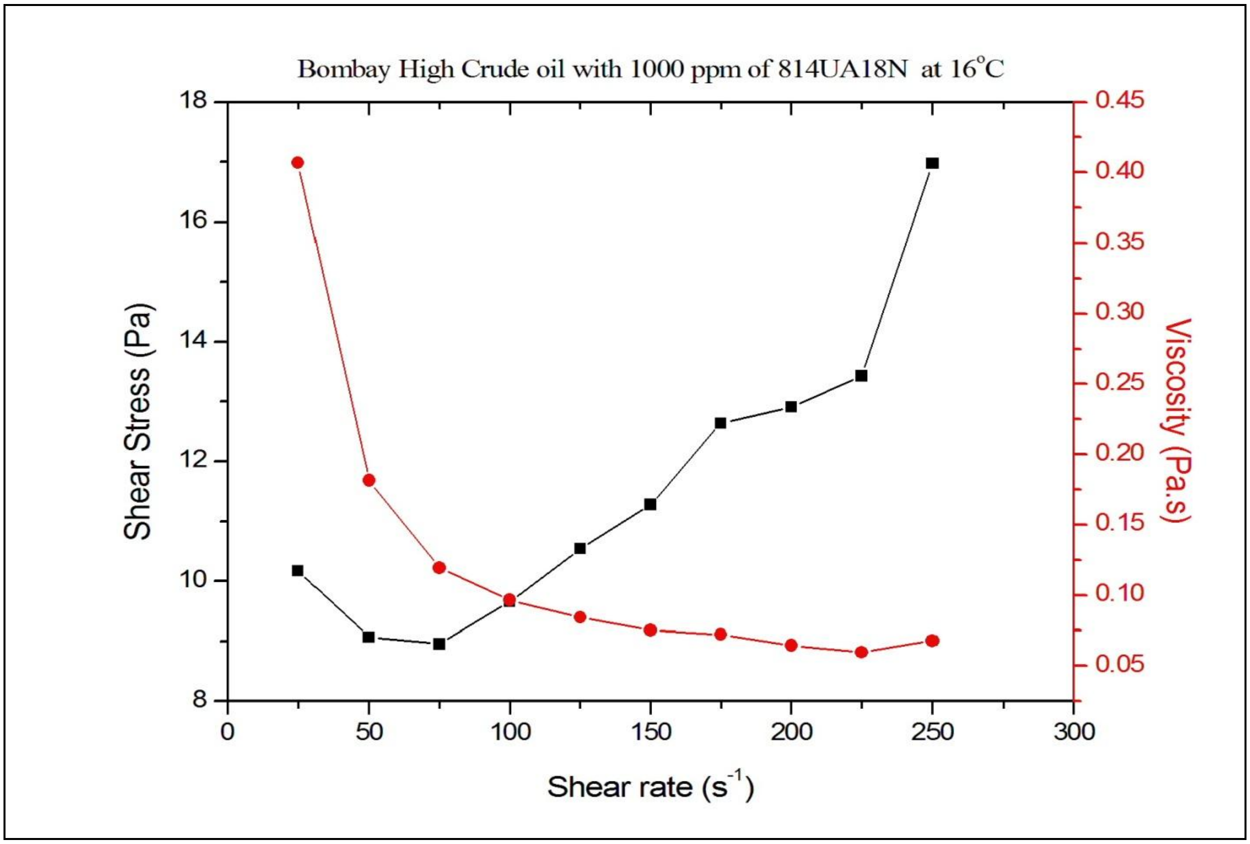

Fig. 3.161 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14UA18N at 16°C

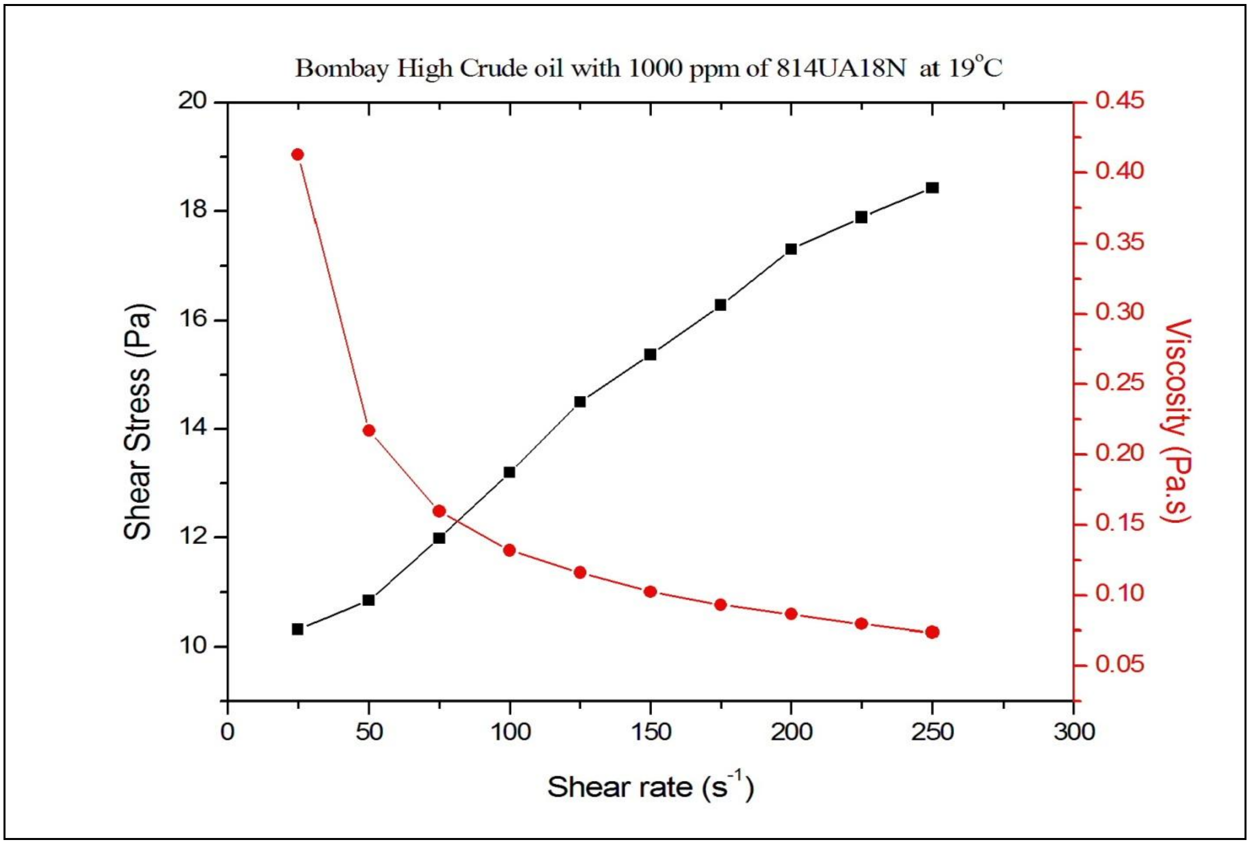

Fig. 3.162 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14UA18N at 19°C

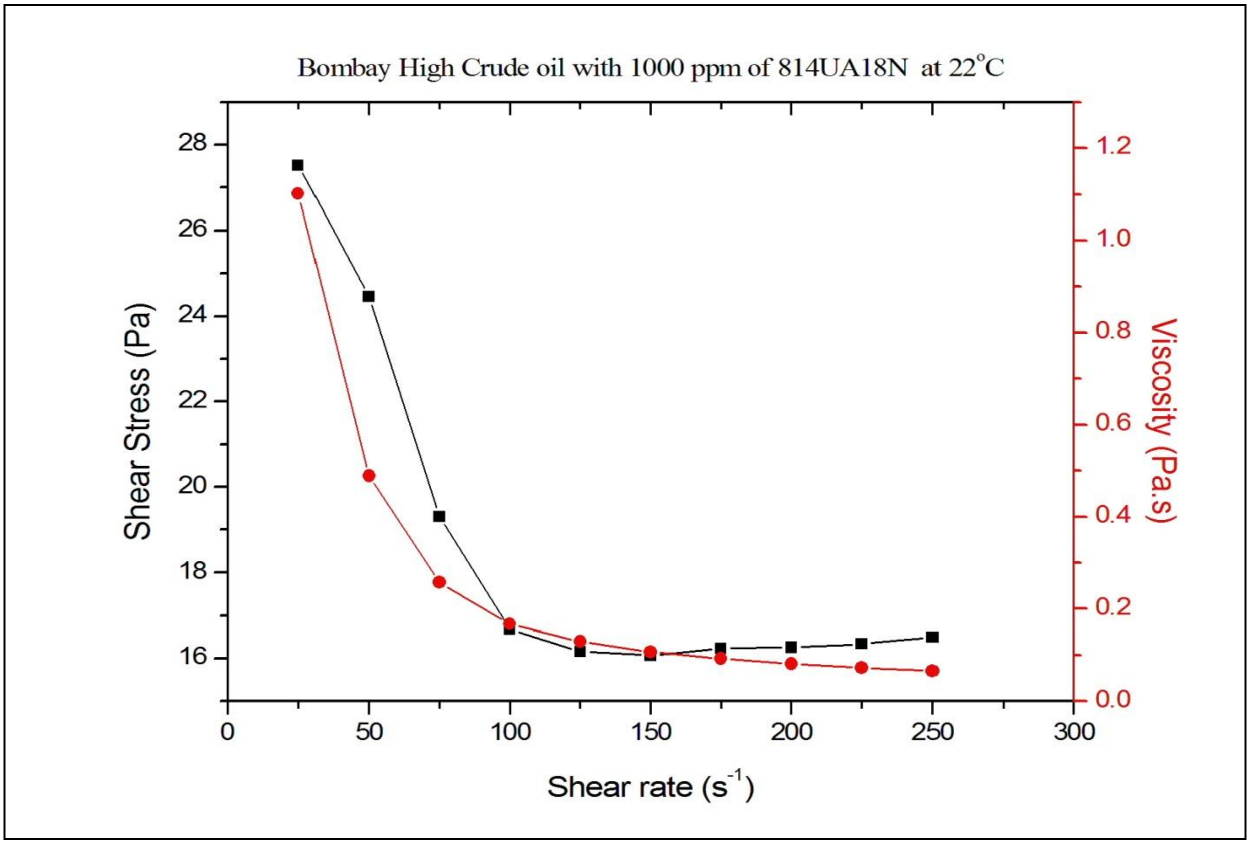

Fig. 3.163 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14UA18N at 22°C

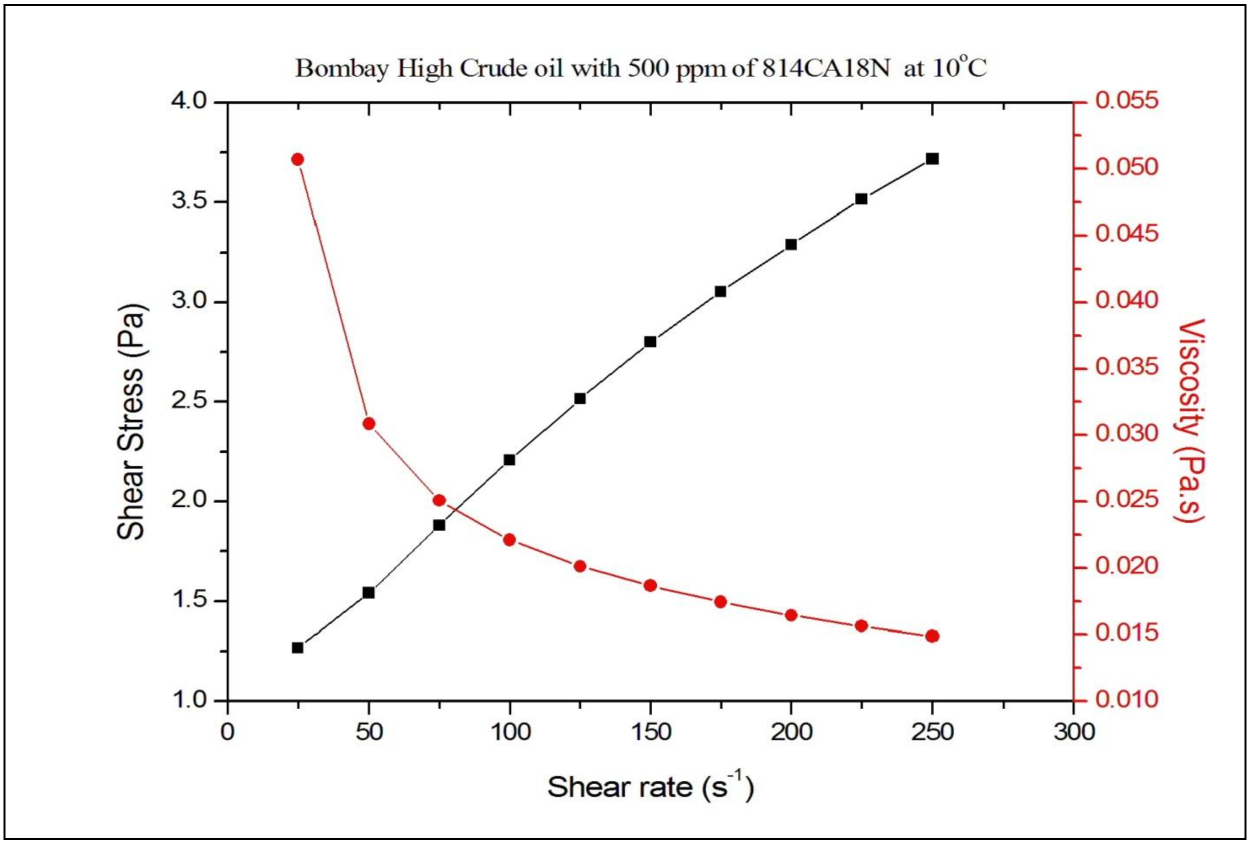

Fig. 3.164 Rheogram of Bombay High Crude oil with 500 ppm of 8-14CA18N at 10°C

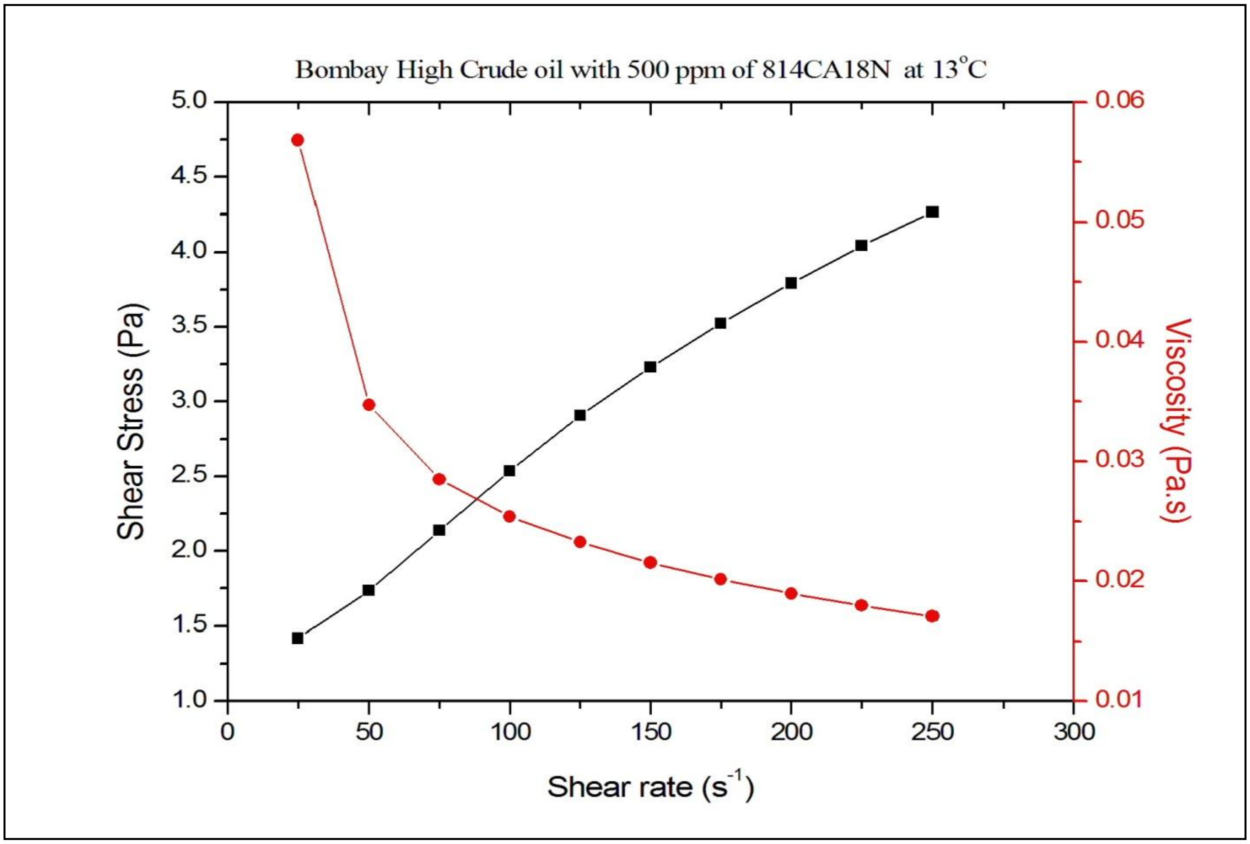

Fig. 3.165 Rheogram of Bombay High Crude oil with 500 ppm of 8-14CA18N at 13°C

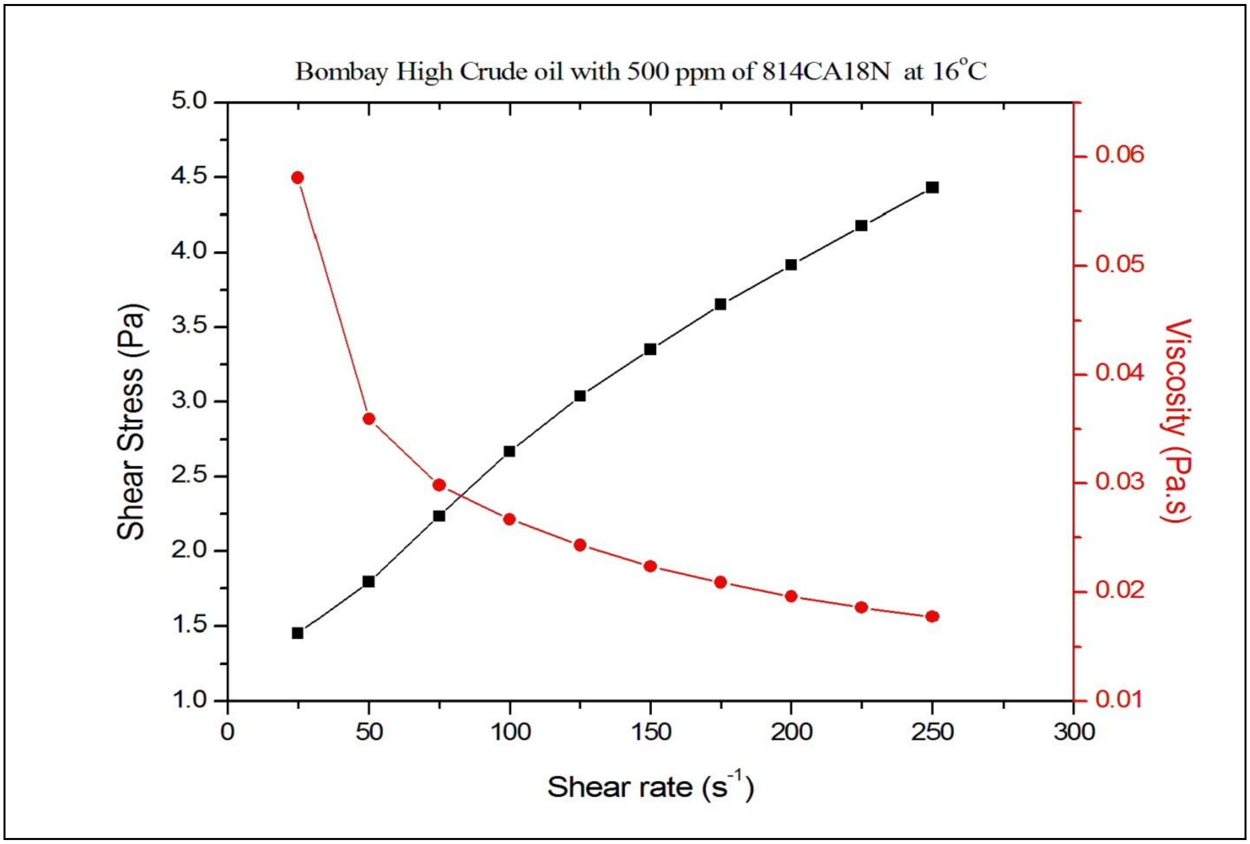

Fig. 3.166 Rheogram of Bombay High Crude oil with 500 ppm of 8-14CA18N at 16°C

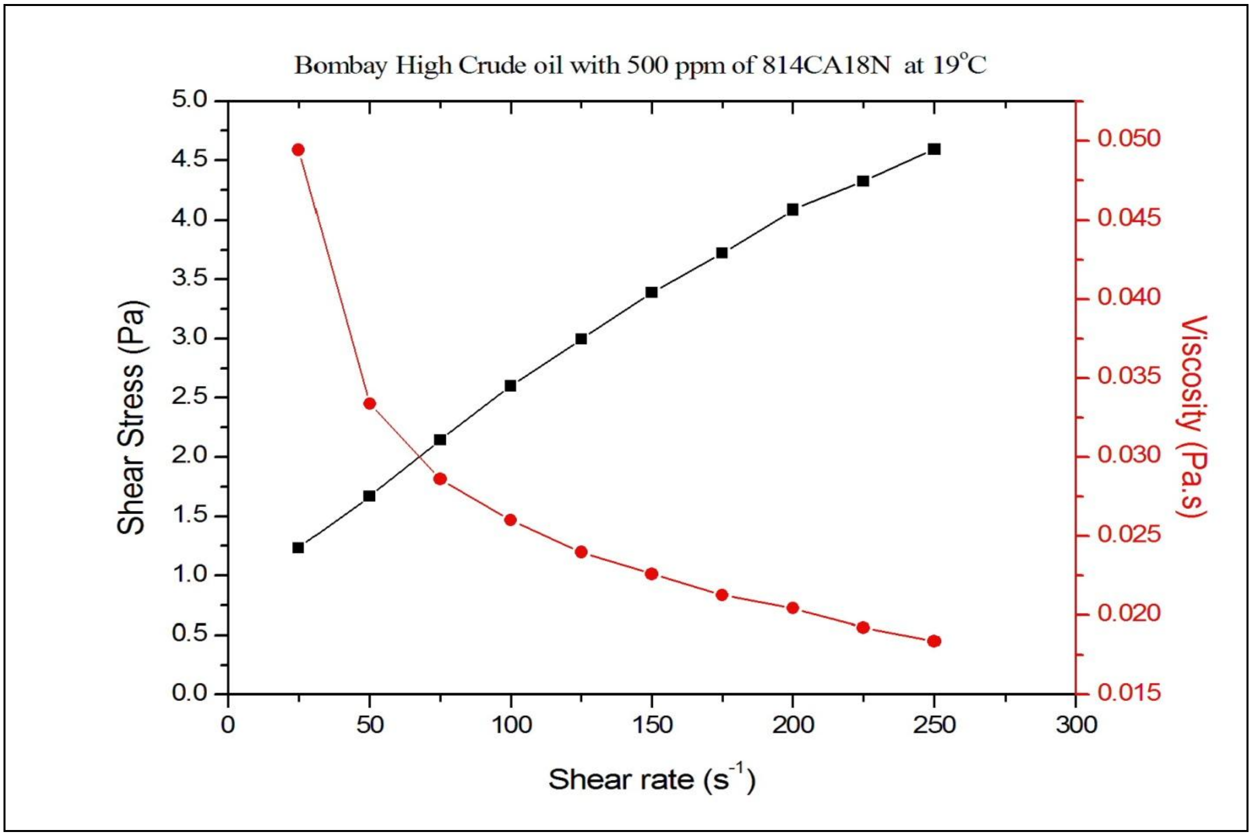

Fig. 3.167 Rheogram of Bombay High Crude oil with 500 ppm of 8-14CA18N at 19°C

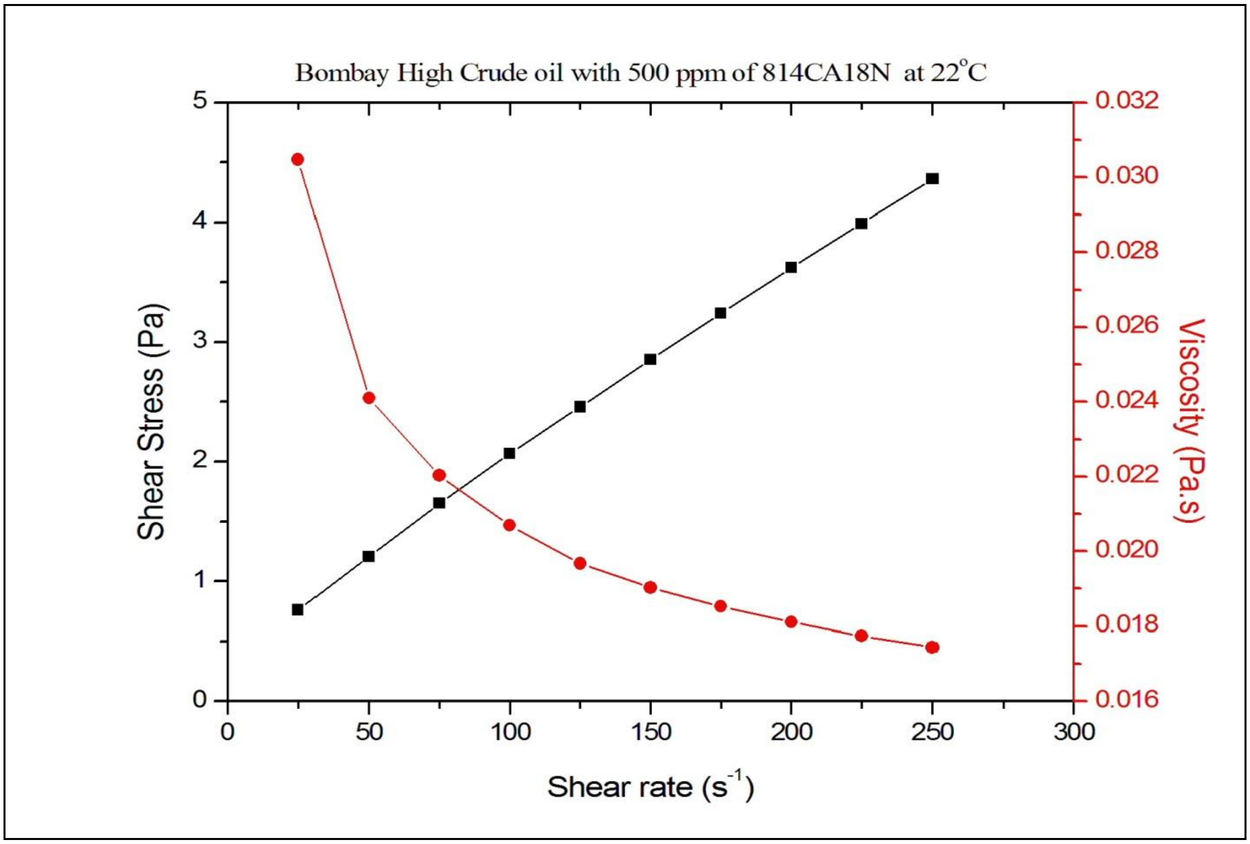

Fig. 3.168 Rheogram of Bombay High Crude oil with 500 ppm of 8-14CA18N at 22^{o}C

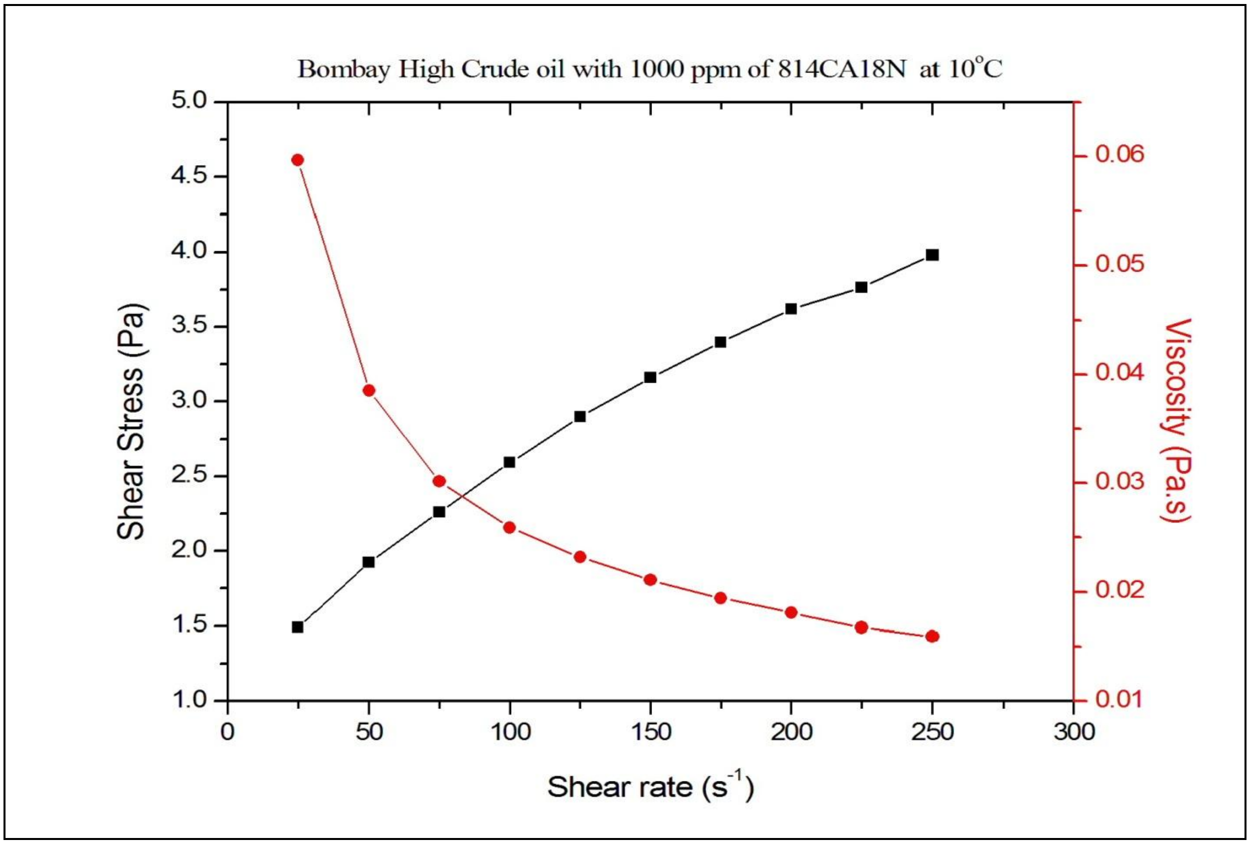

Fig. 3.169 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14CA18N at 10^{o}C

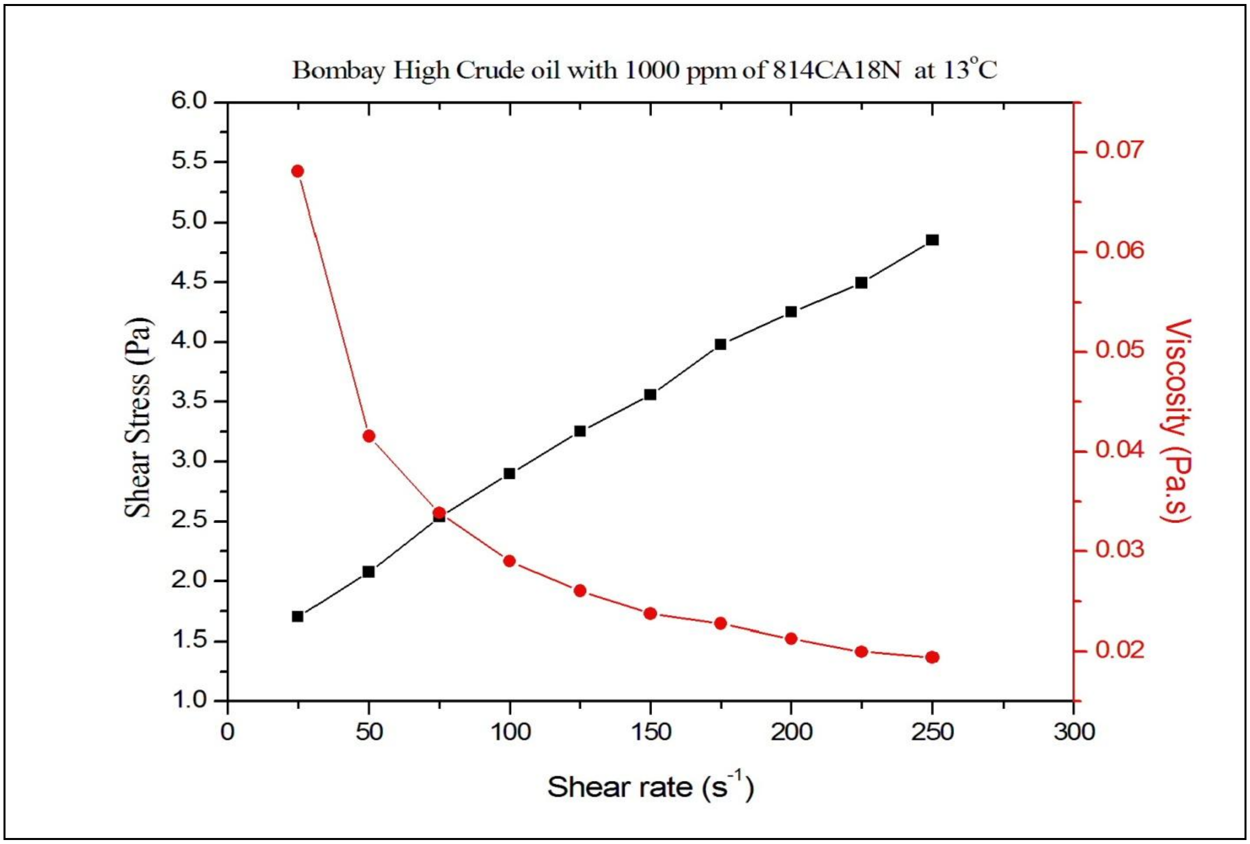

Fig. 3.170 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14CA18N at 13°C

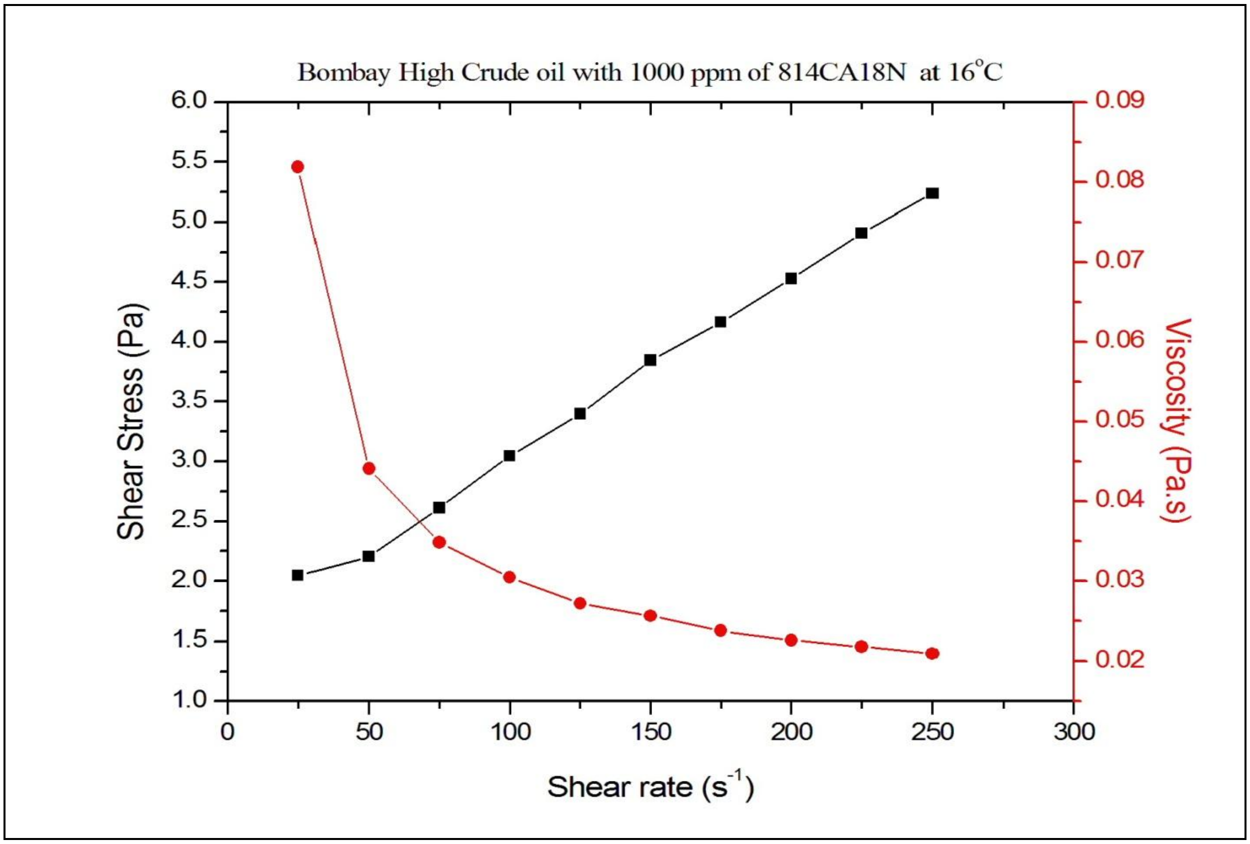

Fig. 3.171 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14CA18N at 16°C

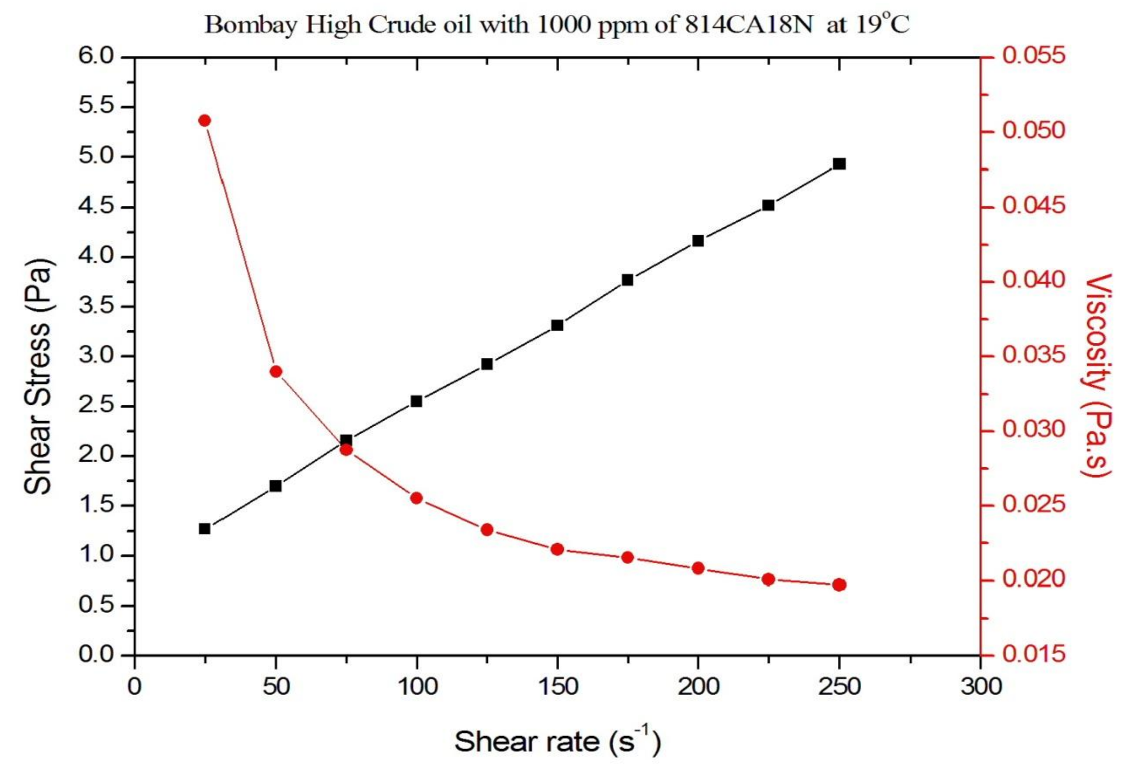

Fig. 3.172 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14CA18N at 19°C

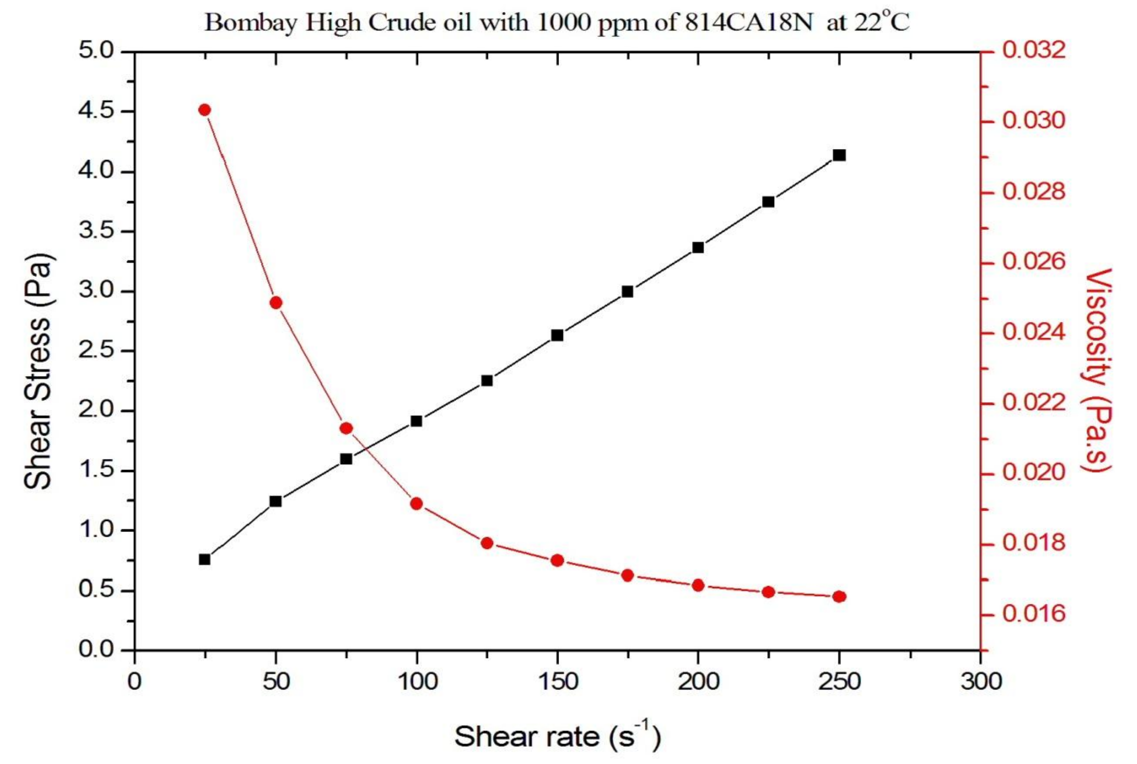

Fig. 3.173 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14CA18N at 22°C

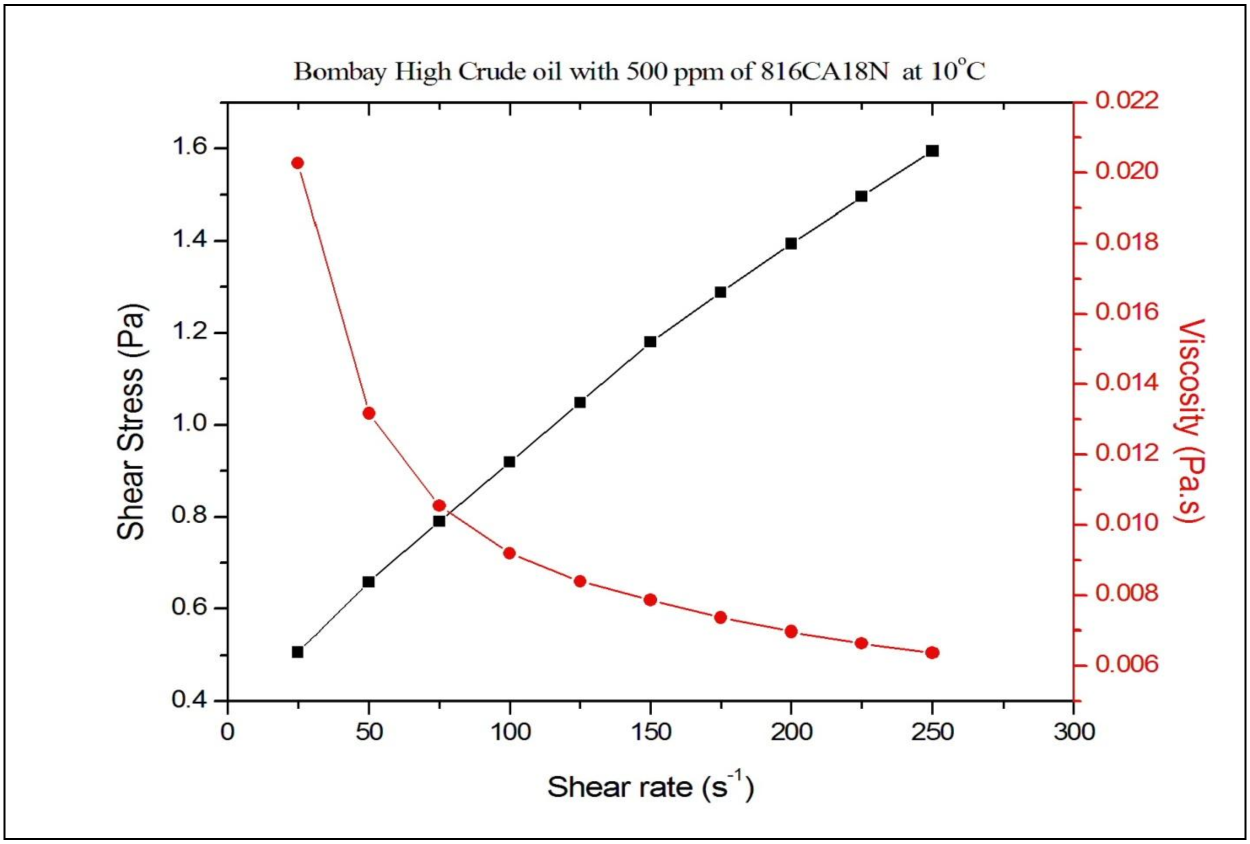

Fig. 3.174 Rheogram of Bombay High Crude oil with 500 ppm of 8-16CA18N at 10°C

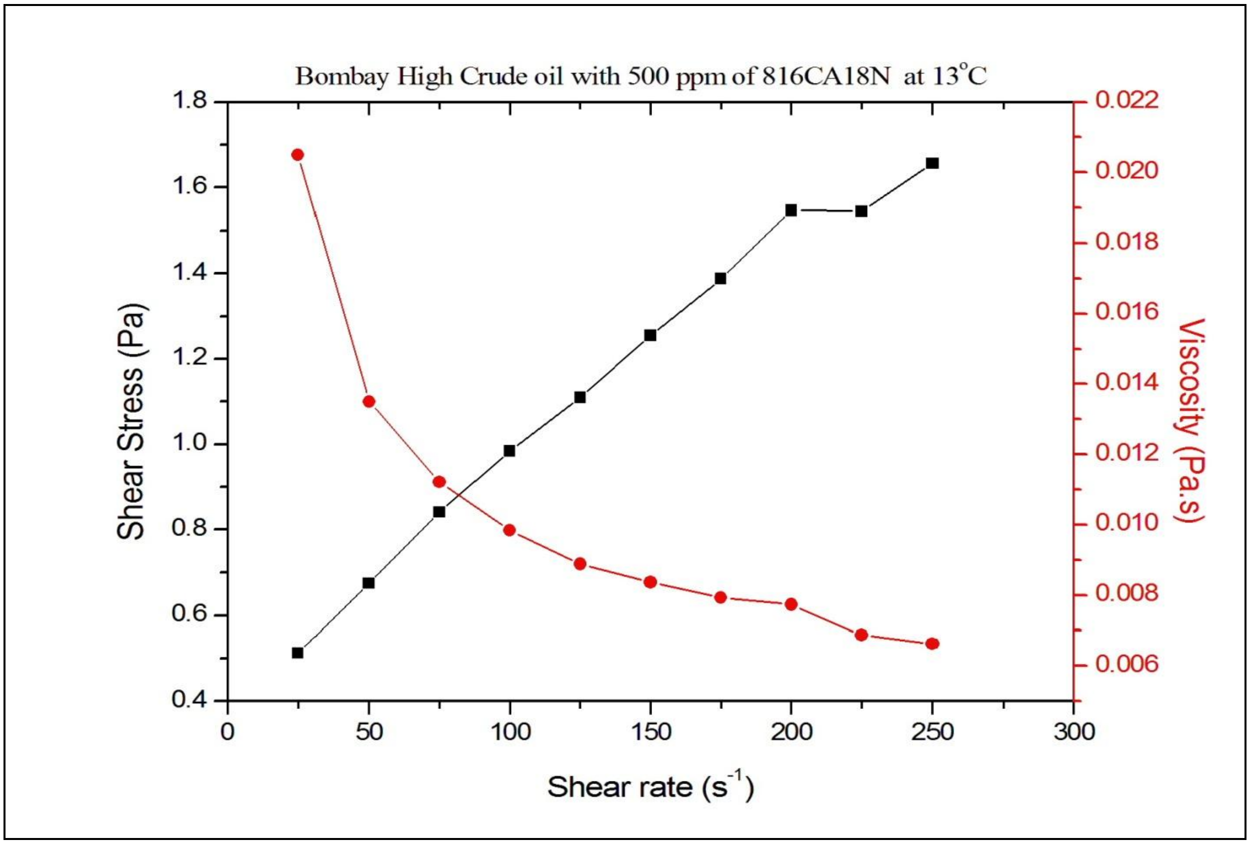

Fig. 3.175 Rheogram of Bombay High Crude oil with 500 ppm of 8-16CA18N at 13°C

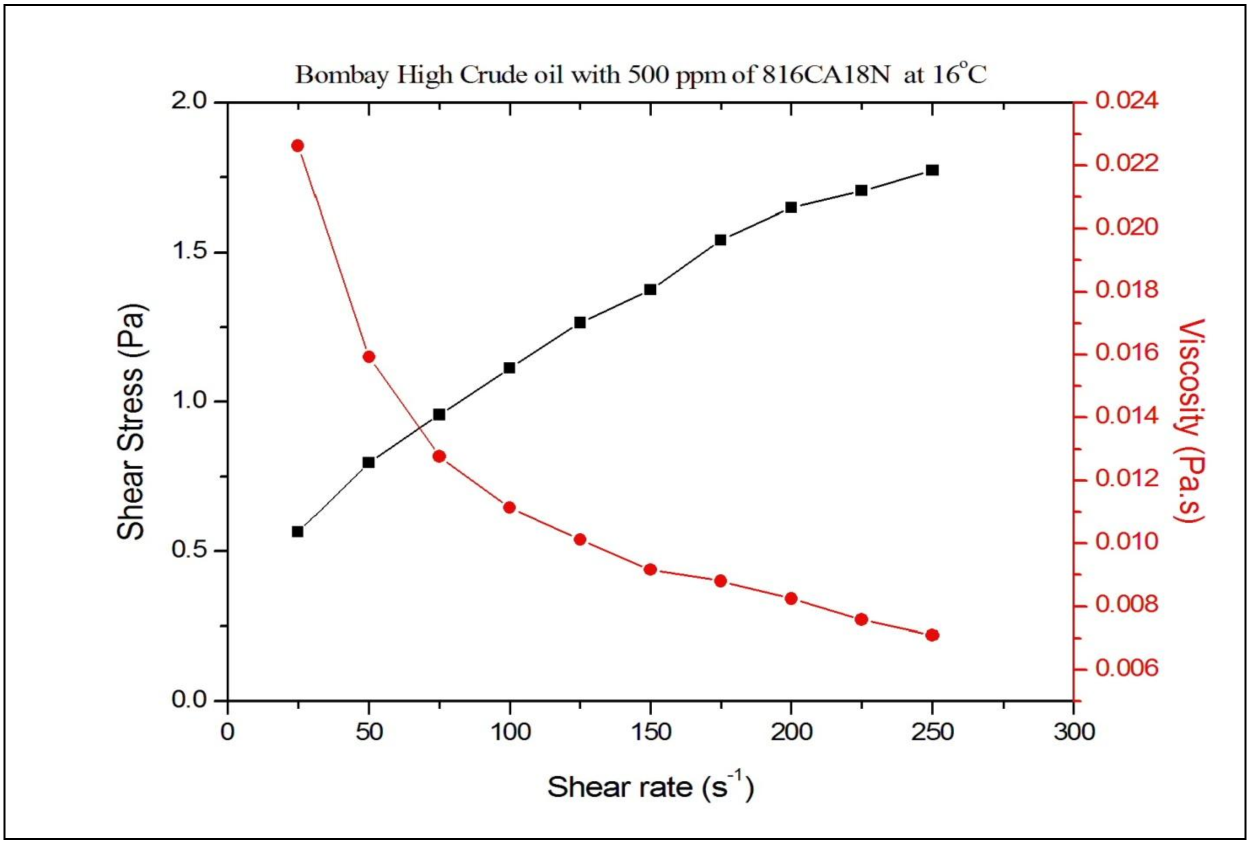

Fig. 3.176 Rheogram of Bombay High Crude oil with 500 ppm of 8-16CA18N at 16°C

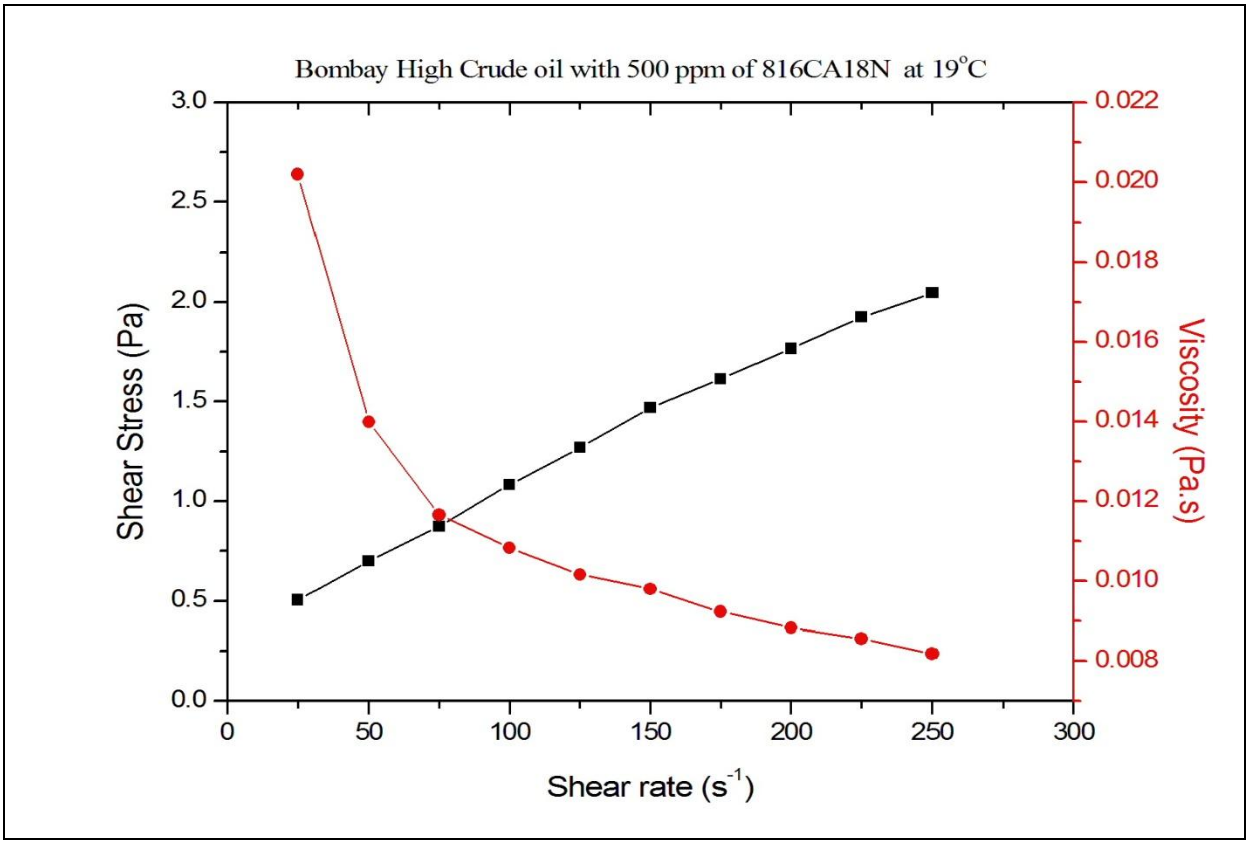

Fig. 3.177 Rheogram of Bombay High Crude oil with 500 ppm of 8-16CA18N at 19°C

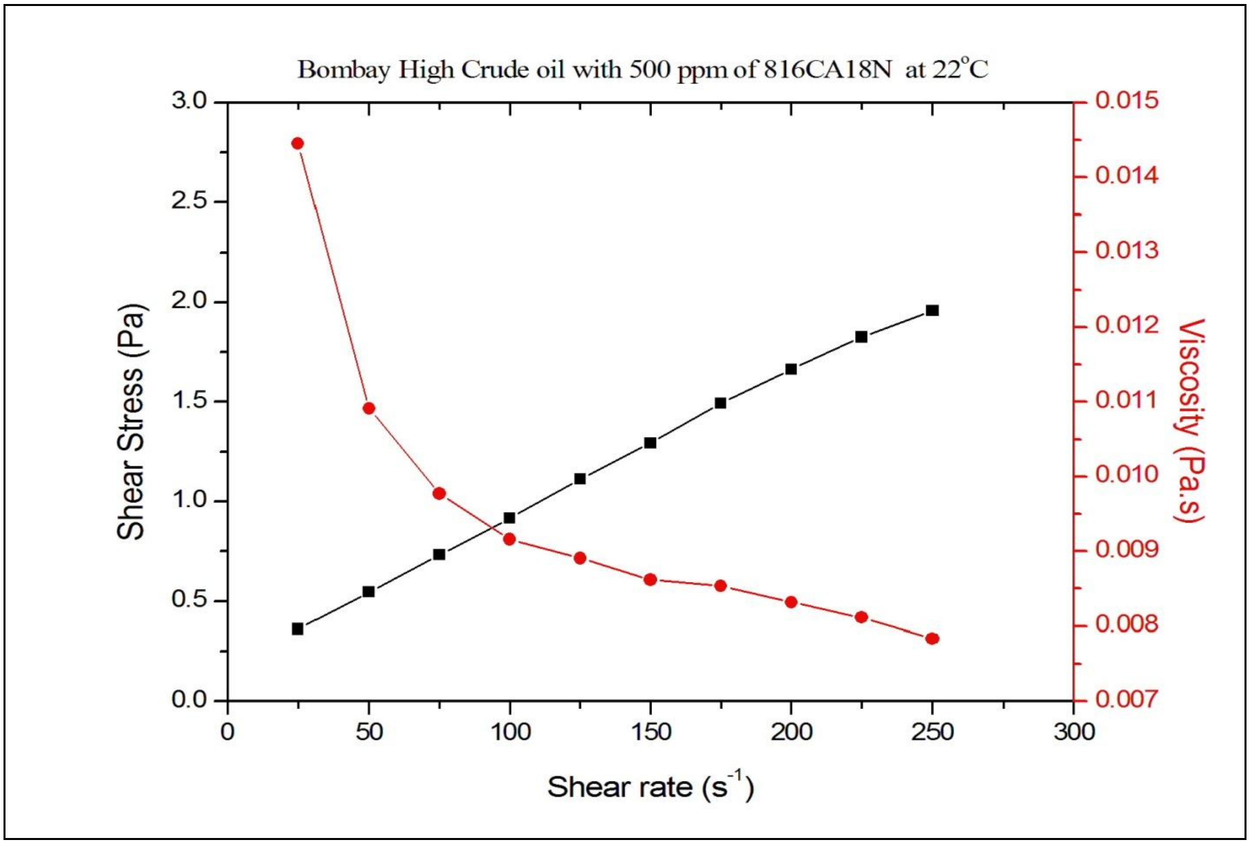

Fig. 3.178 Rheogram of Bombay High Crude oil with 500 ppm of 8-16CA18N at 22°C

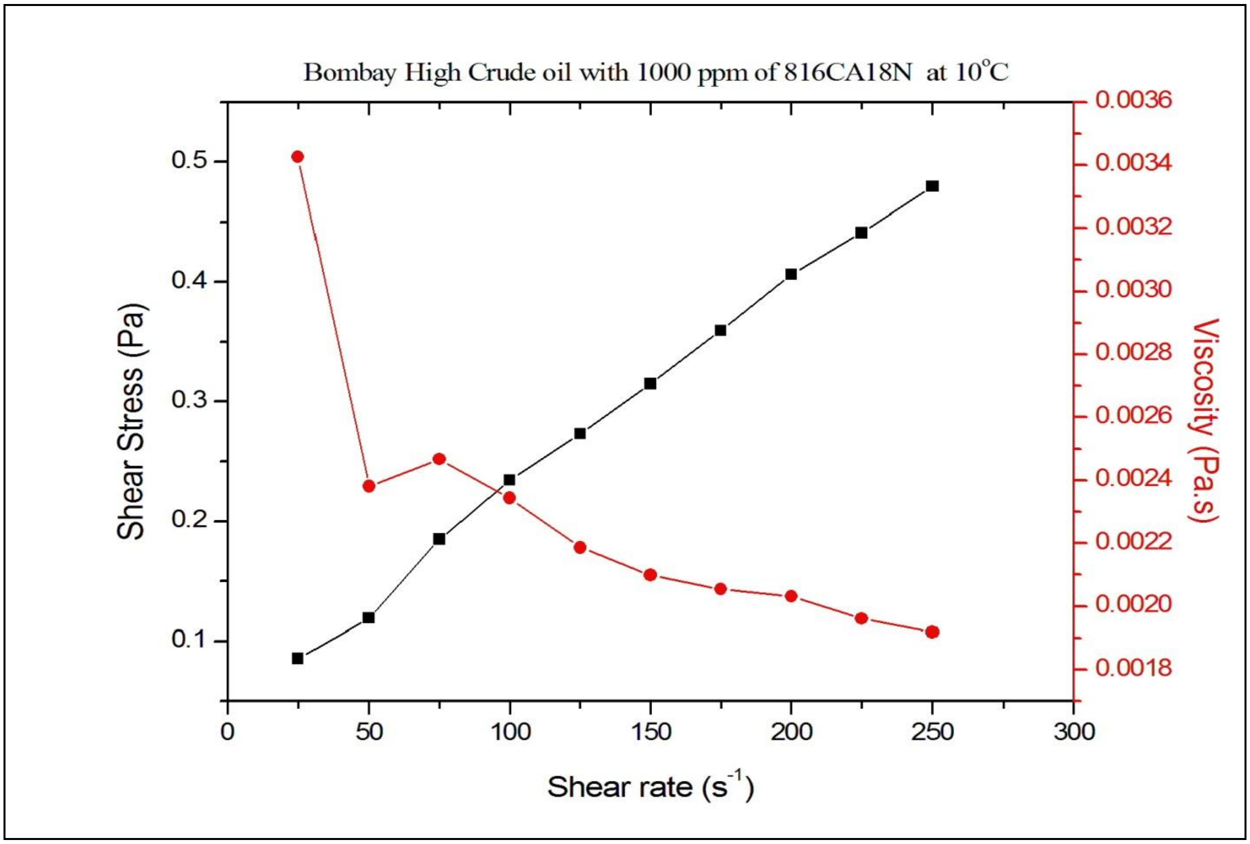

Fig. 3.179 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16CA18N at 10°C

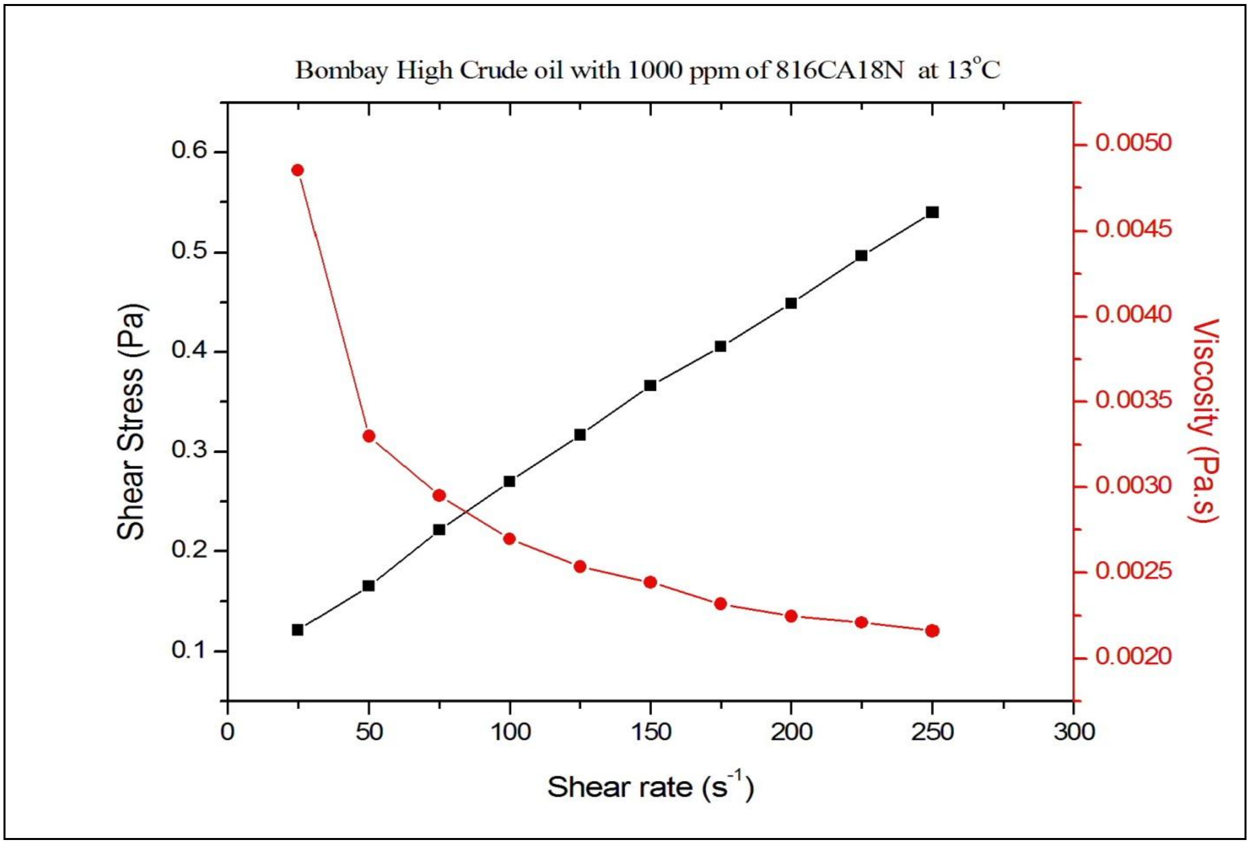

Fig. 3.180 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16CA18N at 13°C

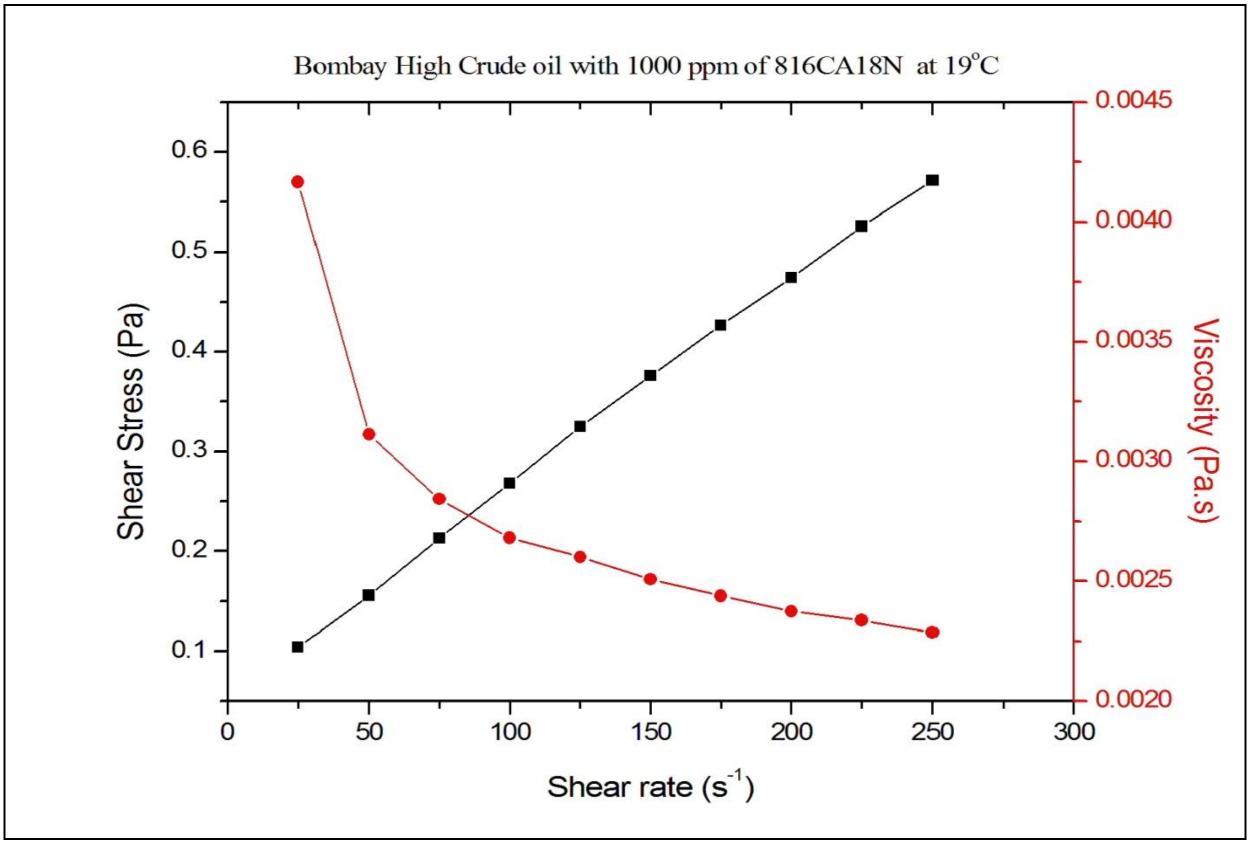

Fig. 3.181 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16CA18N at 19°C

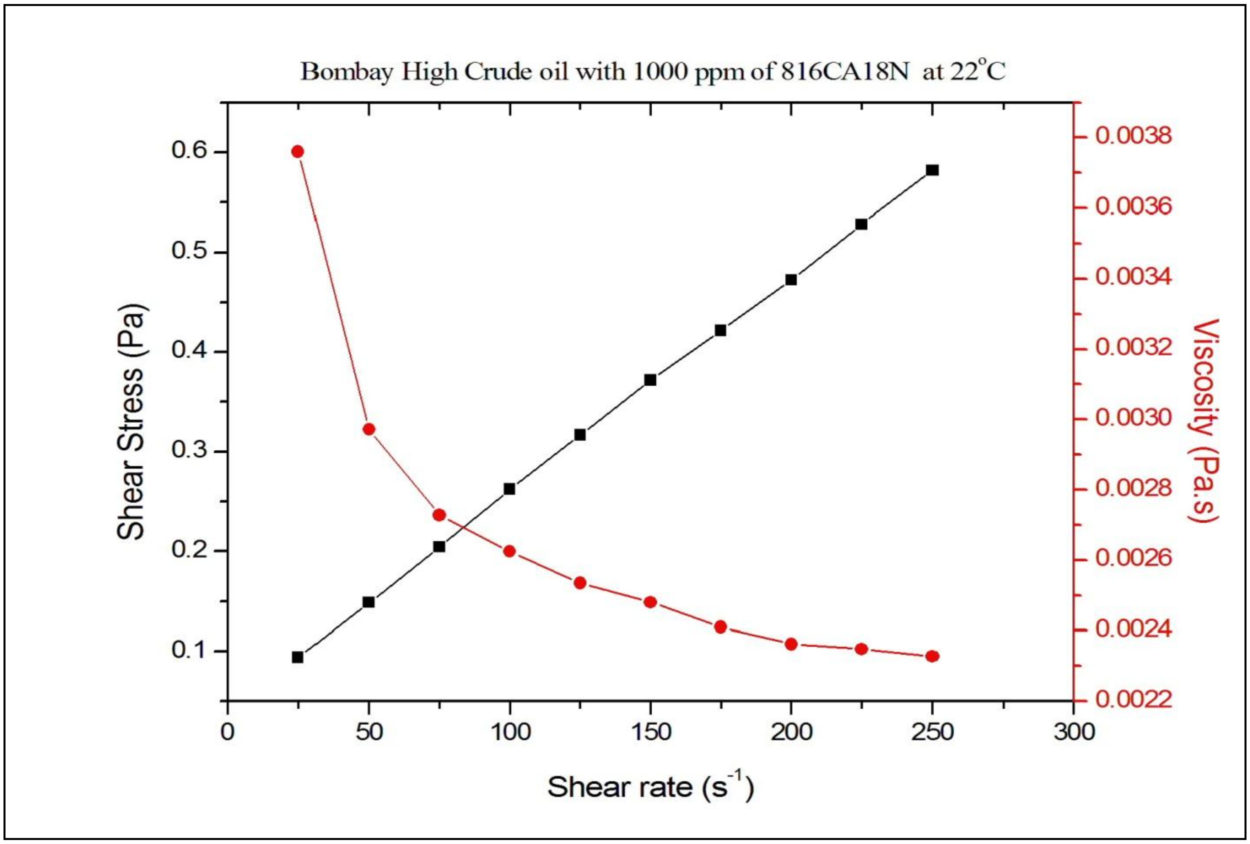

Fig. 3.182 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16CA18N at 22°C

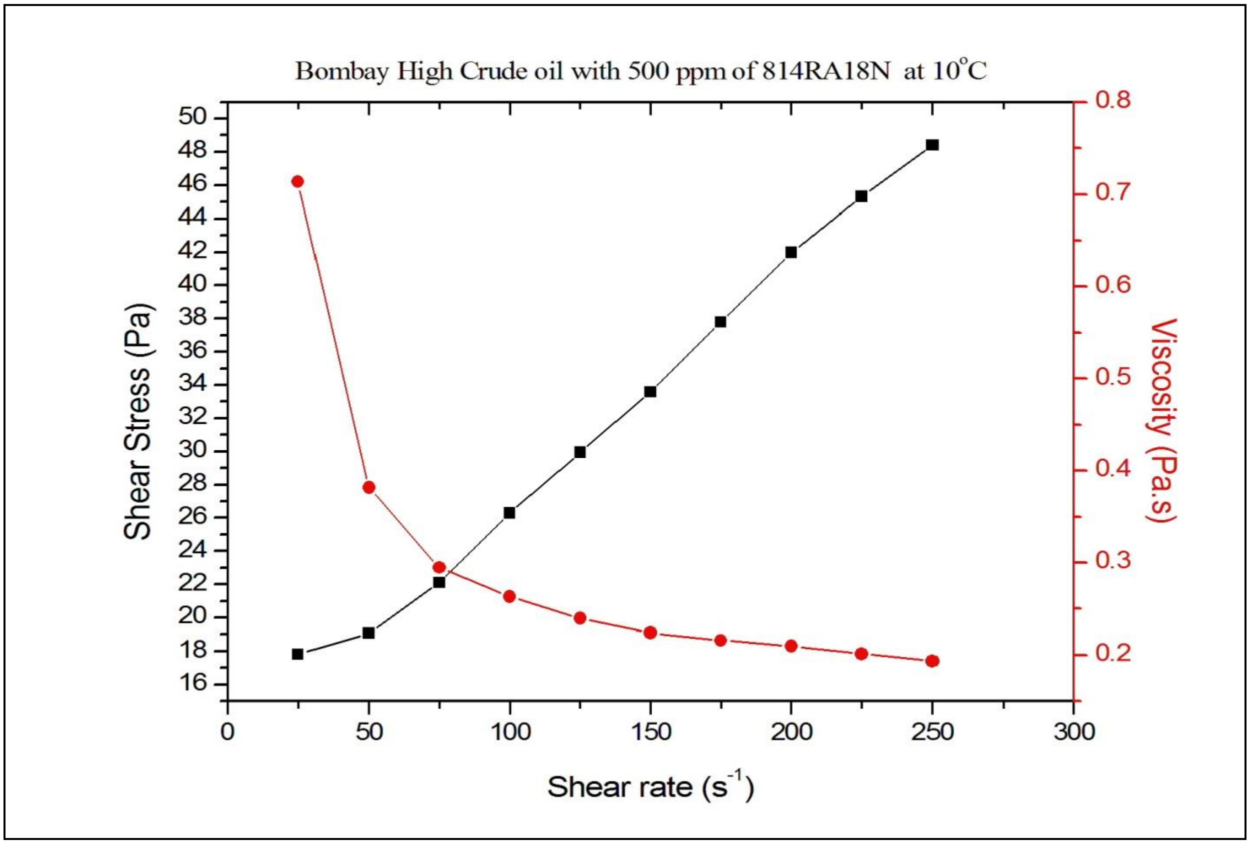

Fig. 3.183 Rheogram of Bombay High Crude oil with 500 ppm of 8-14RA18N at 10°C

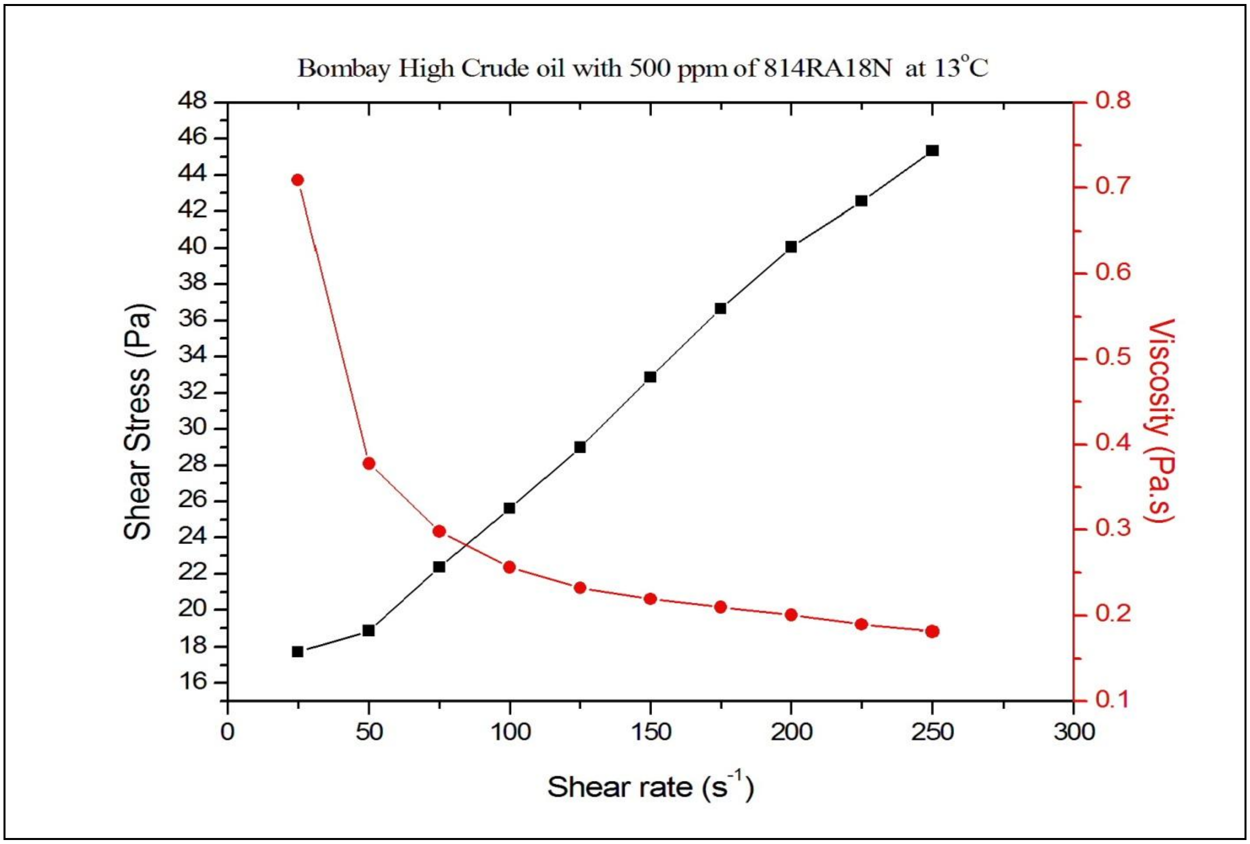

Fig. 3.184 Rheogram of Bombay High Crude oil with 500 ppm of 8-14RA18N at 13°C

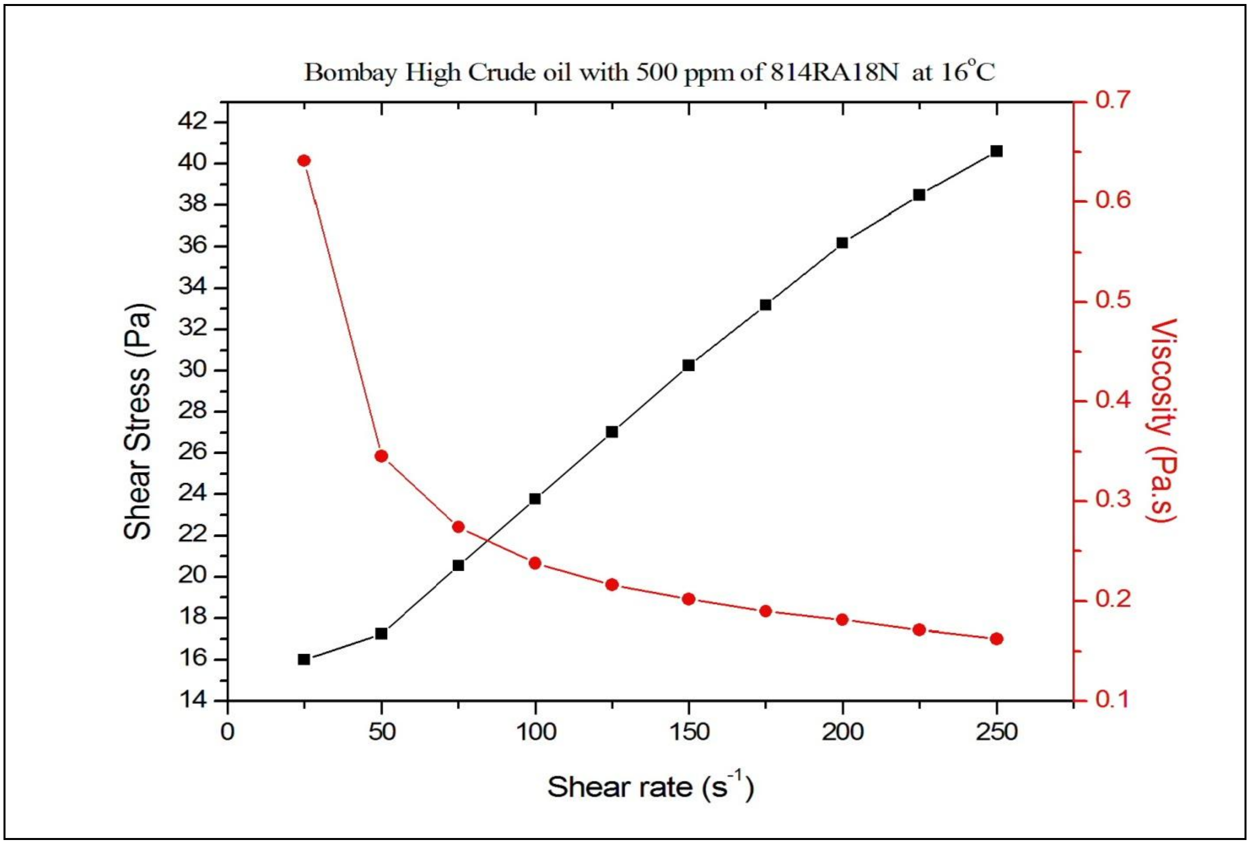

Fig. 3.185 Rheogram of Bombay High Crude oil with 500 ppm of 8-14RA18N at 16°C

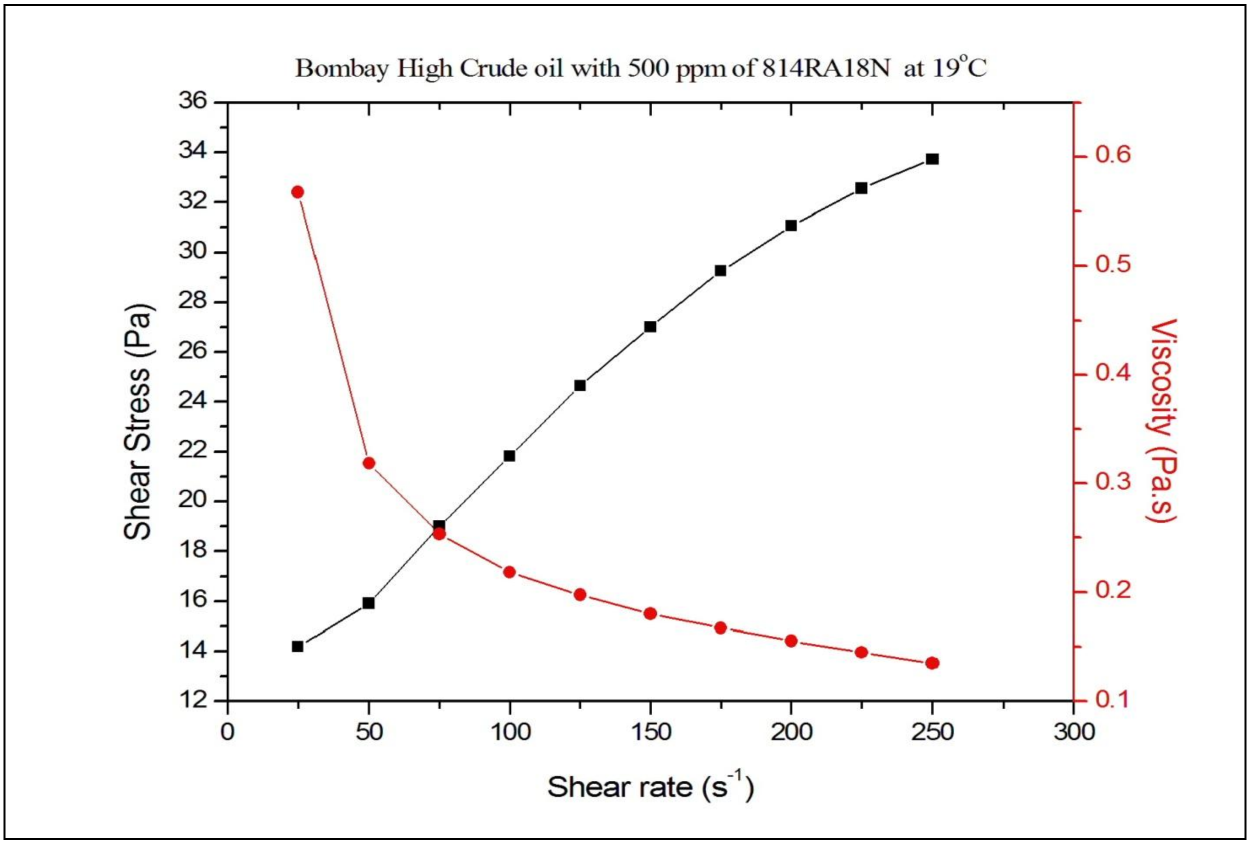

Fig. 3.186 Rheogram of Bombay High Crude oil with 500 ppm of 8-14RA18N at 19°C

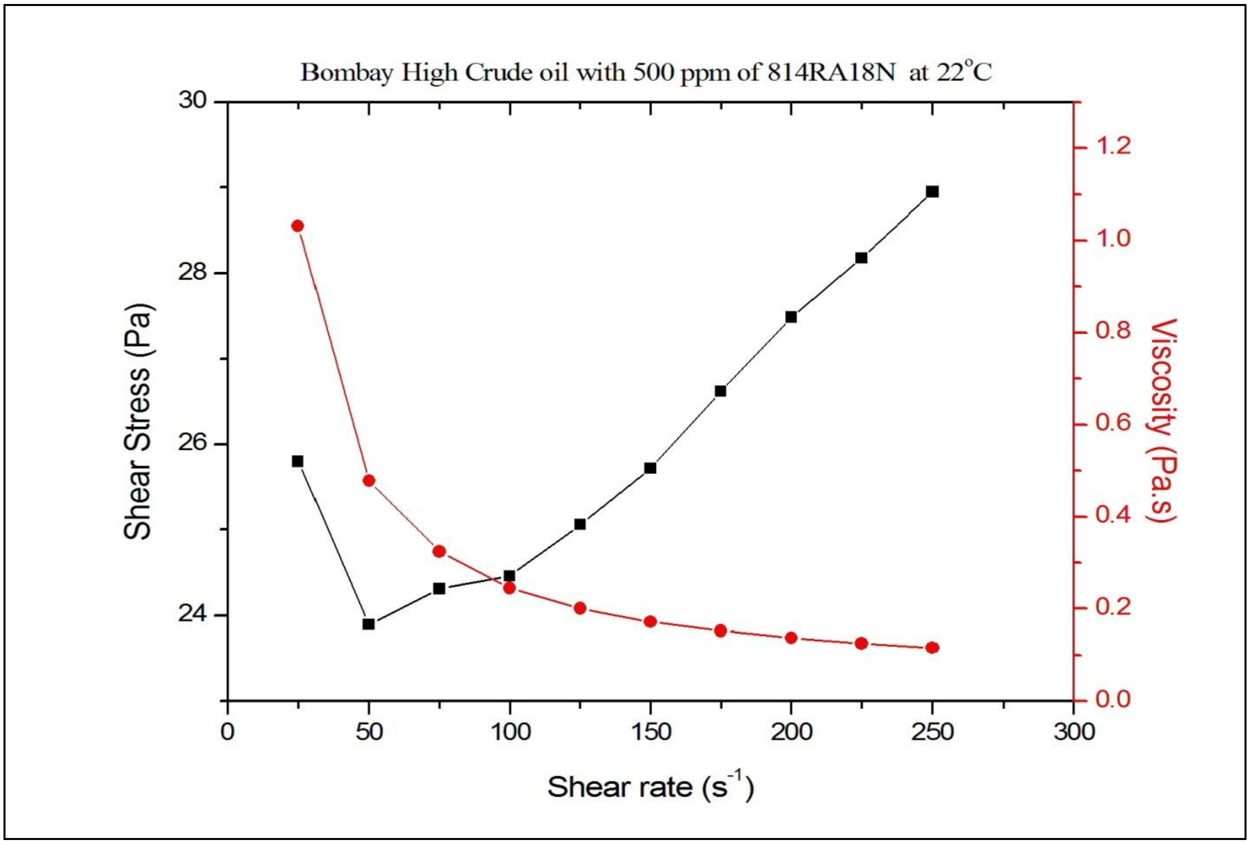

Fig. 3.187 Rheogram of Bombay High Crude oil with 500 ppm of 8-14RA18N at 22°C

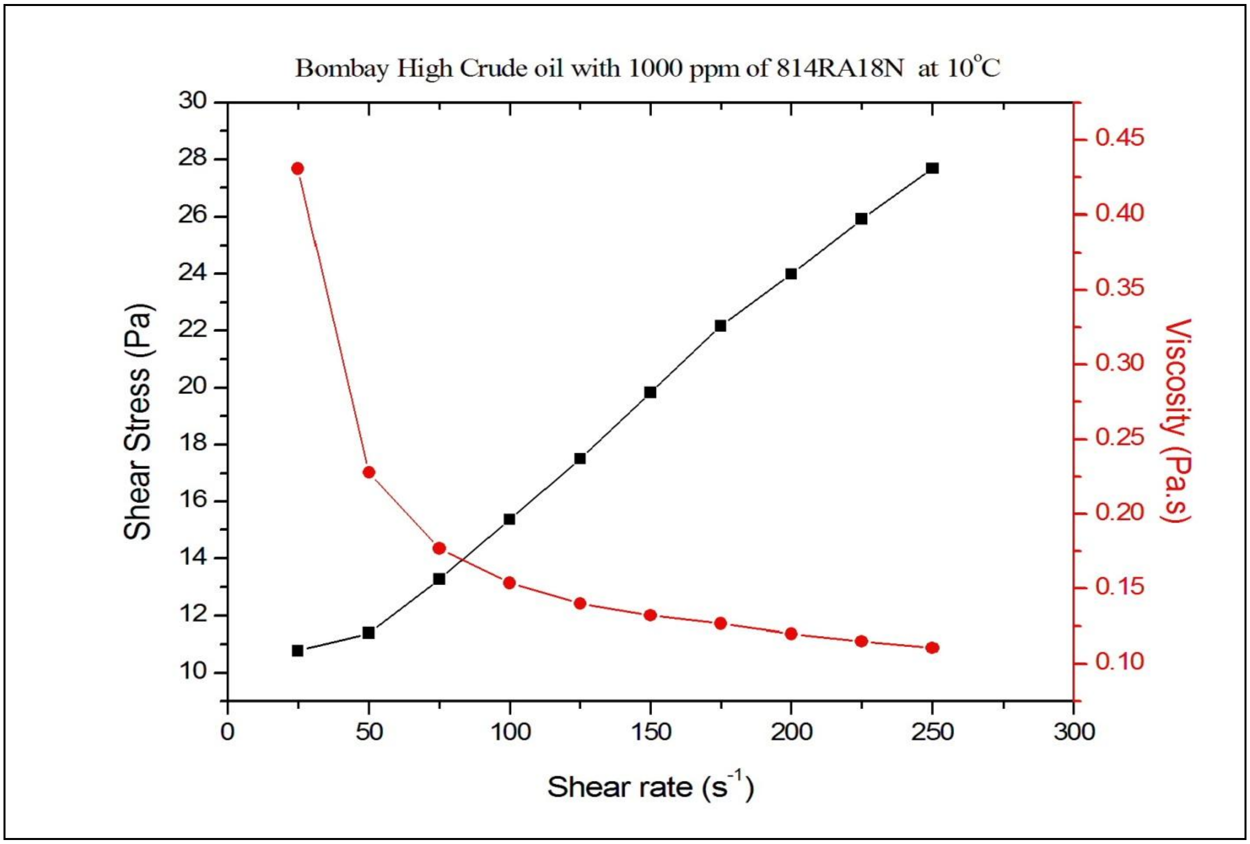

Fig. 3.188 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14RA18N at 10°C

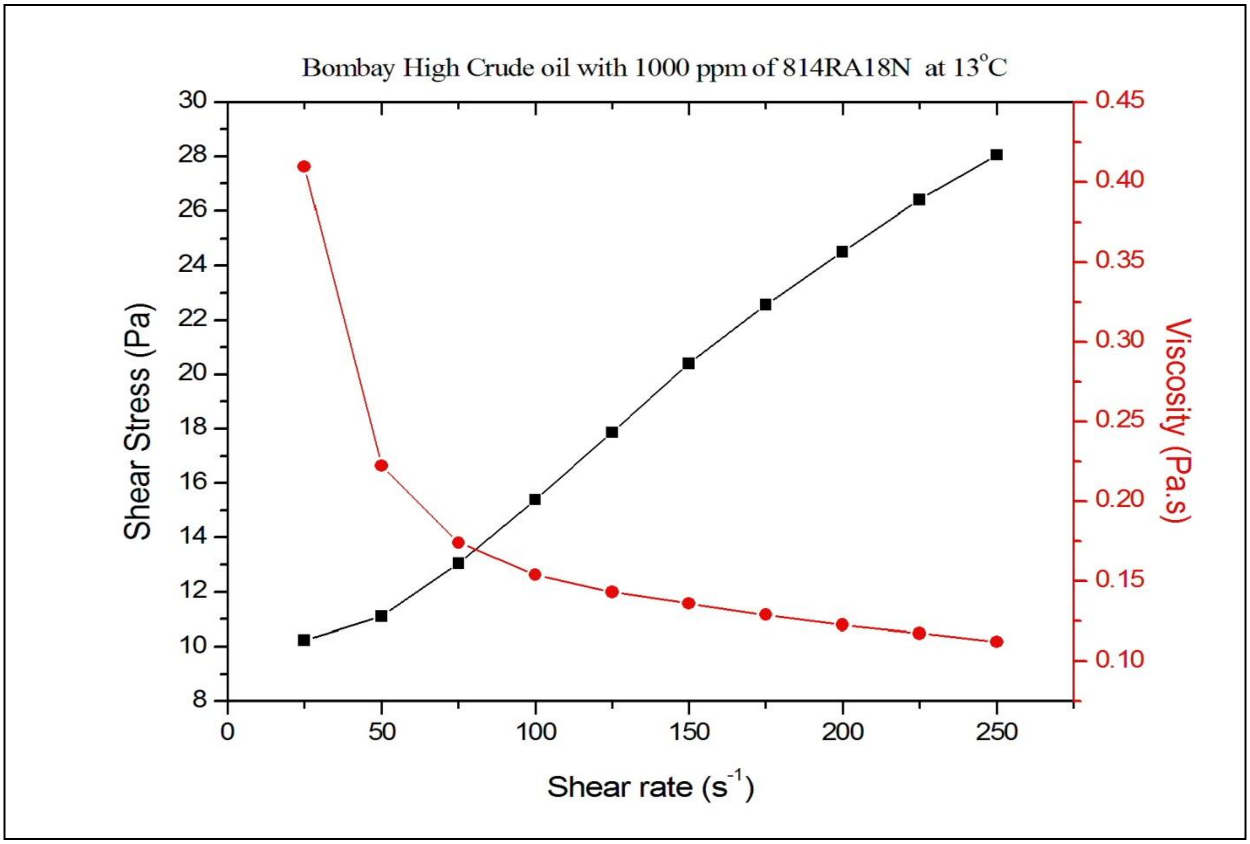

Fig. 3.189 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14RA18N at 13°C

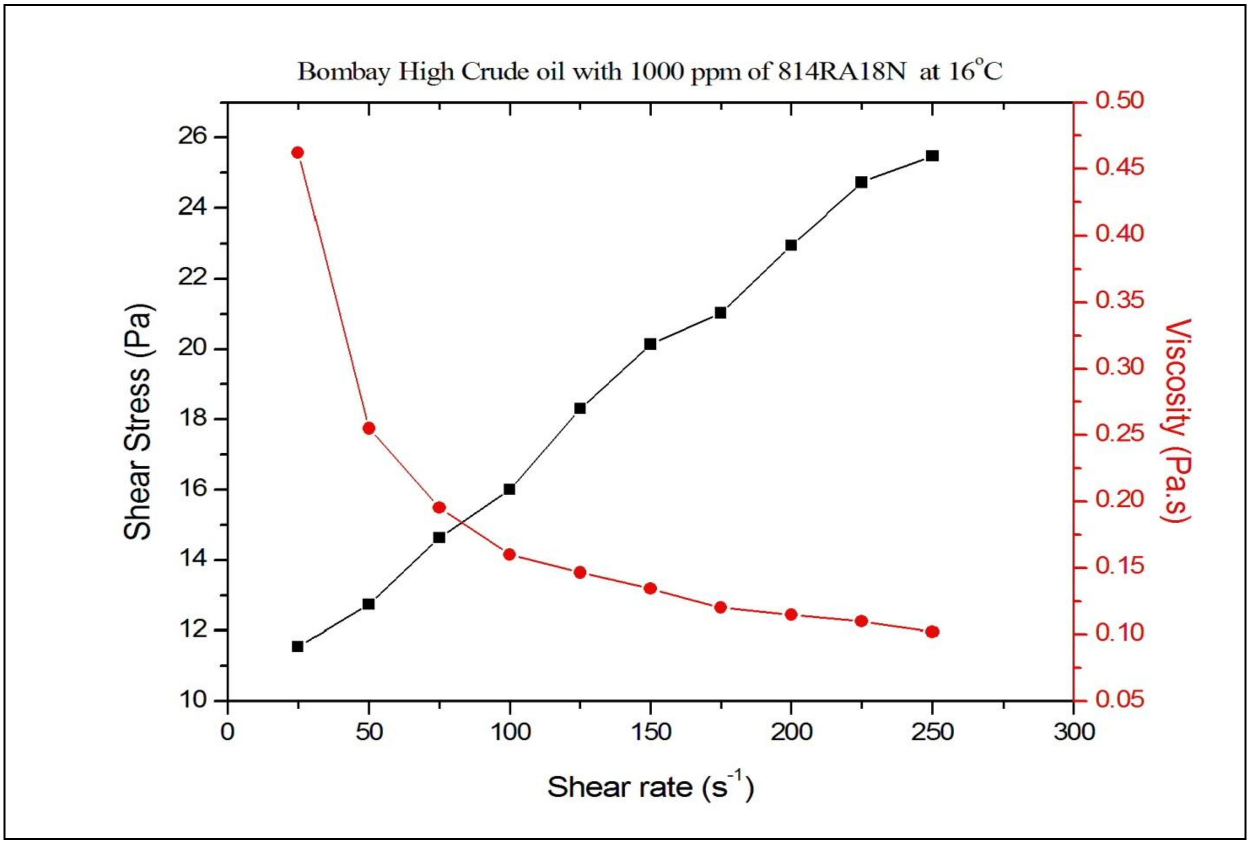

Fig. 3.190 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14RA18N at 16°C

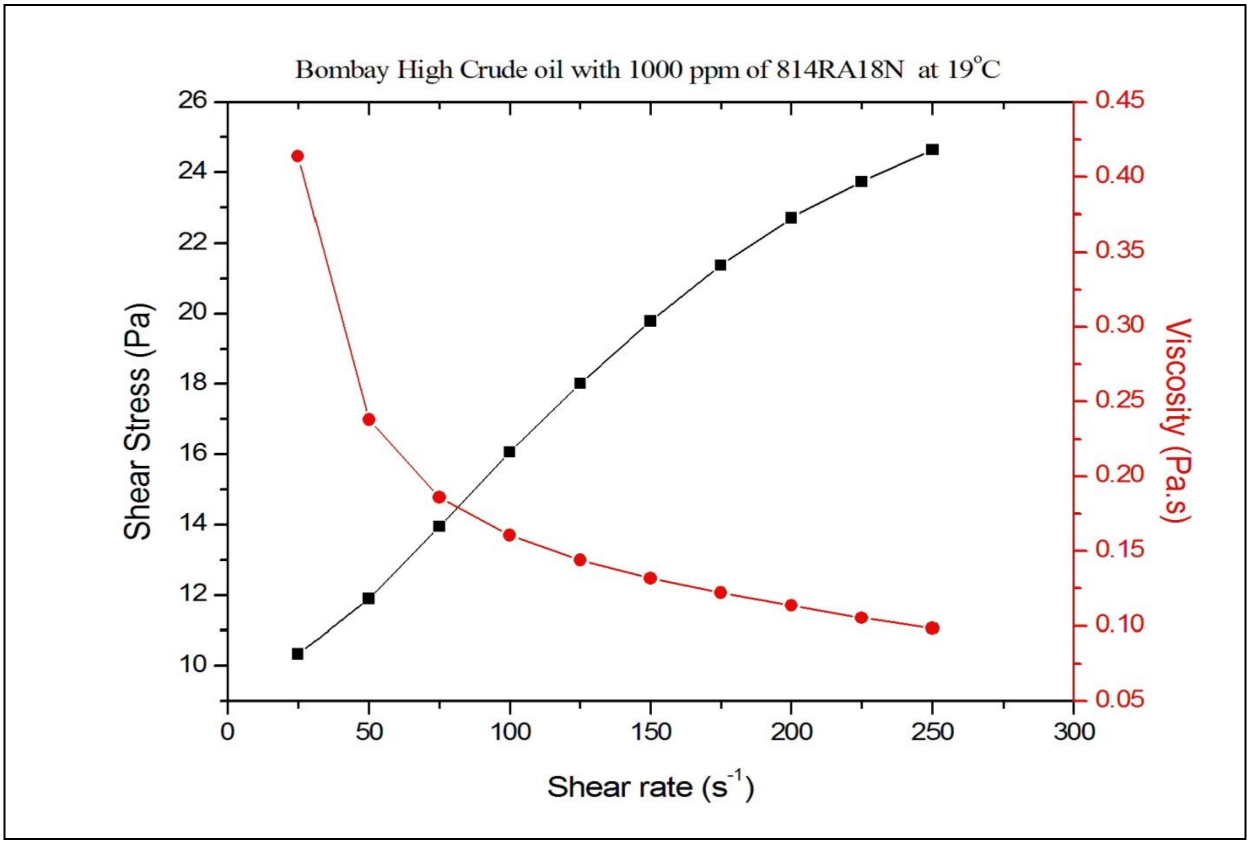

Fig. 3.191 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14RA18N at 19°C

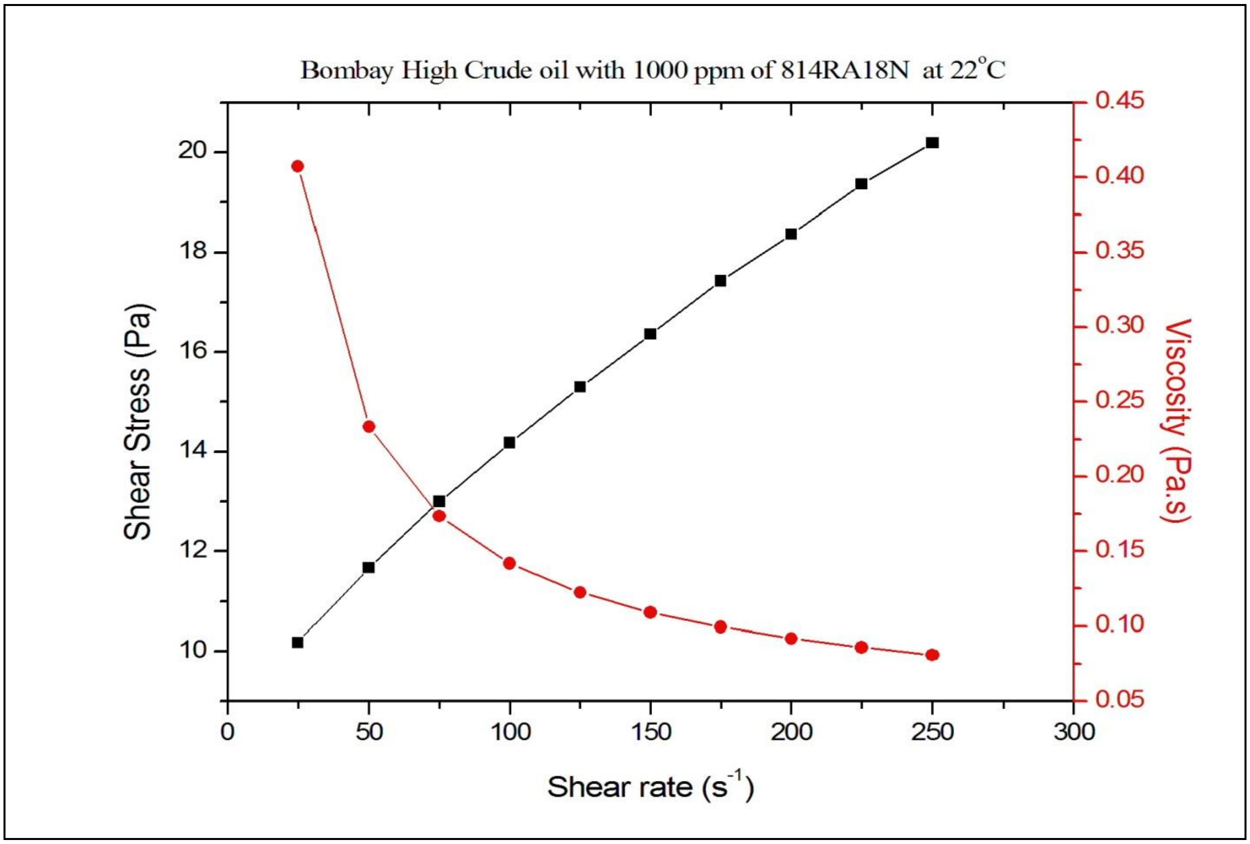

Fig. 3.192 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14RA18N at 22°C

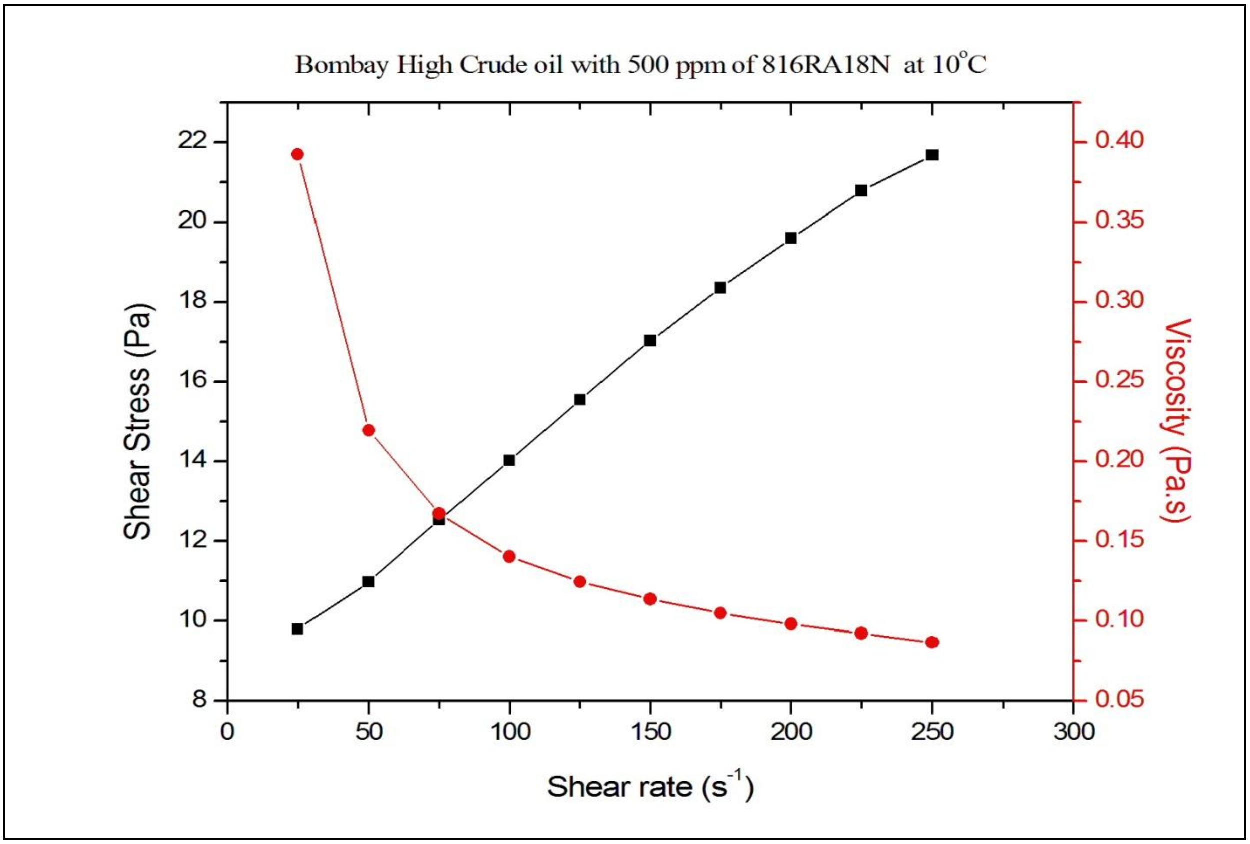

Fig. 3.193 Rheogram of Bombay High Crude oil with 500 ppm of 8-16RA18N at 10°C

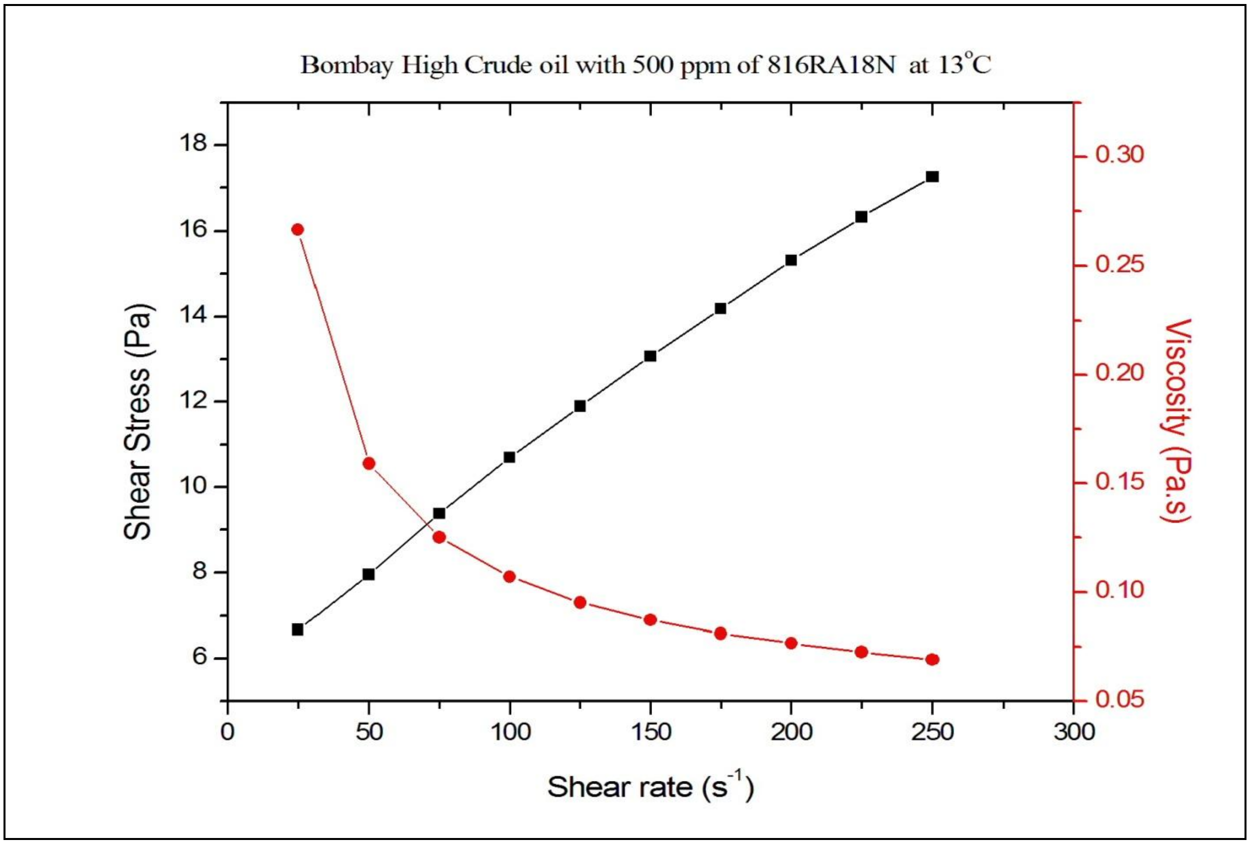

Fig. 3.194 Rheogram of Bombay High Crude oil with 500 ppm of 8-16RA18N at 13°C

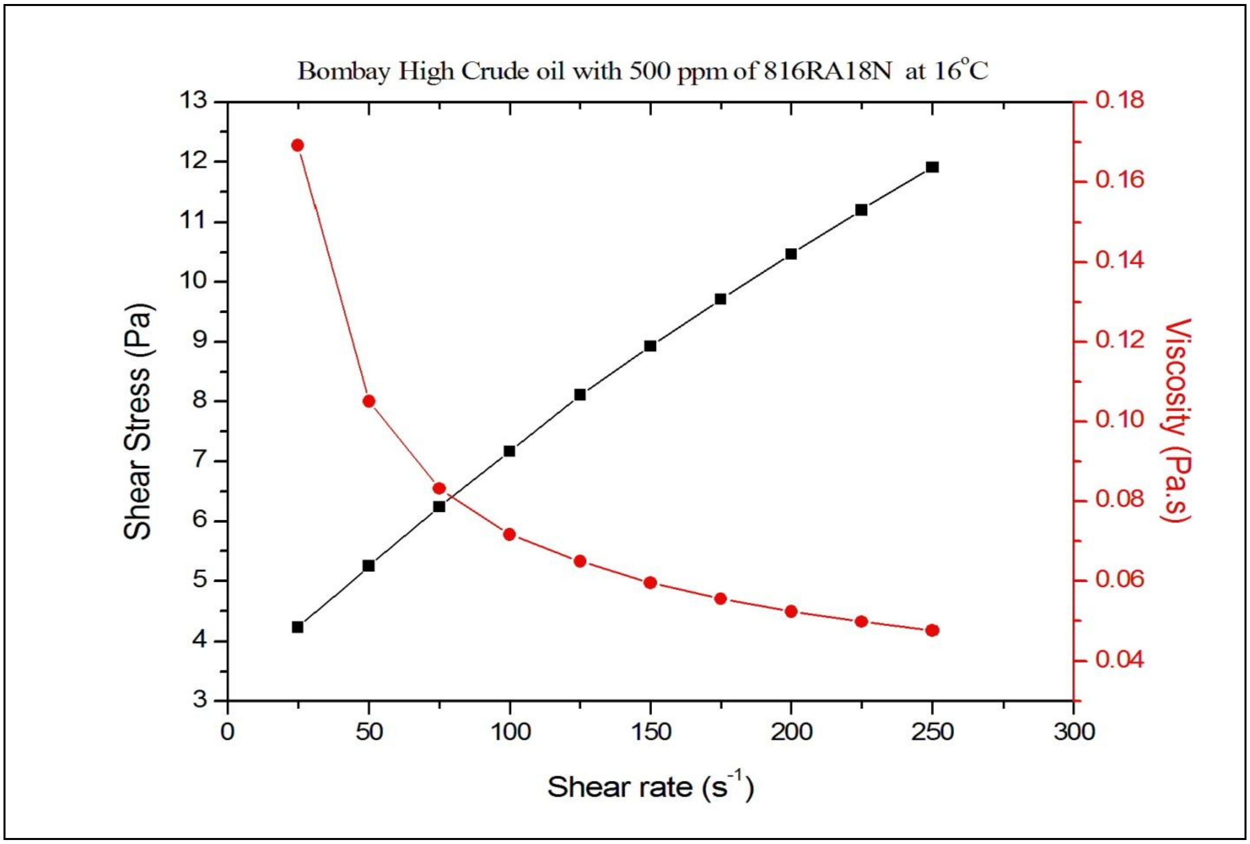

Fig. 3.195 Rheogram of Bombay High Crude oil with 500 ppm of 8-16RA18N at 16°C

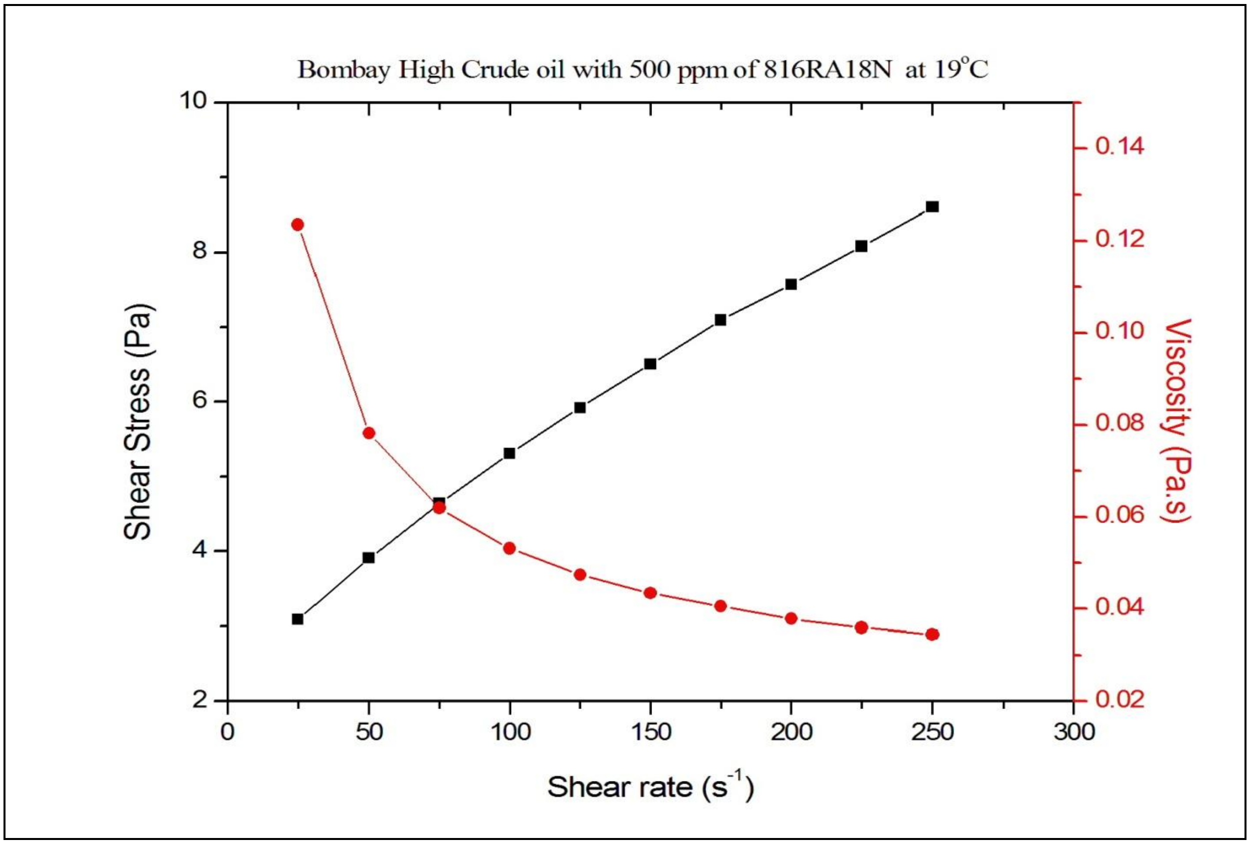

Fig. 3.196 Rheogram of Bombay High Crude oil with 500 ppm of 8-16RA18N at 19°C

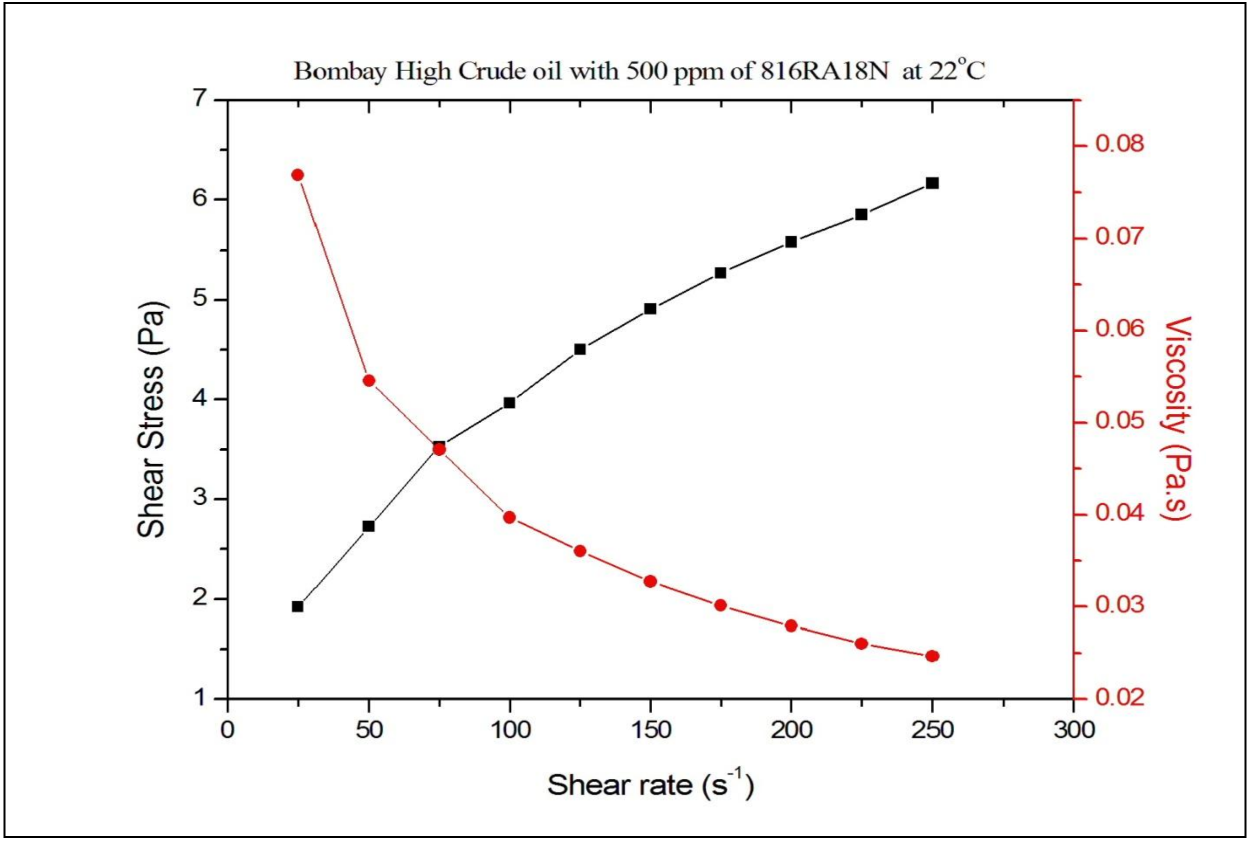

Fig. 3.197 Rheogram of Bombay High Crude oil with 500 ppm of 8-16RA18N at 22°C

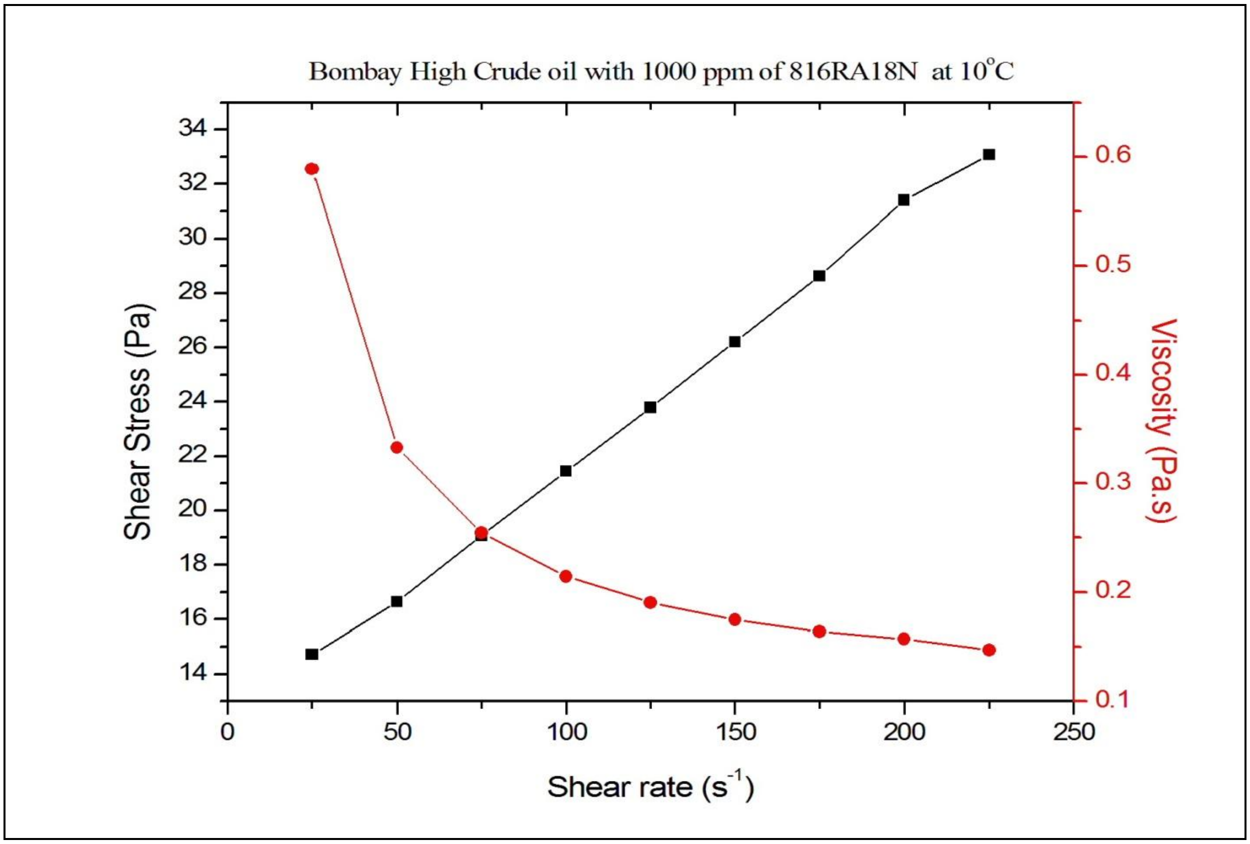

Fig. 3.198 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16RA18N at 10°C

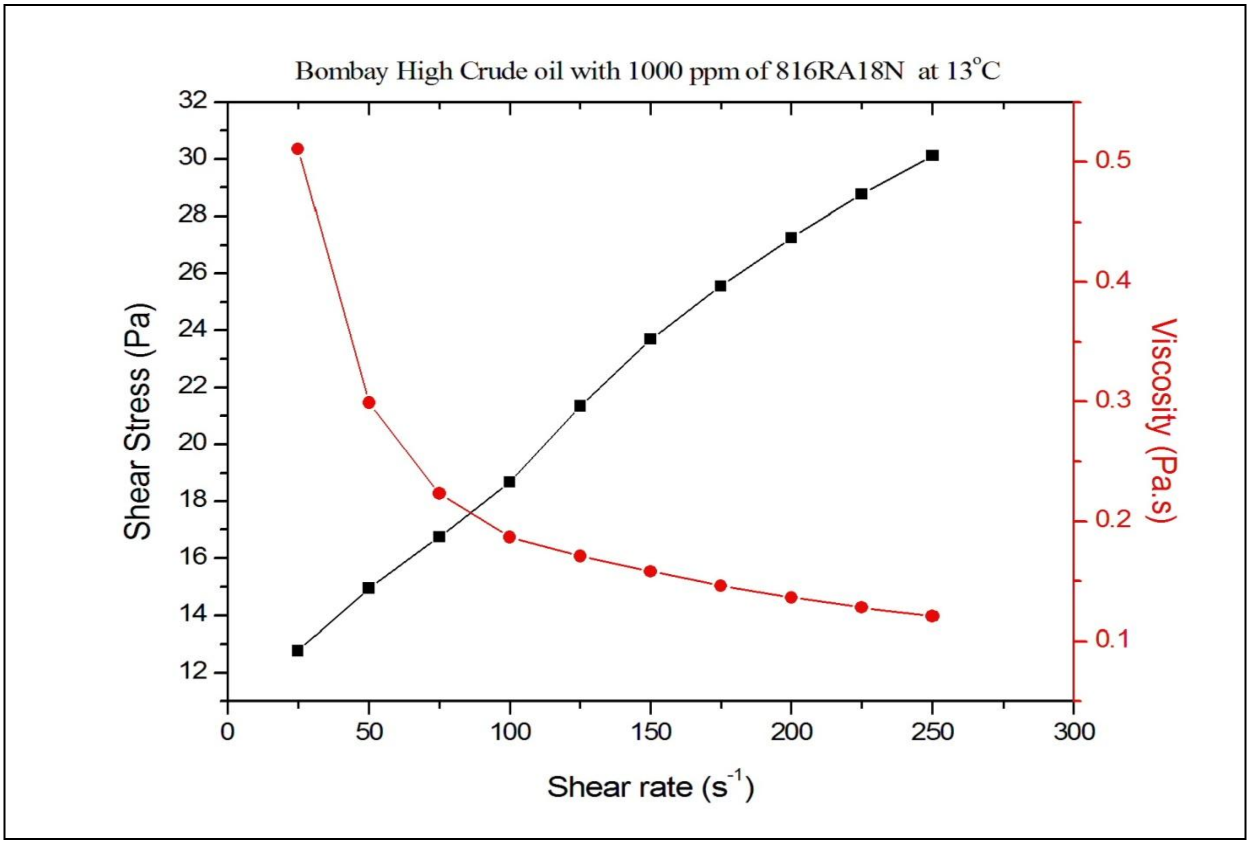

Fig. 3.199 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16RA18N at 13°C

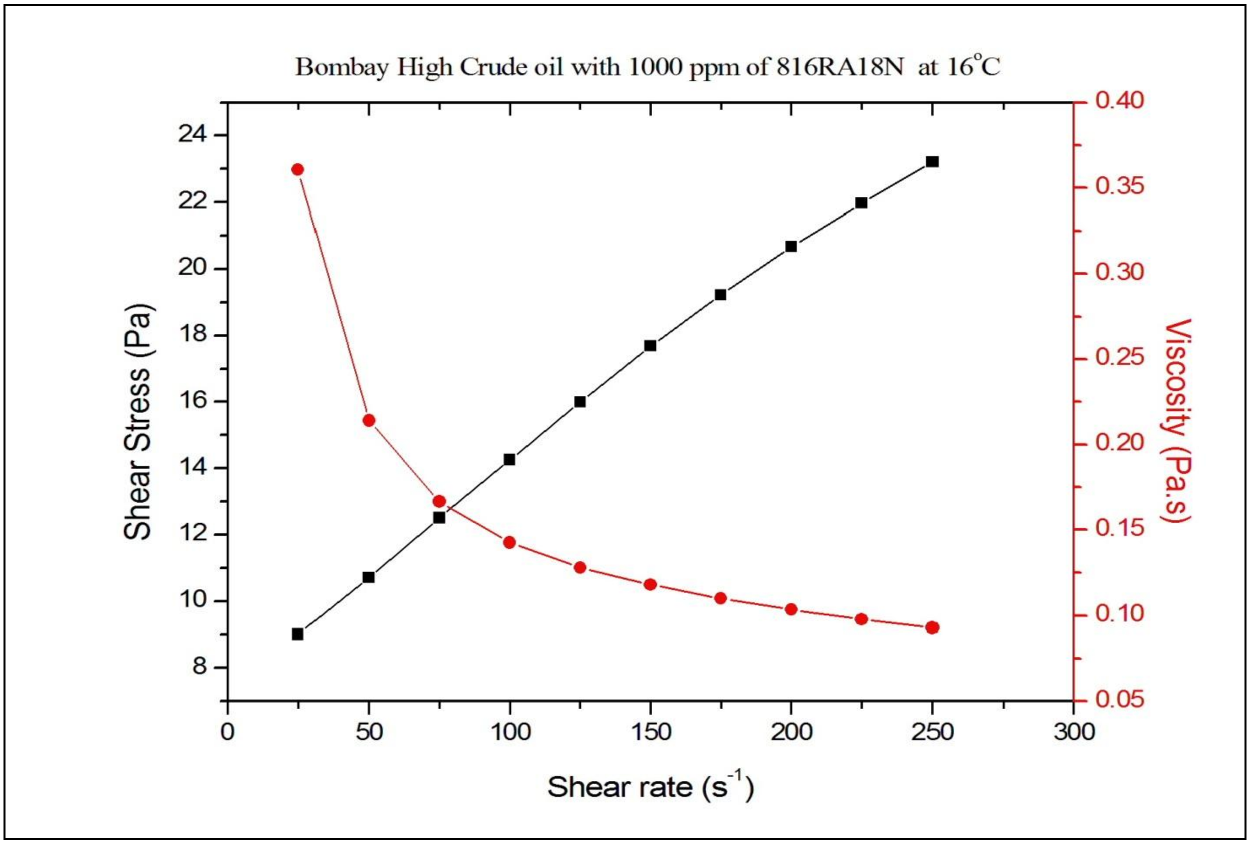

Fig. 3.200 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16RA18N at 16°C

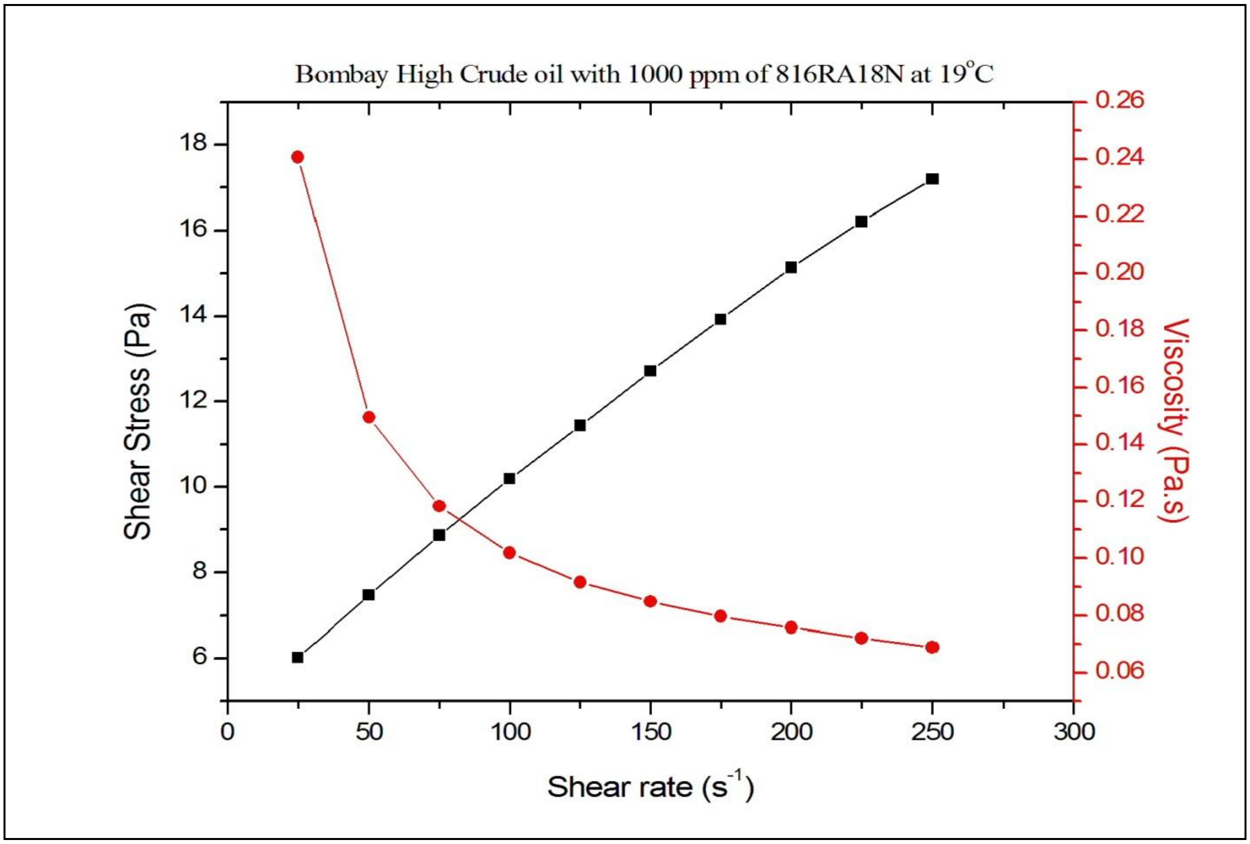

Fig. 3.201 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16RA18N at 19°C

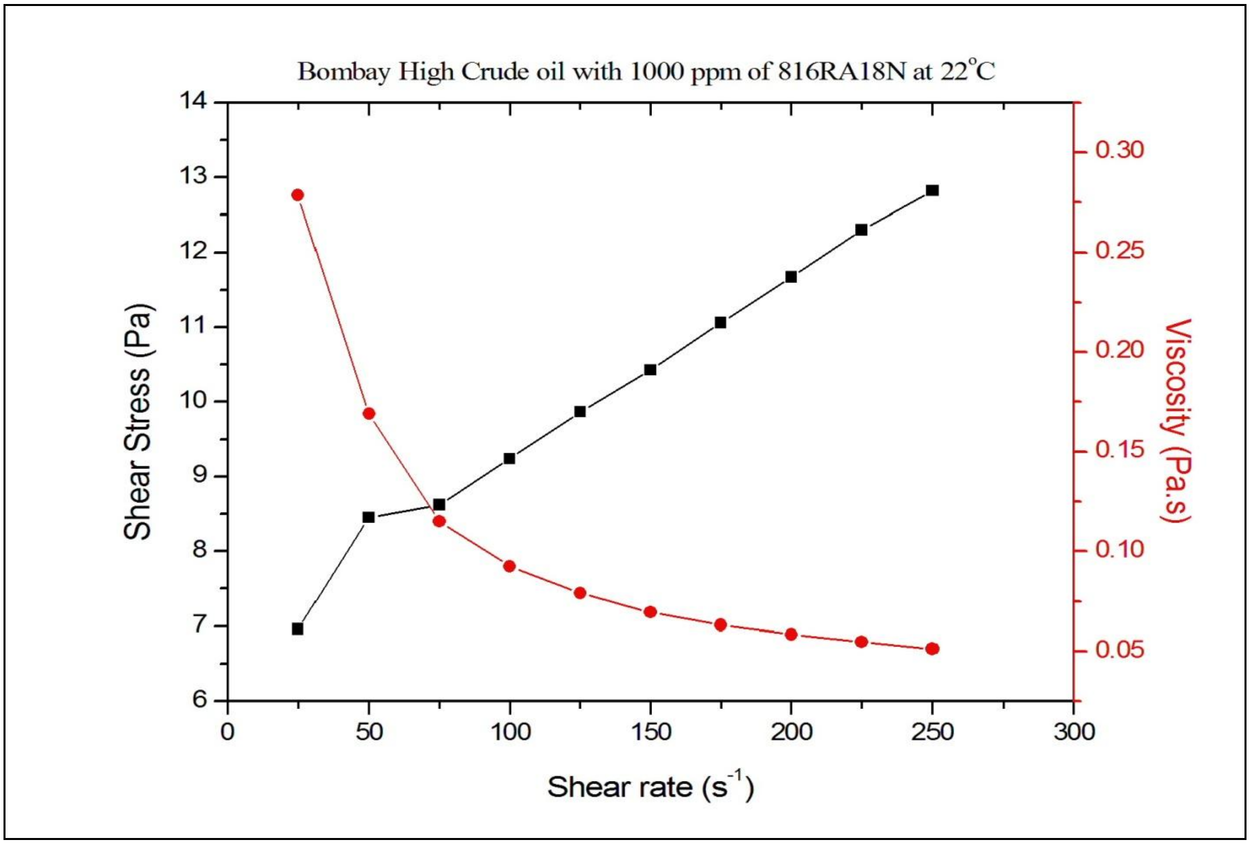

Fig. 3.202 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16RA18N at 22°C

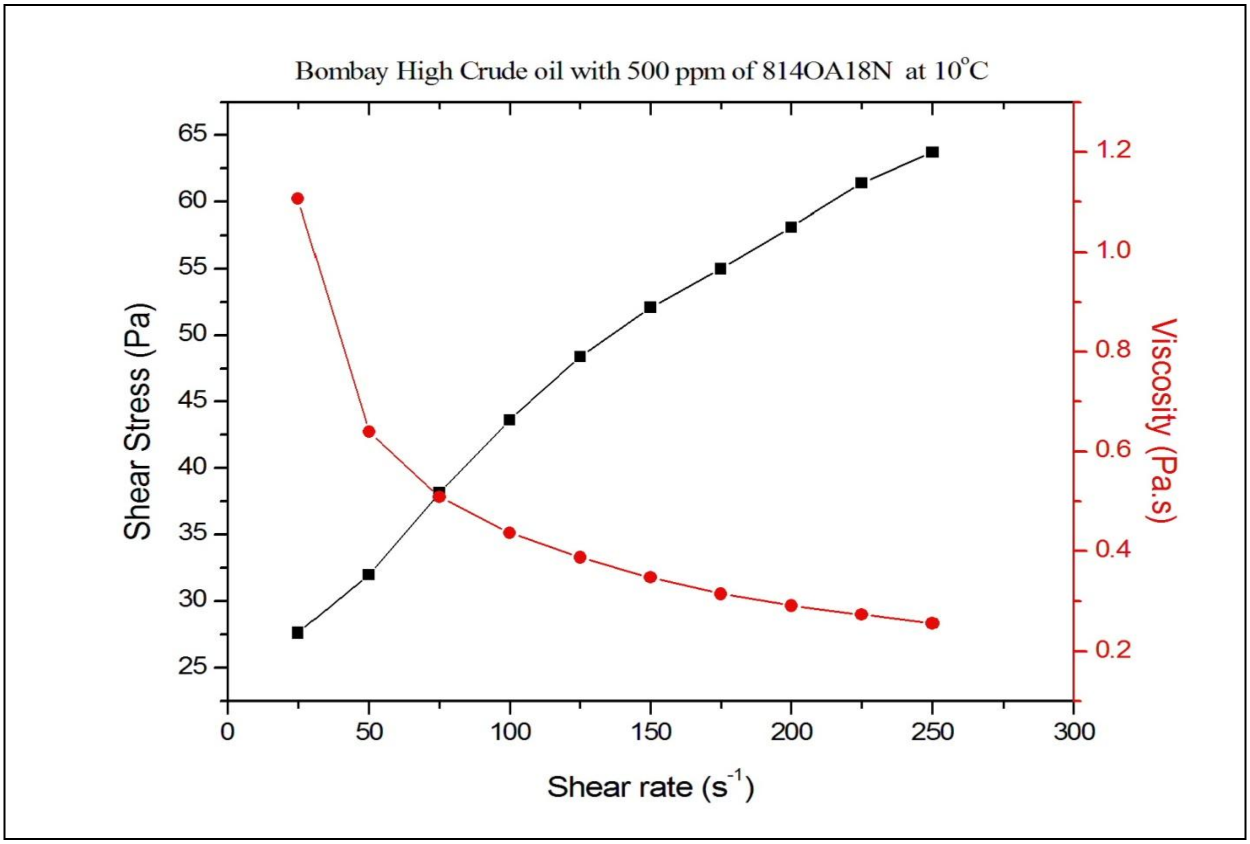

Fig. 3.203 Rheogram of Bombay High Crude oil with 500 ppm of 8-14OA18N at 10°C

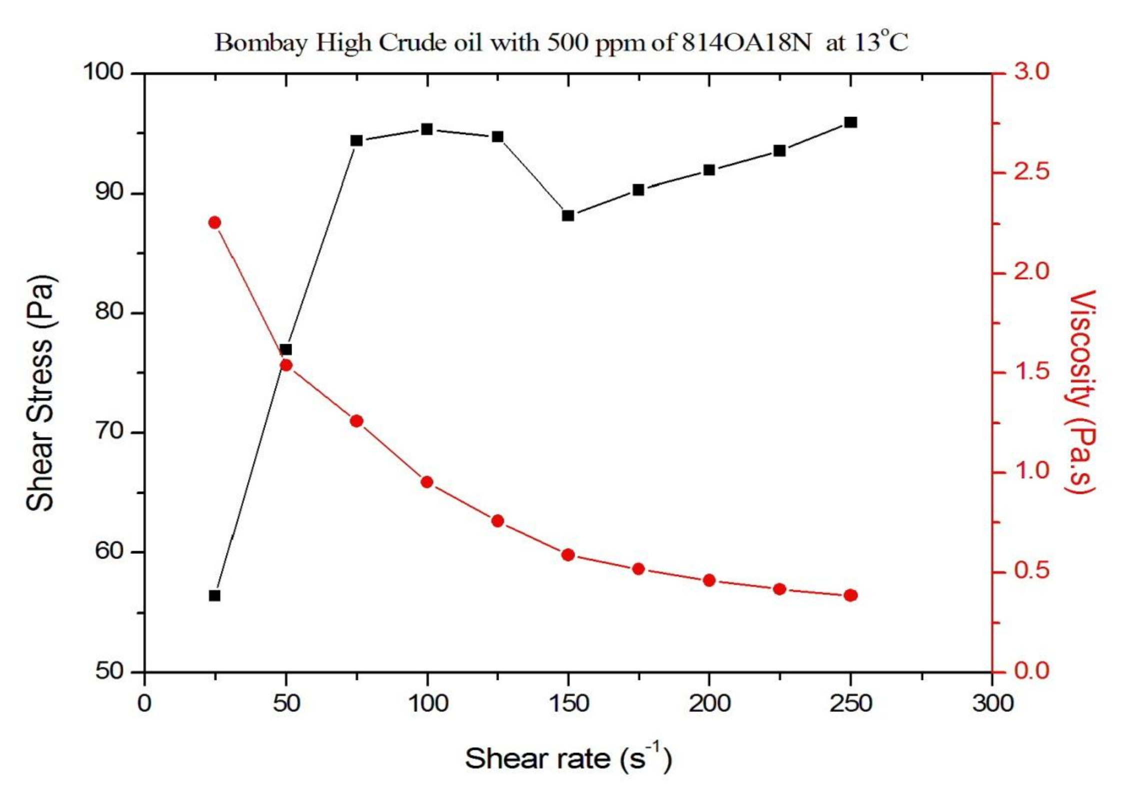

Fig. 3.204 Rheogram of Bombay High Crude oil with 500 ppm of 8-14OA18N at 13°C

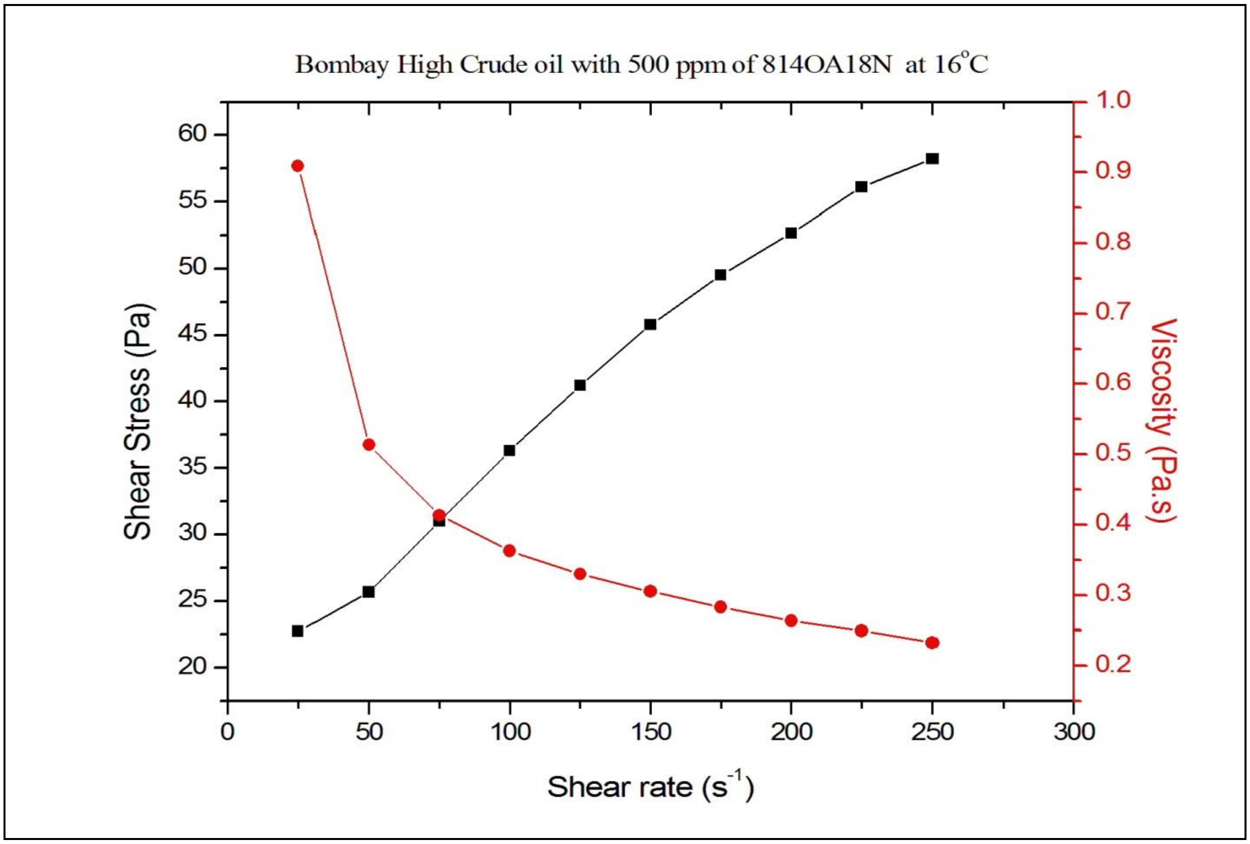

Fig. 3.205 Rheogram of Bombay High Crude oil with 500 ppm of 8-14OA18N at 16°C

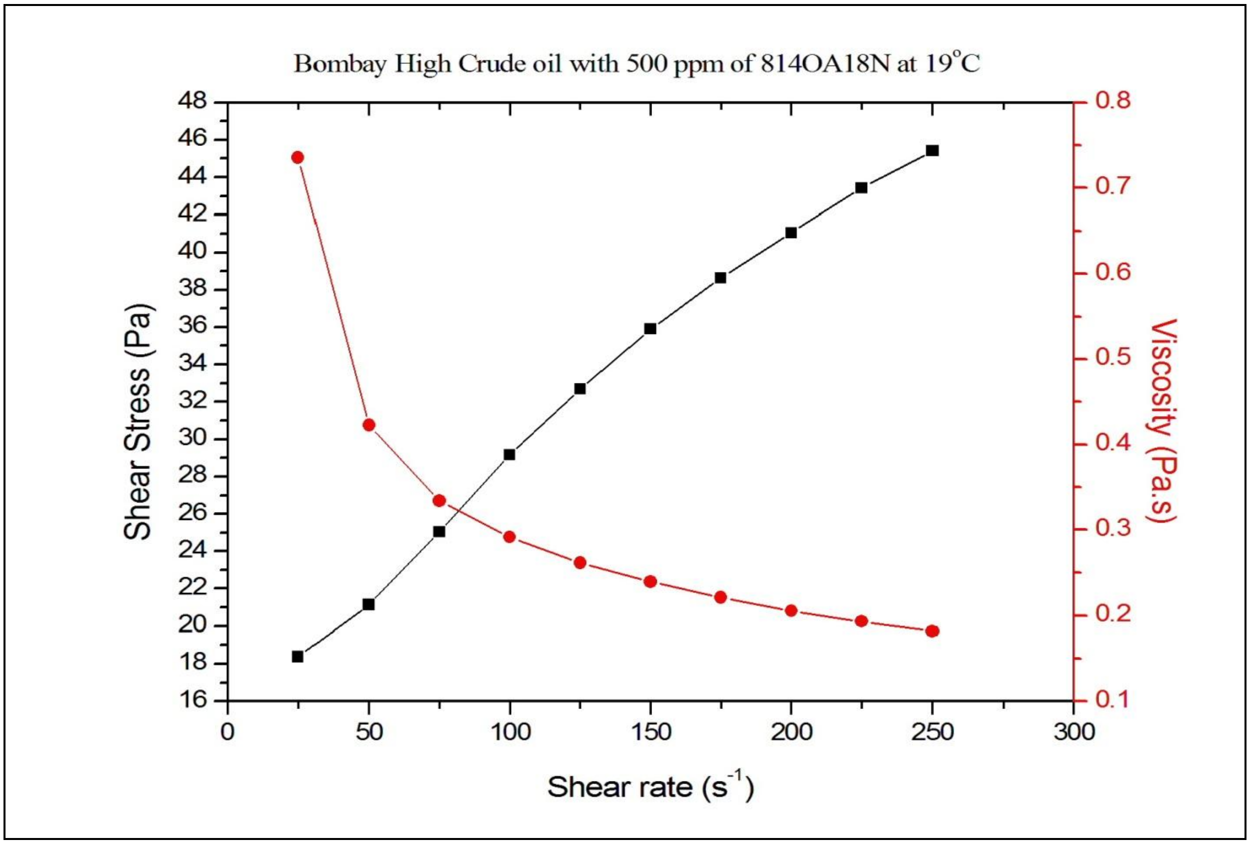

Fig. 3.206 Rheogram of Bombay High Crude oil with 500 ppm of 8-14OA18N at 19°C

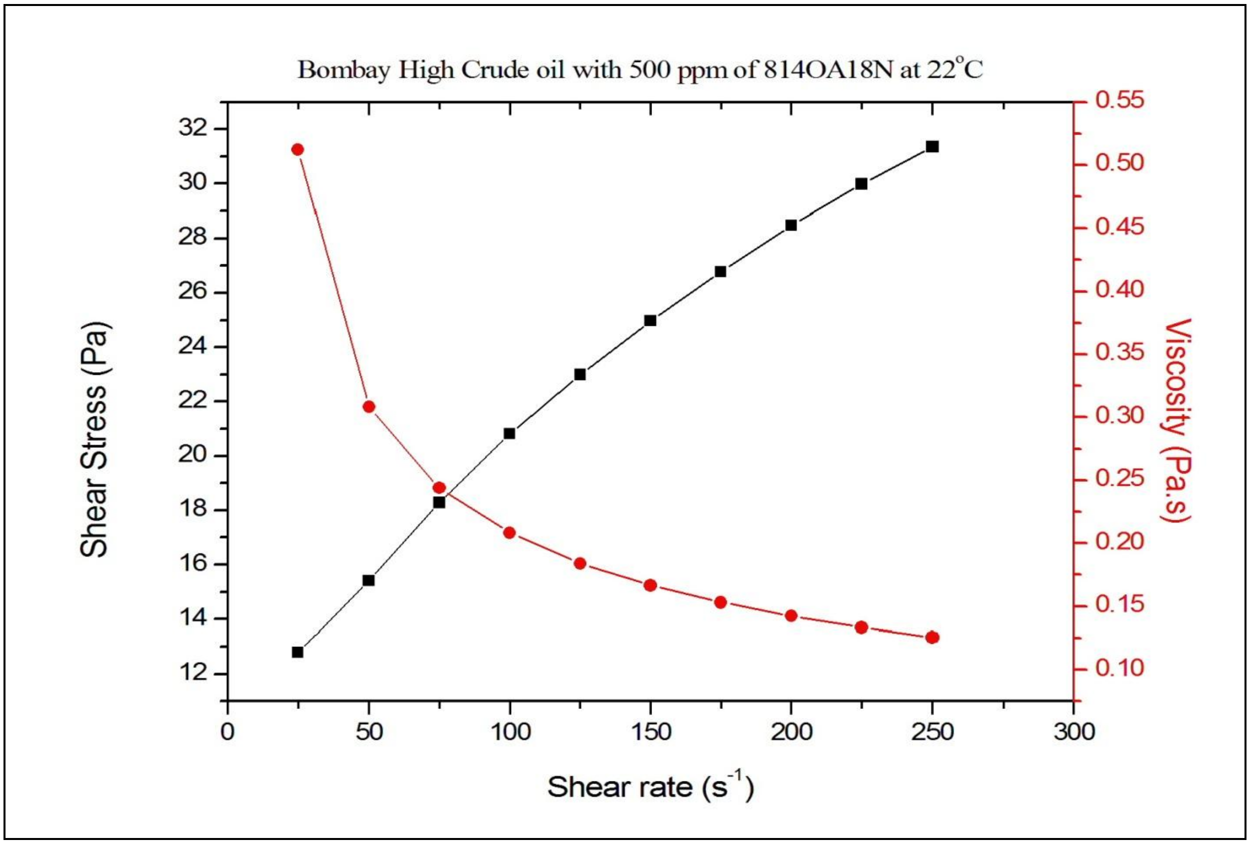

Fig. 3.207 Rheogram of Bombay High Crude oil with 500 ppm of 8-14OA18N at 22°C

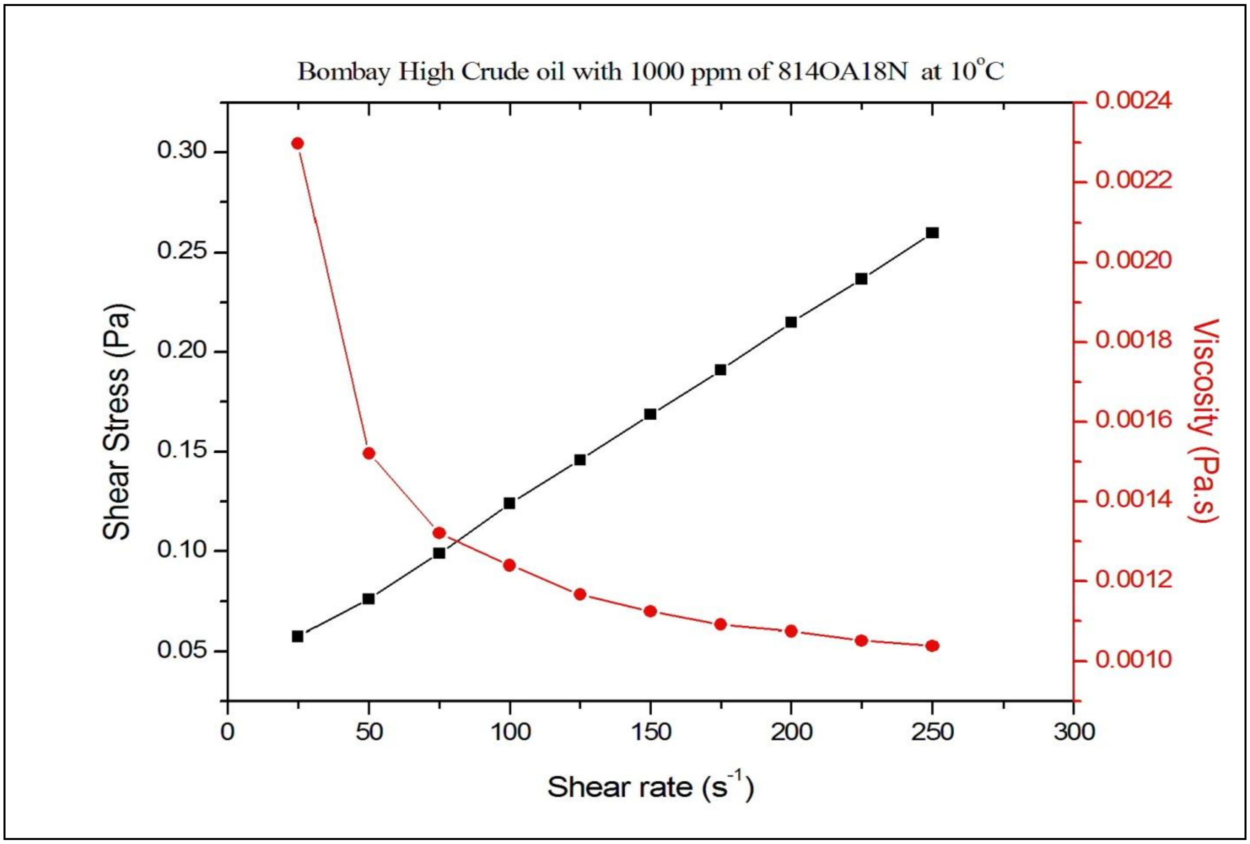

Fig. 3.208 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14OA18N at 10^{o}C

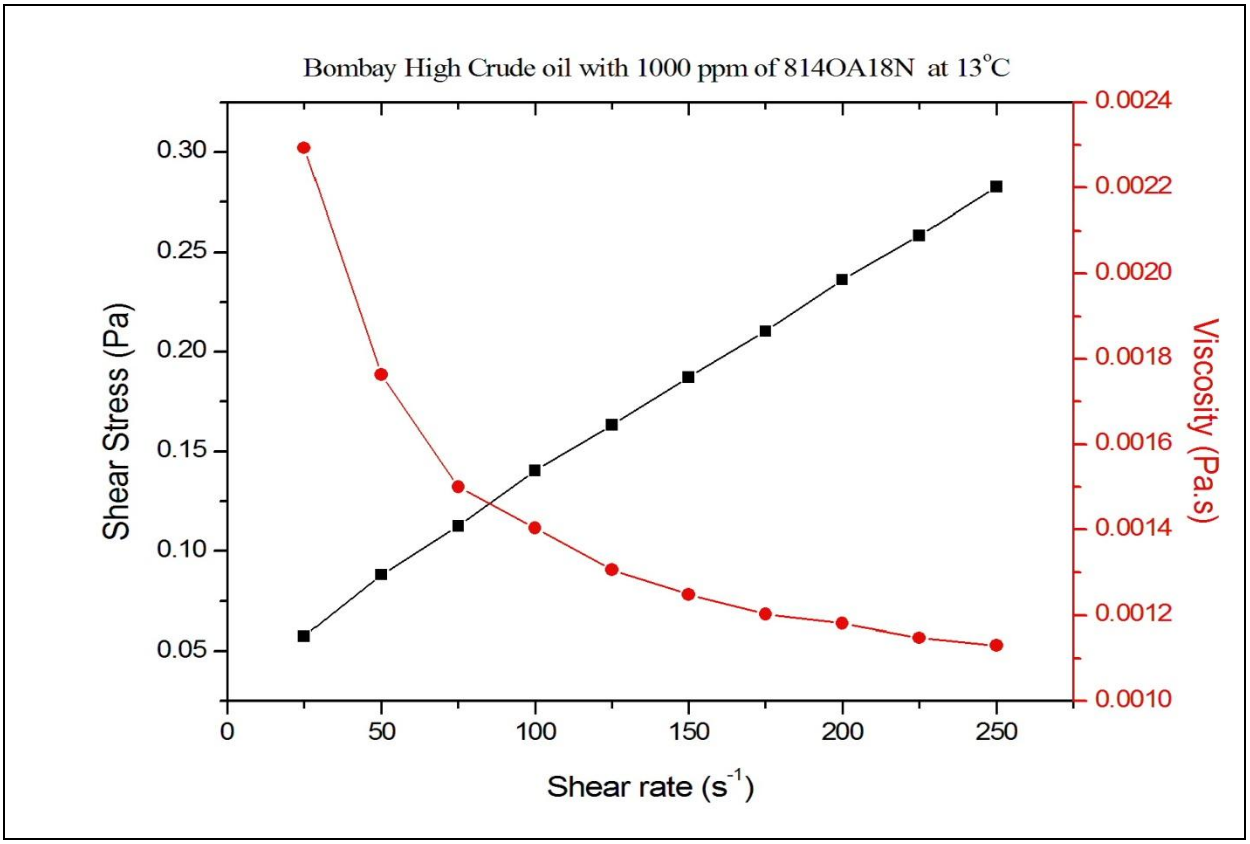

Fig. 3.209 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14OA18N at 13^{o}C

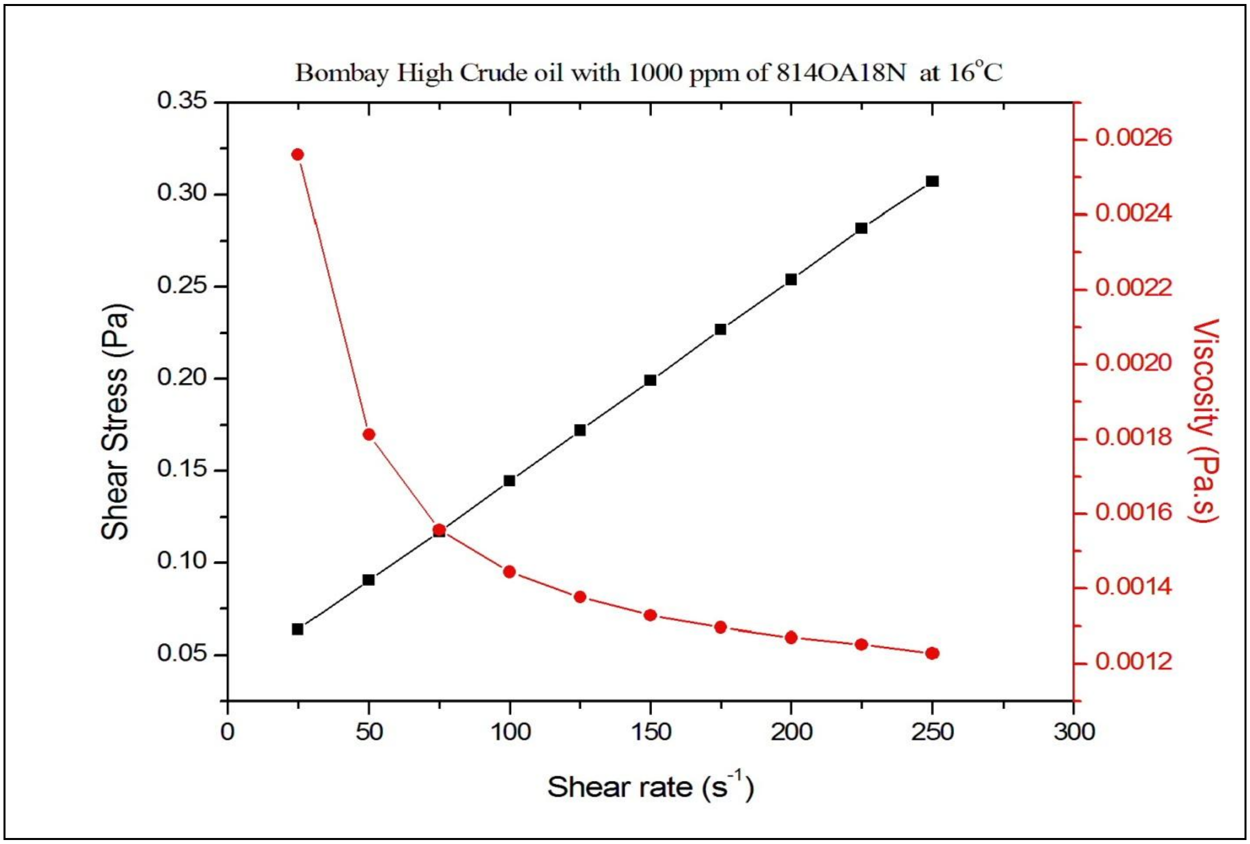

Fig. 3.210 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14OA18N at 16°C

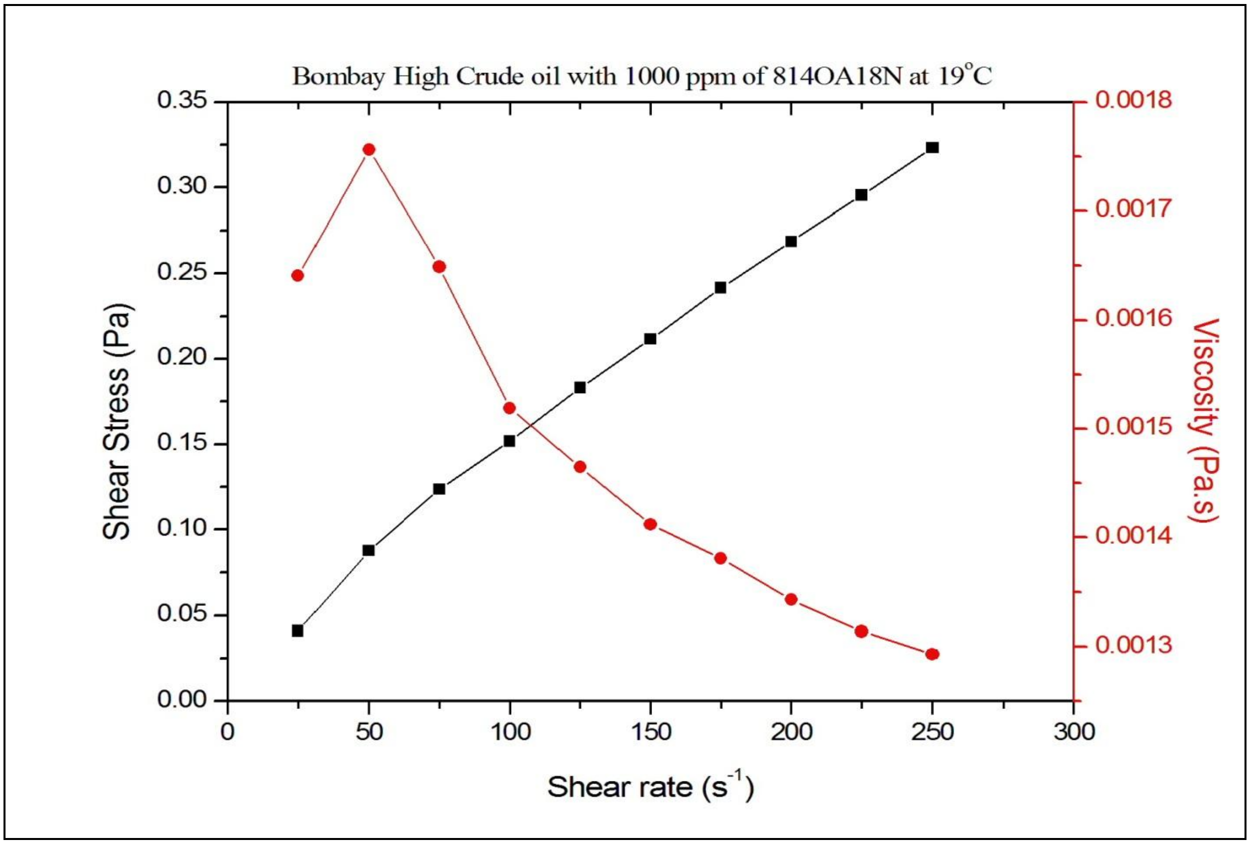

Fig. 3.211 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14OA18N at 19°C

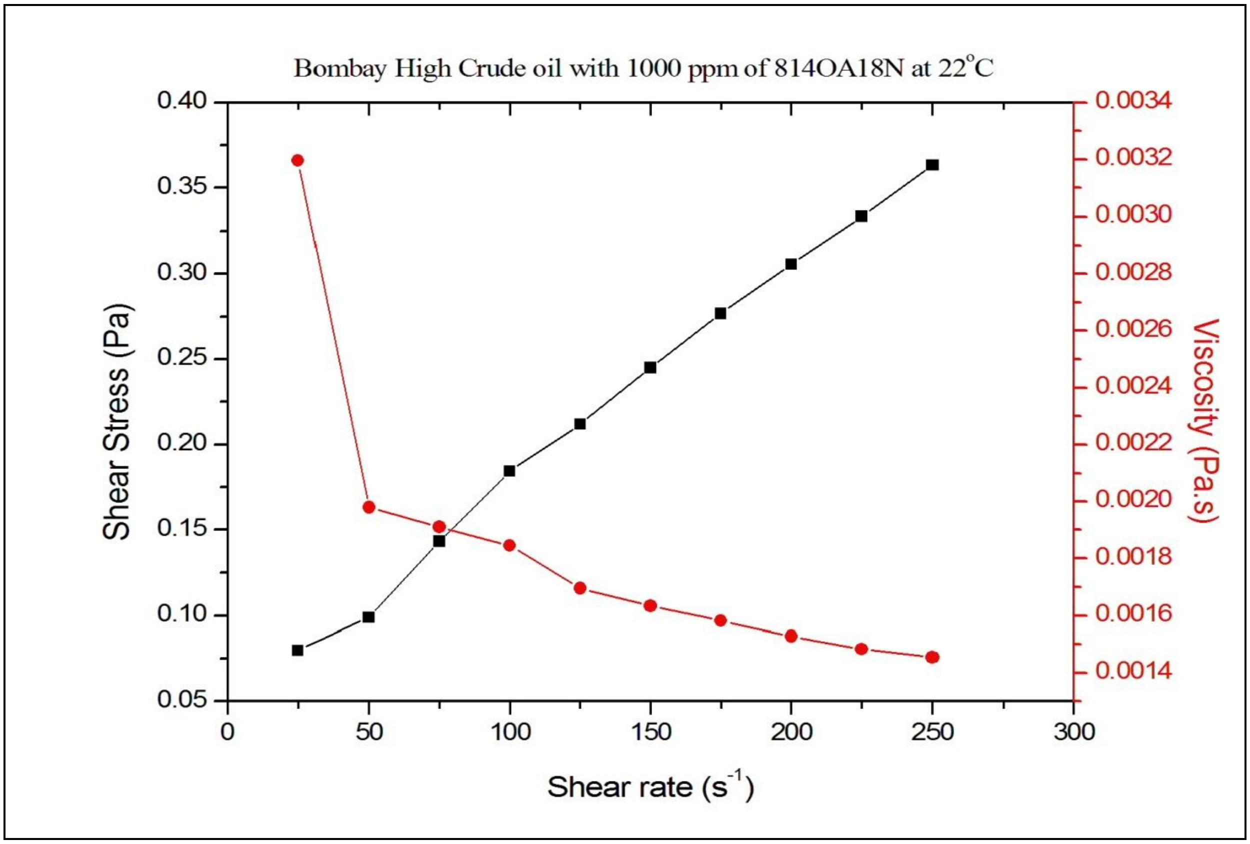

Fig. 3.212 Rheogram of Bombay High Crude oil with 1000 ppm of 8-14OA18N at 22°C

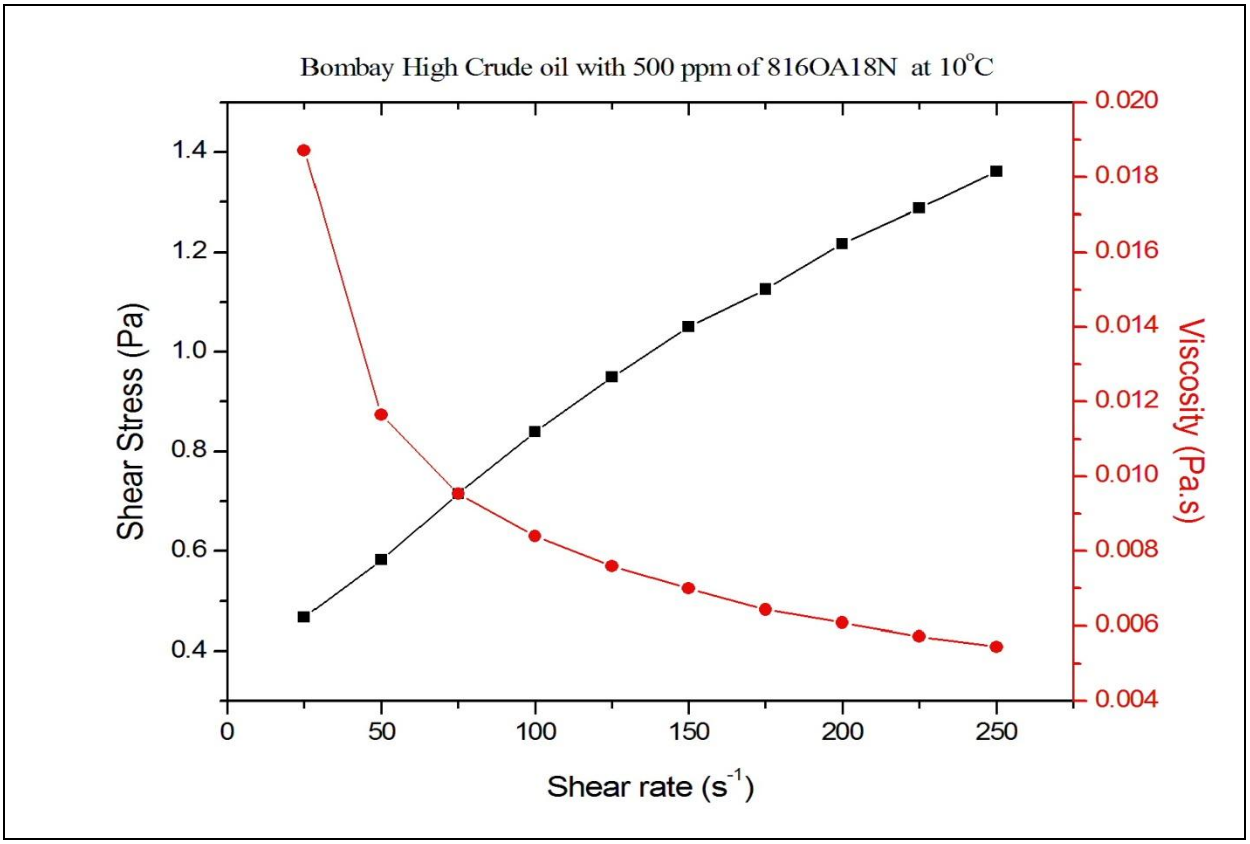

Fig. 3.213 Rheogram of Bombay High Crude oil with 500 ppm of 8-16OA18N at 10°C

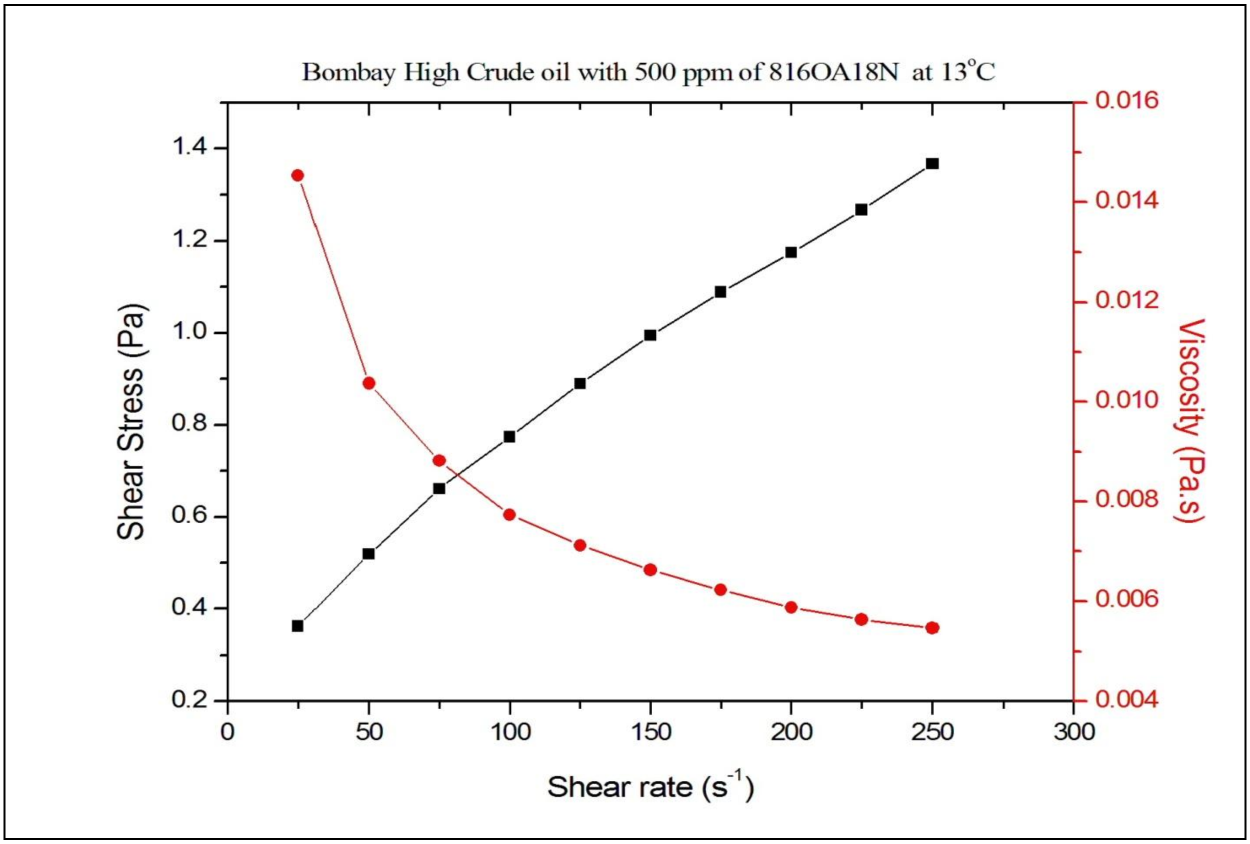

Fig. 3.214 Rheogram of Bombay High Crude oil with 500 ppm of 8-16OA18N at 13°C

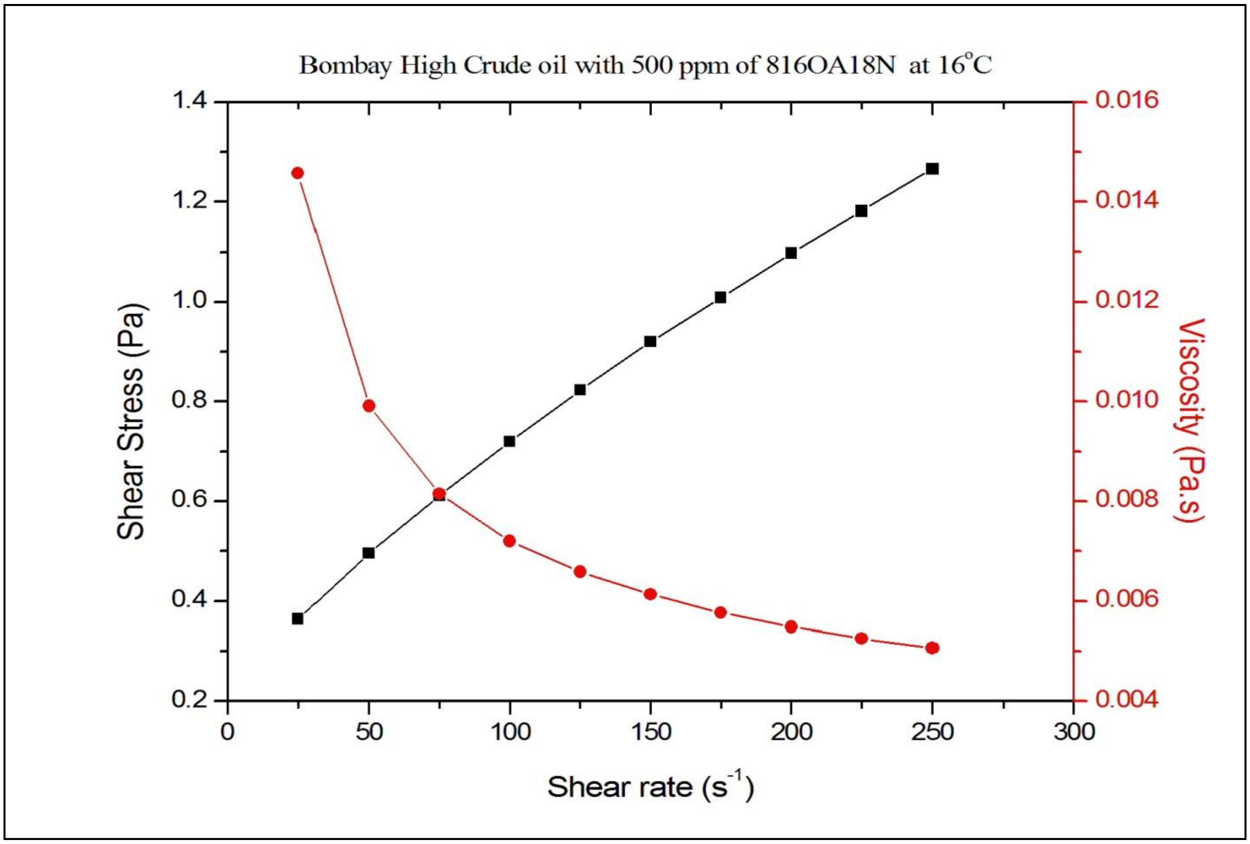

Fig. 3.215 Rheogram of Bombay High Crude oil with 500 ppm of 8-16OA18N at 16°C

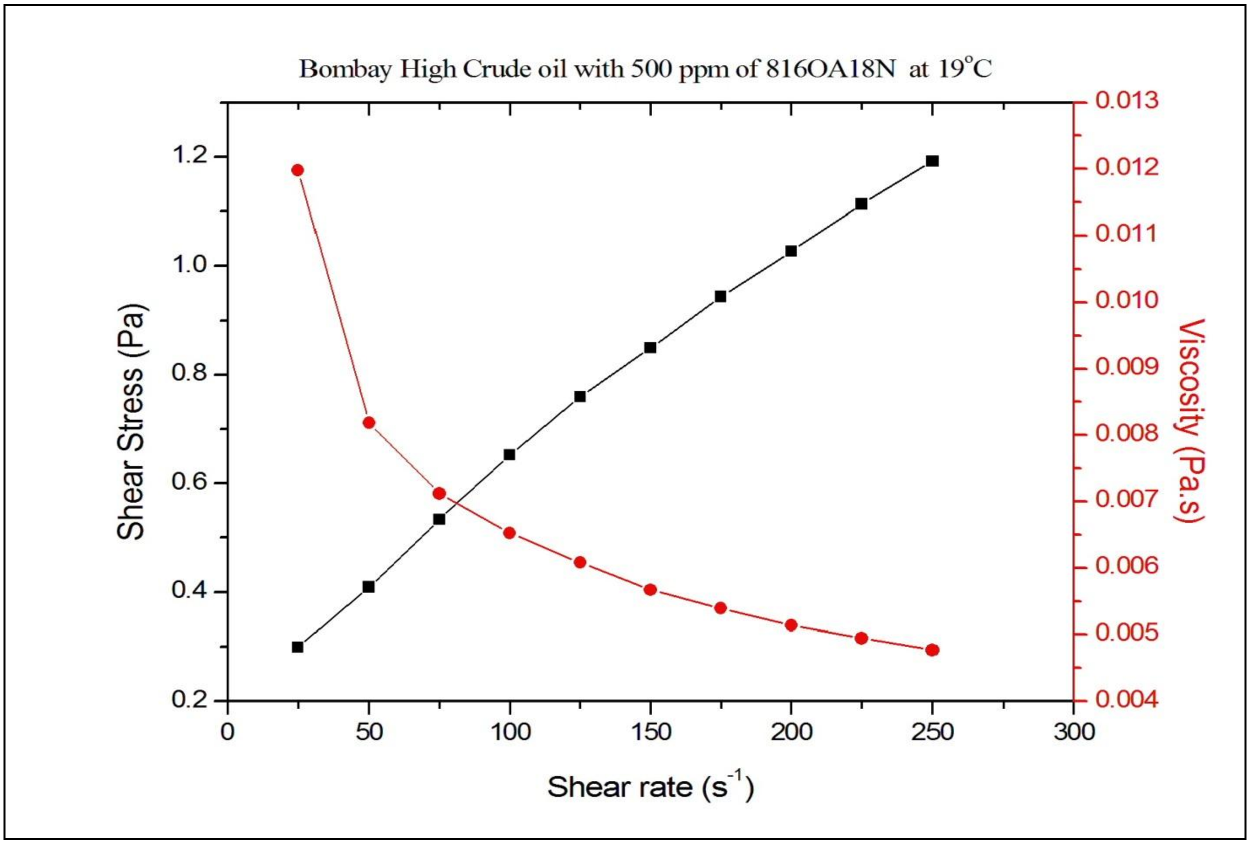

Fig. 3.216 Rheogram of Bombay High Crude oil with 500 ppm of 8-16OA18N at 19°C

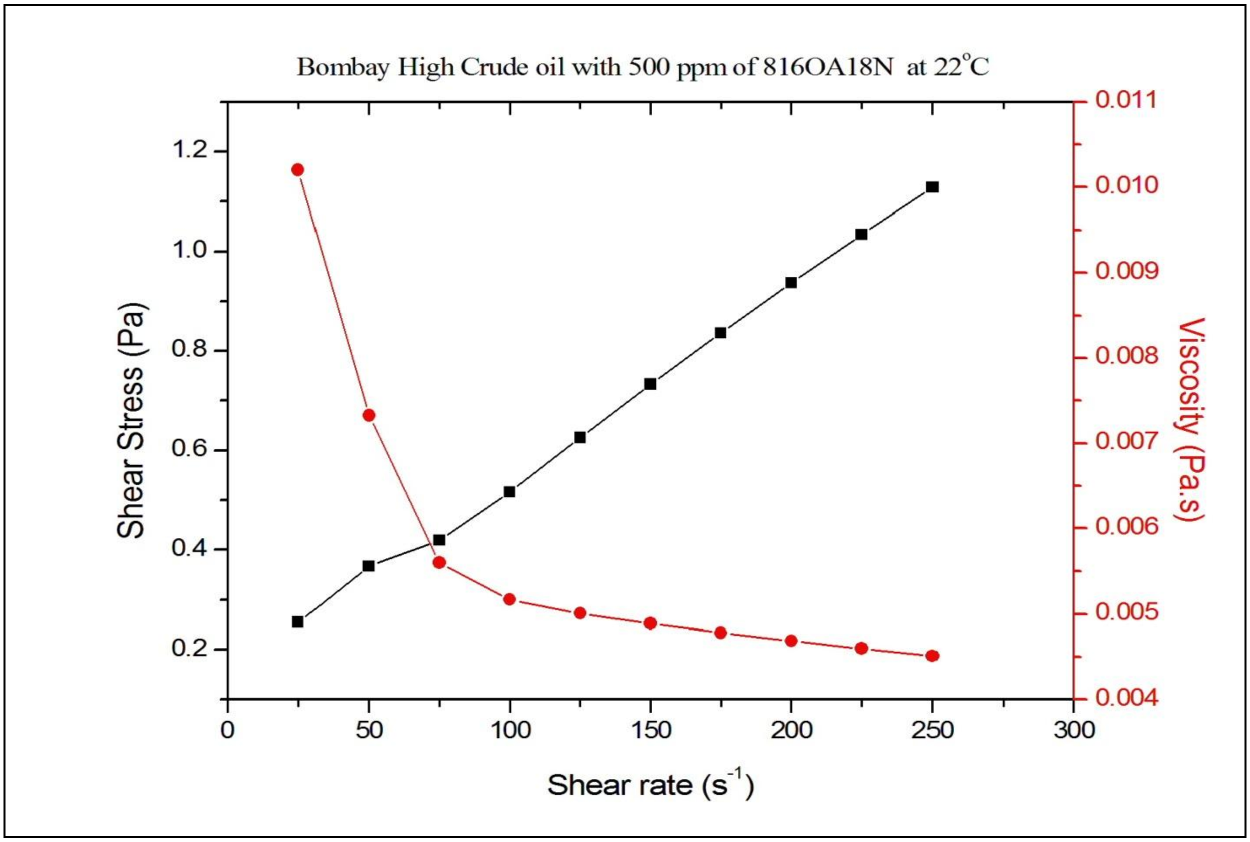

Fig. 3.217 Rheogram of Bombay High Crude oil with 500 ppm of 8-16OA18N at 22°C

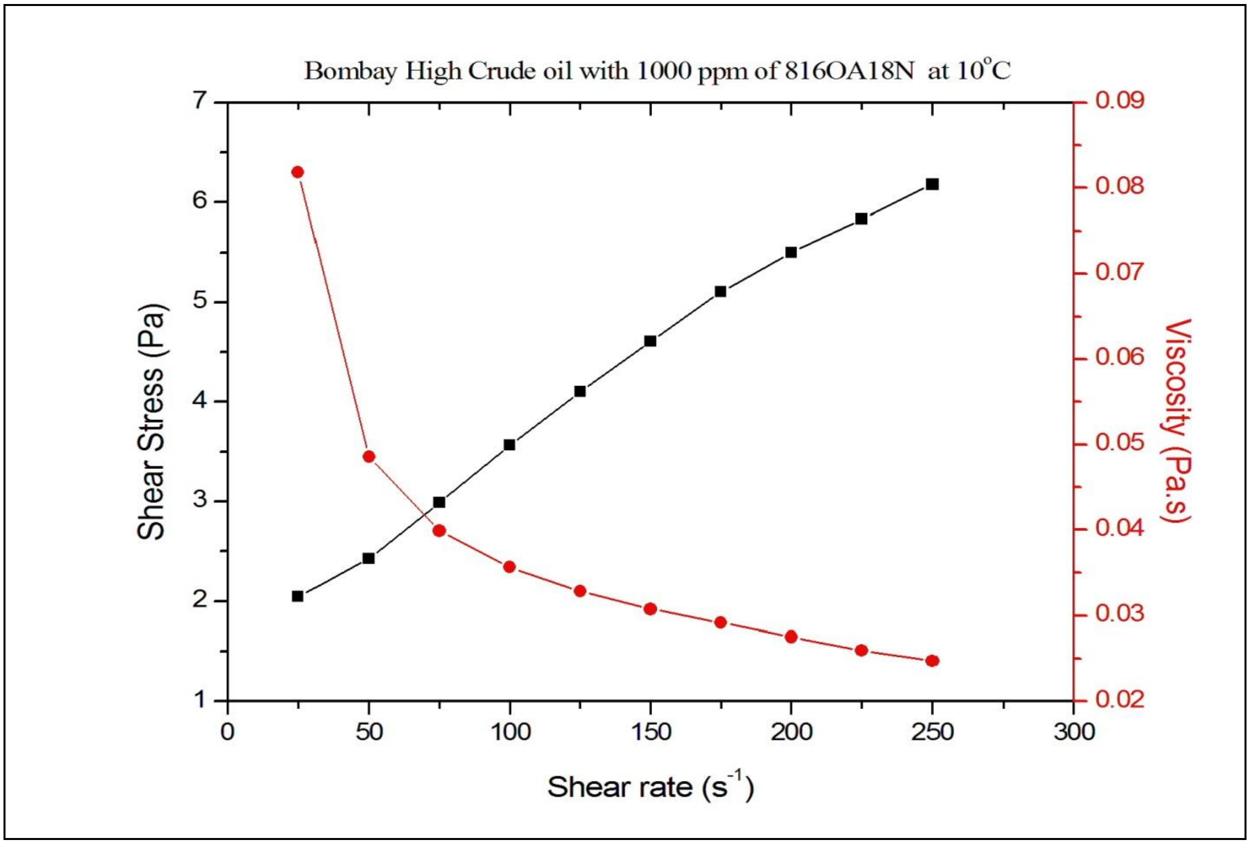

Fig. 3.218 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16OA18N at 10°C

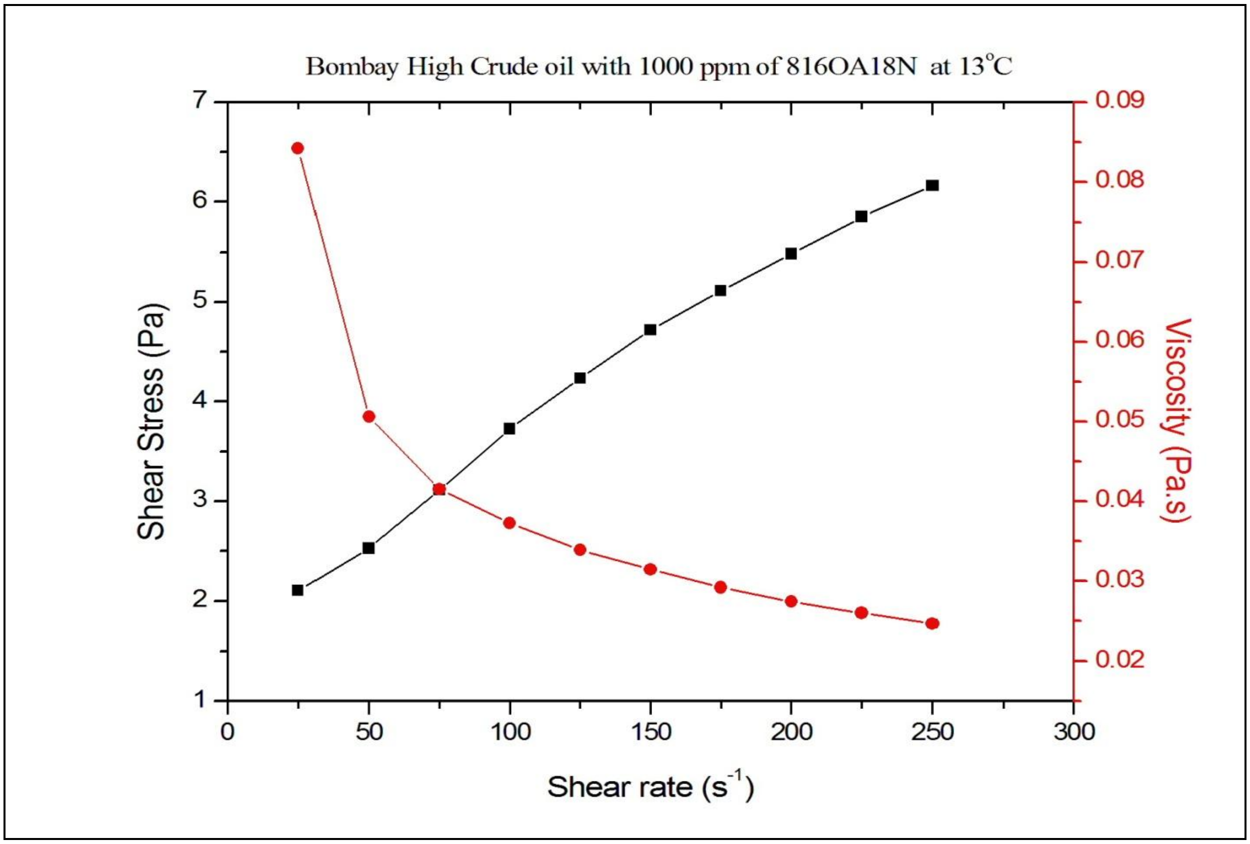

Fig. 3.219 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16OA18N at 13°C

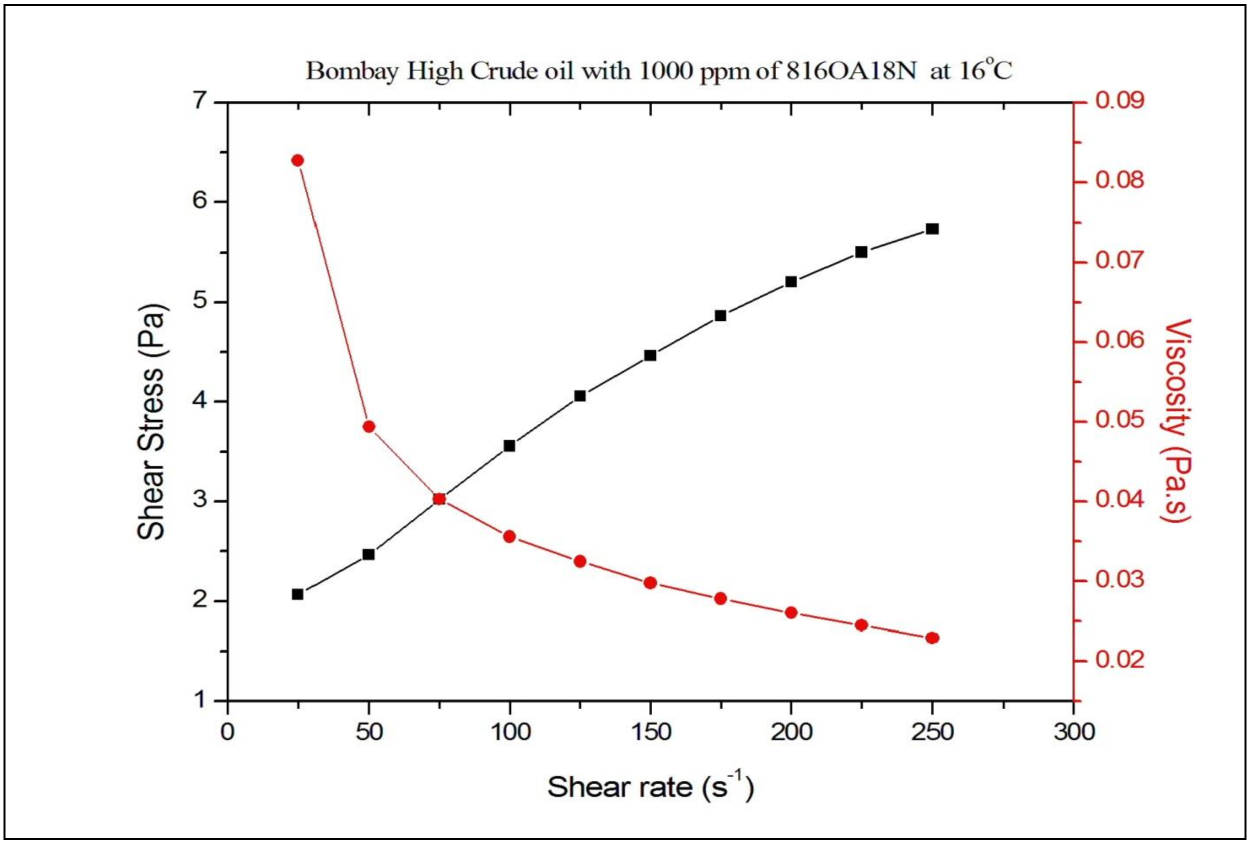

Fig. 3.220 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16OA18N at 16°C

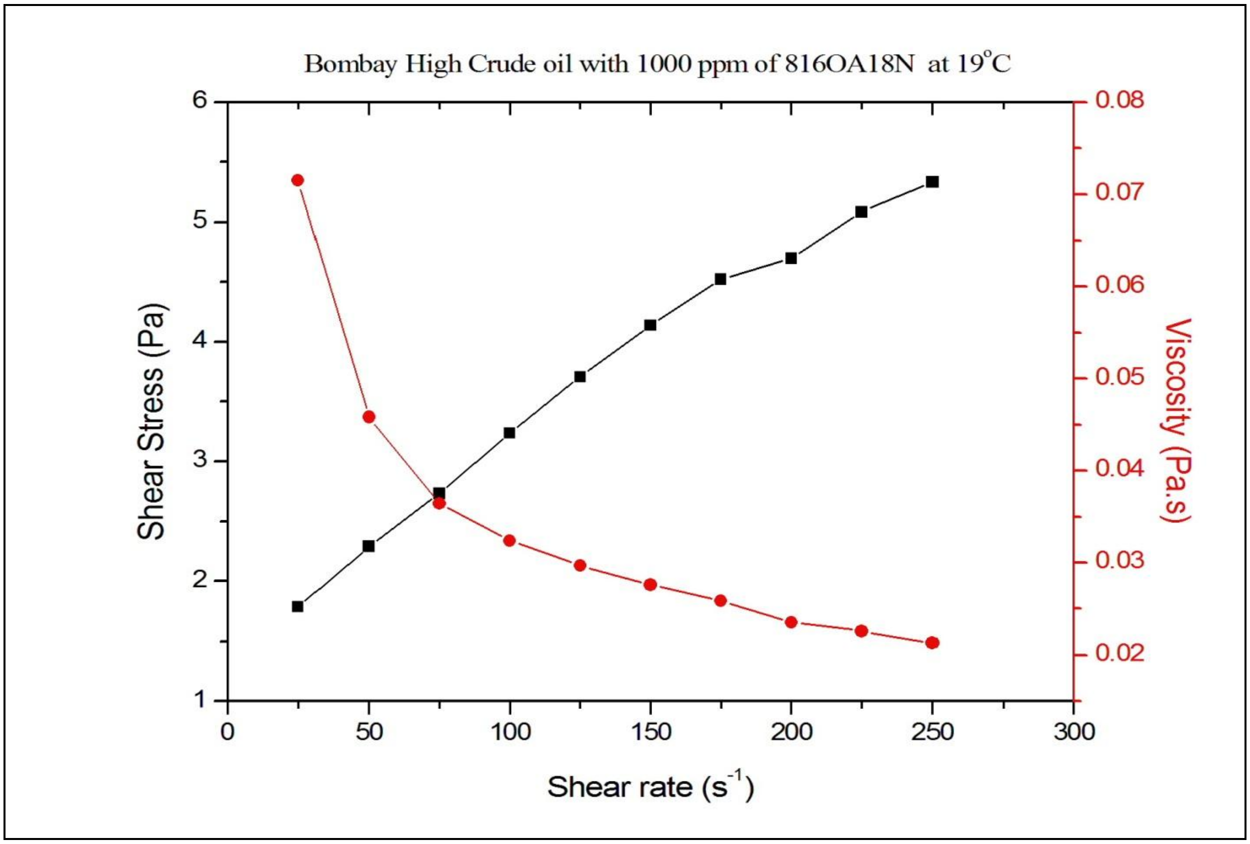

Fig. 3.221 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16OA18N at 19°C

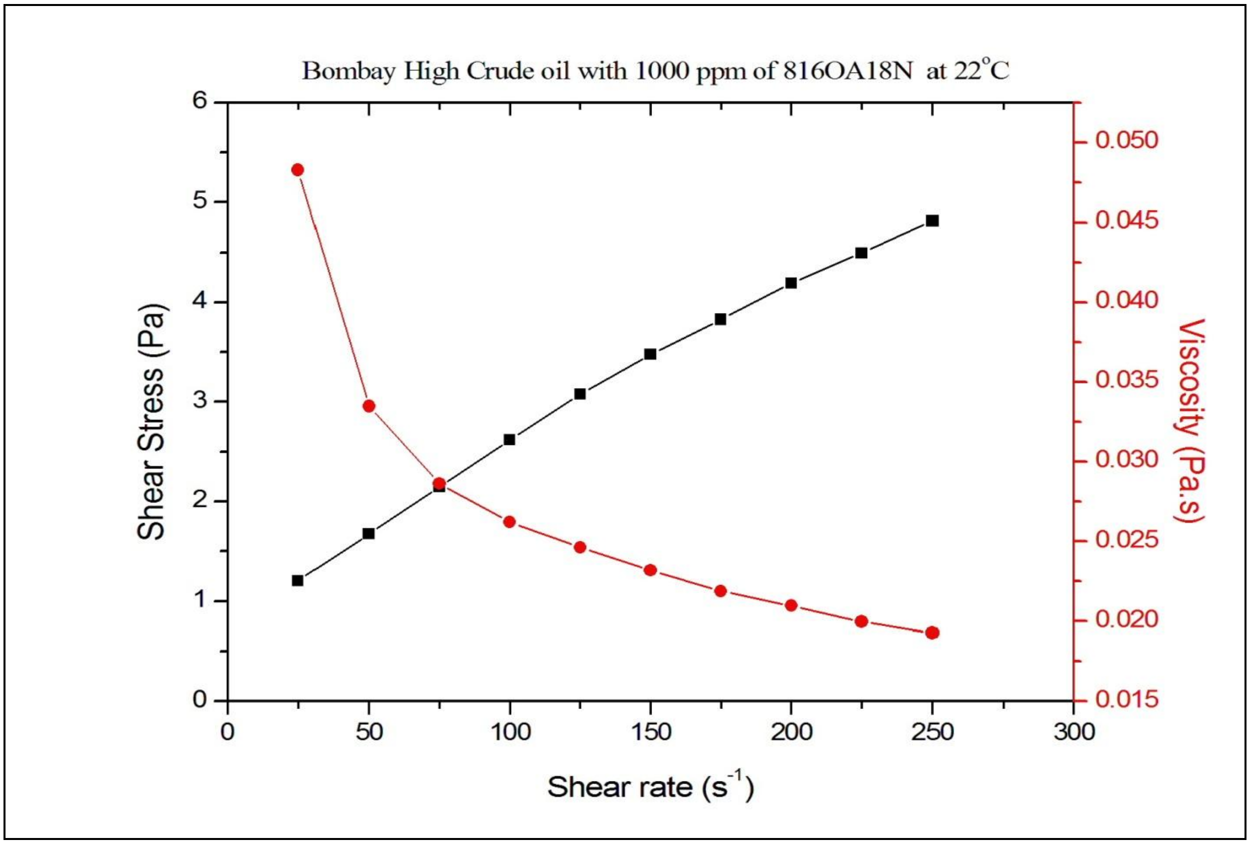

Fig. 3.222 Rheogram of Bombay High Crude oil with 1000 ppm of 8-16OA18N at 22^{o}C

Yield stress and viscosity values of virgin Bombay High crude oil are as shown in Table 3.9. From the shown values, it is clear that at 22^{o}C i.e. pour point of Bombay High crude oil viscosity is 0.1249 Pa-s which increases to 0.3041 Pa-s at 30^{o}C. This clearly reveals that as temperature decreases viscosity increases and vice-versa. Same is the case with yield stress also. It is seen that at 22^{o}C yield stress value is 5.00 Pa which increases to 13.36 Pa at 10^{o}C. So viscosity and yield stress follow same trend in neat condition.

Rheogram of virgin and additive treated crude oil depicts zigzag nature for plot of shear stress v/s shear rate having constant slope overall. Wax crystals present in crude oil stay in the fluid state and show Newtonian behavior at higher shear stress but as shear stress reduces, wax crystallize to impart zigzag nature to curve. Figure 3.140 to 3.143 show Rheogram of virgin Bombay High crude oil at 13^{o}C, 16^{o}C, 19 ^{o}C and 22^{o}C. Fig. 3.143 shows Newtonian behavior of crude oil at 22^{o}C and beyond it, as shear rate v/s shear stress curve passes through origin and viscosity reduces with rise in shear rate and after shear rate 100 s^{-1} it become almost constant. The figure 3.140, 3.141, 3.142 & 3.143 clearly show high value of yield stress as 12.15, 11.03, 10.43 Pa and 5.00 Pa respectively. From such values it can be concluded that at temperature below pour point of crude oil, it shows non-Newtonian behavior, as increase in shear stress is not proportional to shear rate and curve does not pass through origin.

Above mentioned behavior can be explained as follows; at temperatures near pour point and at low shear rates, the energy imparted by shear and dispersed energy in crude matrix tends to break down the wax crystals partially. Secondary bonds form among the flocculated wax structure, thus bringing partial decrease of yield stress and drop in viscosity (thinning effect) without any tendency to flow. By increasing the shear rate, the dispersed energy is high enough to overcome yield stress and start flow, which is evident by increasing the shear stress of flow curve. At lower temperature, the dispersed energy is mostly directed to the decrease of progressive yield stress and thus less amount of energy is given to the decrease of viscosity, hence thinning effect is lowered.

On increasing the shear rate, the size of aggregates decreases and this process releases some of the continuous phase originally immobilized within the aggregates. As a result, the effective dispersed phase concentration decreases and brings decrease of viscosity. The viscosity decreases with increasing the shear rate until the aggregates are completely broken down into the basic particles. So the waxy crude oil system shows non-Newtonian characteristic. [32]

The selection of additives from each series of polymers for further rheological studies was done based on its efficiency to reduce pour point at different concentration ranging from 100 to 1000 ppm. The additive which showed best performance at all concentrations (i.e. from 100 to 1000ppm) was selected which is as shown by circles in table 3.8.

The selected additives are 8-6UA18N, 8-14UA18N, 8-14CA18N, 8-16CA18N, 8-14RA18N, 8-16RA18N, 8-14OA18N and 8-16OA18N were taken at 22^{o}C, 19^{o}C, 16 ^{o}C, 13^{o}C and 10^{o}C at 500 ppm and 1000 ppm concentration and their Rheograms are shown from Figure 3.144 to Figure 3.220. From all the above additives employed 8-14CA18N, 8-16CA18N and 8-16OA18N were capable of reducing rheological parameters of viscosity and yield value to great extent as compared to virgin crude oil at 500 ppm and 1000 ppm concentration respectively.

However, the other additives 8-6UA18N, 8-14UA18N, 8-14RA18N, 8-16RA18N and 8-14CA18N showed variety of behavior by changing viscosity as well as yield value of Bombay High crude oil.

3.3.4 Conclusion:

3.3.4.1 Pour Point of Bombay High crude oil

From Table 3.7 showing pour point data for Bombay High crude oil, it can be concluded that additives 8-6UA18N, 8-14UA18N, 8-14CA18N, 8-16CA18N, 8-14RA18N, 8-16RA18N, 8-14OA18N and 8-16OA18N showed good efficiency as pour point depressants. Probable reason for good efficiency of these additives can be matching of carbon number of the wax present in Bombay High crude oil with pendant chain. These additives successfully adsorbed and co-crystallized on wax surface inhibiting wax crystal growth. Additives having effective PPD behavior were found to have C_{13} to C_{20} pendant alkyl chain length. Also the presence of aromatic ring made molecule more bulky which helped in improving its pour point depressing tendency. Hence it can be concluded that the matching of carbon number, presence of aromatic ring and polar ester, nitrogen group together acted effectively to depress pour point of Kosamba-33 crude oil.

3.3.4.2 Rheological Studies

Rheological behavior of virgin and some additive treated crude oil at various concentration and temperature were studied. The Rheogram shows alteration in viscosity due to additive treatment at different temperatures and shear rates. The results obtained clearly depict that some of additives like 8-14CA18N, 8-16CA18N & 8-16OA18N brought significant reduction in viscosity of Bombay High crude oil. Also as viscosity of crude oil decreases then the yield stress needed to start flow also decreases and so it is possible to keep crude oil in flowing condition even at low temperature. 8-14CA18N at 500 ppm reduced viscosity to 0.0208, 0.0263, 0.0274, 0.0264 and 0.0231 Pa-s at 22^oC, 19^oC, 16^oC, 13^oC and 10^oC respectively. Also at 1000 ppm concentration the viscosity values registered are 0.0198, 0.0266, 0.0333, 0.0305 and 0.0270 Pa-s at 22^oC, 19^oC, 16^oC, 13^oC and 10^oC respectively. Also for 8-16CA18N at 500 ppm concentration 0.0095, 0.0111, 0.0113, 0.0101 and 0.0096 Pa-s viscosity values were reported at 22^oC, 19^oC, 16^oC, 13^oC and 10^oC respectively. When concentration increased to 1000 ppm 0.0026, 0.0027, 0.0027, 0.0025 and 0.0023 Pa-s at 22^oC, 19^oC, 16^oC, 13^oC and 10^oC respectively were observed. For 8-14CA18N additive the values of yield stress are also in the range of 0.43 Pa to maximum 1.56 Pa. And for 8-16CA18N additive the yield stress values found to be in range of 0.045 to 0.54 Pa. Similar low values of Viscosity and Yield Value were observed for 8-

16OA18N. Both the values of viscosity and yield stress for above additives observed are pretty low as compared to virgin crude oil. Hence these additives can be successfully employed for Bombay High crude oil.

This behavior may be explained by the two reasons: on one hand PPD have changed the morphology of paraffins in crude oil, resulting in decrease of pour point, thereby reducing temperature at which viscosity increases. On the other hand, intermolecular forces between paraffins, asphaltenes and resins becomes weaker when PPDs are added because of nucleation in case of paraffins and H-bonds between PPDs, asphaltenes, resins which keeps these molecules in dispersed phase. As a result, viscosity is reduced.

Now the other additives coded 8-6UA18N, 8-14UA18N, 8-14RA18N, 8-16RA18N and 8-14OA18N have given reverse results that is increased the viscosity of Bombay High crude oil. It can be observed from the table 3.9 that with increase in pendant alkyl chain length and concentration of additive the viscosity and yield stress has been increased. Flow behavior is reduced to considerable extent. The yield stress has increased to as high as 73.16 Pa indicating reverse effect of additive. So it is very much clear that above mentioned additives are not suitable for Bombay High crude oil. The reason for such high values of rheological parameters may be such that the polymer additive becomes insoluble in crude oil and forms aggregates, which precipitate out from the crude along with wax crystal without being properly adsorbed on the surface. Due to this they cannot make a change in the crystal structure but instead, the pendant chains of polymers interlock into one another like a zipper. Now the polymer molecules cannot slide over one another which results in an increase in viscosity and yield value of the crude oil. [25, 35]