Improvement in transportability of Indian heavy crude oil using novel surfactant

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Rheological behaviour of Indian heavy crude oil has been investigated using novel surfactant, Brij 30. The results have been compared with addition of dilutants namely mineral oil and 3-pentanol. The effect of addition of additives on viscosity, yield stress and viscoelastic behaviour including non-Newtonian viscosity, elastic modulus, loss modulus, phase angle and complex viscosity and thixotropy are studied. The most efficient additive among the three is found to be Brij 30. Addition of 10% 3-pentanol, mineral oil and Brij-30 reduce the viscosity of crude oil by 79.75, 42.1 and 87%, respectively at 25°C. Yield stress reduces by 98% after addition of Brij 30. Thixotropotic area for crude is reduced to 9.11 kPa/s from 326.53 kPa/s after addition of 10% Brij 30. Brij-30 dropped interfacial tension of crude to a greater extent compared to other additives. FTIR studies show disappearance of C=O, C=C and NO₂ groups in surfactant-crude mixture which indicate effectiveness of the Brij-30 surfactant. Brij 30's efficiency as a surfactant may be employed to improve rheological characteristics of heavy crude oil for proper pipeline transportation.

Keywords: Indian Heavy crude, Yield Stress, Thixotropy, Viscoelastic behaviour, Brij 30

In today's growing world, crude oil is one of the most actively traded commodities. It has great impact on both economy and politics of the whole world. Demand growth is prominent in developing countries like India and China, whose economies witnessed a remarkable growth in the last few years. Heavy crude oil plays a significant role in world's recoverable oil resources. Heavy crude oil is defined as the crude oil having API gravity equal or lower than 20°API. According to the statistics presented by OPEC (Organisation of Petroleum Exporting Countries), heavy crude oil solely represents almost 50% of the recoverable oil resources¹. Heavy crude oil in highly viscous and poses great difficulty in pipeline transportation leading to high economic losses. Several methods have been identified in the past to tackle this problem. Those methods have been compared to find the best method for reducing the viscosity of waxy crude oil for easier transportation².

Pipelines are the most economical and convenient way for the transportation of crude oils and their products. The viscosities of heavy crude at 25°C might reach more than 10⁵ mPas. For easy pipeline transportation viscosity of crude oil should not exceed 400 mPas^{3,4}. The transportation through pipelines also becomes difficult because of lower mobility and flowability at higher viscosity⁵. Crude oils are mainly

composed of carbon, hydrogen, altering amount of waxes and small amount of asphaltenes. Additionally, traces of nitrogen, sulfur, oxygen, nickel and vanadium might be present in different forms. Moreover, properties of crude oils vary from region to region^{6,7}. These properties make conventional pipelining unsuitable for transporting heavy crude oils from the reservoir to refinery. Preheating of crude followed by heating of pipelines, water sheath injection around highly viscous crudes, use of pour point depressants (PPD) and the formation of oilwater emulsion are other alternative methods employed for easier transportation^{8,9}. However, the higher cost of equipment and difficulty in restarting after shutdown makes heating of economically non-viable. The disadvantage associated with emulsifier is the separation of water from crude oil at the utilization end. PPDs function better when used with mechanical methods such as pigging. Evidently, all of these methods have some technical or economical drawbacks.

A suitable alternative for reducing viscosity is dilution. It consists of the addition of lighter liquid hydrocarbons typically condensates from natural gas production; lighter crude and different solvents to heavy crude oils. Dilution increases the pumping and pipeline cost due to increase in transport volume.

Separation of additives is also difficult at the utilization end. Again, addition of condensate or light oil may affect the stability of asphaltenes and paraffins and cause precipitation and pipeline clogging¹⁰. To overcome this disadvantage 3-pentanol and mineral oil are used which are very effective in reducing viscosity. The present investigation consists of reducing the viscosity of heavy crudes by diluting them with polar solvents namely 3-pentanol, mineral oil and a surfactant Brij-30 and their comparative effectiveness of viscosity reduction. 3-pentanol is an effective solvent in reducing the viscosity of heavy crudes in comparison to other additives like toluene, due to hydrogen bond interactions with the hydroxyl groups present in some of the asphaltenes. Usually, for greater relative reduction of viscosity of crude oil, we need a solvent with lower polarity of the hydrogen bonding parameter¹¹.

This was due to hydrogen bond interactions with the hydroxyl groups that characterize some of the asphaltenes. The above mentioned polar solvents have very little hydrogen bonding which is highly recommended for reduction in viscosity of the crude oil^{12,13}.

Experimental Section

Materials

The heavy Crude oil sample was procured from O.N.G.C., Ahmedabad asset, India. Mineral oil and 3-pentanol was bought from Otto Chemie, Mumbai, and Across Organics, Mumbai, respectively and were used as solvent. Brij-30 was obtained from Loba Chemie Pvt. Ltd., Mumbai. India. Heavy crude oil is characterized by density, acid number, API gravity, pour point, interfacial tension and their composition. The density and acid number of this crude are 997 kg/m³ and 1.726 g KOH/ g oil respectively, at 20°C. API gravity was measured using the ASTM D 28 method and it was 19.32 at 60°F. Pour point of the pure crude was 12°C. Composition of the crude oil in terms of Saturates, Aromatic, Resins and Asphaltanes was measured using SARA analysis and results are depicted in Table 1. FTIR spectroscopy techniques provided the reliable information regarding the functional groups present in pure crude and crude additive mixture.

Sample preparation

Heavy crude oil was mixed with 3-pentanol, mineral oil and Brij-30 to form a stable homogeneous mixture of 5% w/w and 10% w/w of different additives. The

measured weight of heavy crude was placed in a container and thoroughly mixed using MC-MSC-WH magnetic stirrer with a speed of 1500 RPM.

Experimental Procedure

The rheological properties of heavy crude as well as a diluted mixture were measured using Physica MC01 rheometer, manufactured by Helmat-Hirth-Str. (Model no-6 - D 73760) Ostfildern, Germany. The temperature was maintained by magnetic transducer for cone-plate method and by using a water bath for bob and cylinder methods. The US200 software (MK 22 Seriennummer: 416) was used to control the experimental parameters. For measuring Thixotropy behaviour, Complex modulus, Elastic and Viscous modulus, Rheometer from Malvern Instruments (Model No-GEM-200-913), Germany was used. Interfacial tension was measured by Dunoy ring method using Kruss Easy Dyne Tensiometer (Kruss GmbH, Germany; Model: K20, Easy Dyne). Perkin-Elmer Spectrum Two FTIR was used to determine functional groups present in the solvent as well as in the surfactant which are responsible for the reduction of viscosity and yield stress. KBR standard pellets were used and spectra were recorded with 64 scans and 2 cm⁻¹ resolution.

Results and Discussion

Rheological studies

The flow behaviour of the heavy crude oil sample was investigated over a shear rate range between 0.1 s⁻¹ to 1000 s⁻¹ and temperature 25 to 60°C. The measurement was conducted under controlled rate with the rate of shear increasing every 30 s.

Three rheological models, i.e., Power law, Bingham and Casson. [Eqs (1)-(3) respectively] were used to investigate the flow behaviour of the crude oil sample.

$$\tau = k\gamma^n$$
 ... (1)

$$\tau = \tau_0 + n\gamma$$
 ... (2)

Table 1 — Characterization of heavy crude oil and its mixture Characteristics Amount Experimental Unit method Saturates Wt % 58.41 **SARA** Aromatics Wt % 8.99 SARA Resins Wt % 13.47 **SARA** Asphaltenes Wt % 5.19 **SARA** Pour point °C 12 ASTM D5853 mN/m 32.5 **Dunoy Ring** Surface tension at 30°C 0API **API** Gravity 19.32 ASTM D28

$$\tau = (\tau_0^{0.5} + (\gamma n)^{0.5})^2 \qquad ... (3)$$

where τ =applied shear stress (Pa), γ =shear rate (s⁻¹), K = consistency index (Pa sⁿ), n=flow behaviour index, τ_0 =apparent yield stress (Pa), η =apparent viscosity (Pa s). The results of the modeling analysis are presented in Table 2. From the Table it was concluded that the Power Law model is the best to describe crude flow behaviour over a known range of shear rates.

Effect of temperature on viscosity

Temperature is one of the most important factors in rheological characteristics of crude oil ^{17,18}. There were huge differences in viscosity of crude oil when temperature was elevated from 25 to 60°C. To express viscosity reduction Extent of Viscosity Reduction (EVR %) was introduced. EVR% is calculated as below:

$$EVR\% = (Nr-Nc) *100 /Nr$$
 ... (4)

where, N_r is the reference viscosity (i.e., the value of viscosity at which all the viscosity readings were taken to compare) at 81.75 s⁻¹ shear rate and 25°C, N_c is the viscosity at 81.75 s⁻¹ shear rate and corresponding temperature.

Table 3 reports the EVR% in the temperature range of 25-60°C. Over the examined temperature range, there was a noteworthy enhancement in EVR% up to 81%. Several contributing factors might be responsible for this. First of all, the temperature has a major effect on the viscosity of the heavy components present in crude oil. High temperatures destroy the prearranged chemical structure of heavy components in the crude oil phase, hence viscosity is reduced 19,20.

| Table 2 — Modelling analysis of Eqs. (1)- (3) | | | | | | | |
|---|--------------------|-----------|----------------|--|--|--|--|
| Power law model | m= 11.048 | n = 0.860 | $R^2 = 0.9935$ | | | | |
| Bingham model | $\tau_0 = 393.516$ | n=3.716 | $R^2 = 0.9778$ | | | | |
| Casson model | $\tau_0 = 51.045$ | n= 1.8146 | $R^2=0.9857$ | | | | |

Furthermore, it was found that the viscosity of the heavy crude oil depends on the shear rate. The viscosity reaches low values at high shear rates. This means that the flow encounters less resistance at higher shear rates. This is due to the molecular chains found in the heavy crude oil. As the shear rate increases, the chain type molecule gets disentangled, and reoriented parallel to the driving force and hence reduces heavy crude oil viscosity²¹.

Effect of addition of mineral oil, 3-pentanol and Brij-30 on crude oil viscosity

Effect of addition of different additives on viscosity at a particular temperature is shown in Fig. 1. As evident from the figure, the flow is shear thinning up to 500 s⁻¹ and after that it is Newtonian. Addition of 5% w/w and 10% w/w of Brij-30 to crude oil reduced the viscosity by 72.57 and 81.68% respectively at 40°C. Mineral oil addition is effective in reducing the

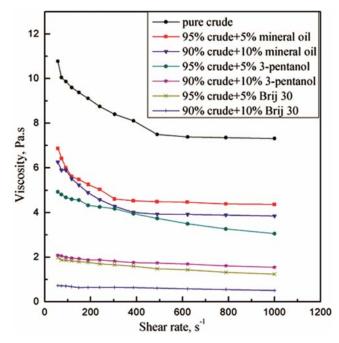


Fig. 1 — Effect of additives in crude oil at 25°C

Table 3 — EVR% over a temperature range of 25 to 60°C

| Temperature, | Viscosity (at 81.75 s ⁻¹ Shear rate) for | | | | | | | | | | | | | |
|--------------|---|-------|------------|-------|-------------|-------|------------|-------|------------|-------|---------|-------|---------|-------|
| (°C) | Pure | EVR | 95% | EVR | 90% | EVR | 95% | EVR | 90% | EVR | 95% | EVR | 90% | EVR |
| | crude | (%) | Crude | (%) | Crude | (%) | Crude | (%) | Crude | (%) | Crude | (%) | Crude | (%) |
| | | | oil+5% | | oil+10% | | oil+5% | | oil+10% | | oil+5% | | oil+10% | |
| | | | Mineral oi | 1 | Mineral oil | | 3-pentanol | | 3-pentanol | | Brij 30 | | Brij 30 | |
| 25 | 10.10 | 0 | 6.30 | 37.61 | 5.85 | 42.04 | 4.67 | 53.73 | 2.04 | 79.75 | 2.77 | 72.57 | 1.85 | 81.68 |
| 30 | 8.32 | 17.52 | 4.25 | 57.87 | 4.17 | 58.68 | 3.33 | 67.02 | 1.41 | 85.98 | 1.86 | 81.58 | 1.28 | 87.32 |
| 40 | 6.03 | 40.29 | 2.19 | 78.28 | 2.32 | 76.96 | 1.70 | 83.15 | 0.72 | 92.78 | 0.91 | 90.99 | 0.64 | 93.66 |
| 50 | 4.63 | 54.10 | 1.07 | 89.38 | 1.53 | 84.80 | 0.91 | 90.93 | 0.48 | 95.17 | 0.36 | 96.43 | 0.29 | 97.12 |
| 60 | 2.85 | 71.69 | 0.54 | 94.60 | 0.72 | 92.79 | 0.77 | 92.30 | 0.31 | 96.91 | 0.25 | 97.52 | 0.11 | 98.91 |

viscosity of crude oil as shown in Table 3. The addition of 10% 3-pentanol reduced the viscosity from 10 Pas to 2.1 Pa s (79%). The reduction in viscosity of crude oil may be due to interaction between the hydroxyl group of alcohol and similar functionalities present in asphaltenic group. With increase in temperature, EVR% increases significantly in almost all the cases. By increasing the temperature from 25°C to 60°C, EVR% increases from 72.57% to 96.15% after addition of 5% w/w Brij 30.

At 60°C, EVR% increases significantly when Brij-30 was used with crude oil. At higher temperature, the flow is completely Newtonian even at low shear rates²².

The Brij-30 is highly effective as higher the polarity of the surfactant, greater is the relative viscosity reduction on crude oil. So, the flowability of crude oil improved by adding Brij 30, as a surfactant. The results obtained show that this method is preferable to other methods of viscosity reduction. At 60°C, addition of 5% w/w and 10% w/w mineral oil reduced viscosity from 6.3 Pa s to 0.7 Pa s and 0.5 Pa s respectively.

Measurement of yield stress

Yield stress is the stress corresponding to the transition from elastic to plastic deformation²³. When applied stress is lower, structural deformation make crude elastic in nature. However, when applied stress cross the yield point, the deformation causes the sample to flow²⁴. Measurement of yield stress was carried out at 40°C by adding 5% and 10% w/w mineral oil, 3-pentanol and Brij-30 to pure crude oil.

Figure 2 shows the yield stress measurements of crude oil with mineral oil, 3-pentanol and Brij 30. It illustrates the relationship between shear stress vs. shear rate plot for crude oil with and without additives. It was observed that the yield point of crude oil decreases after the addition of 5% Brij-30 and other additives. The reduction in yield stress of crude oil after the addition of 10% Brij-30 at 40°C was 98.6% which is even lesser than the yield stress of pure crude at 70°C. On the other hand addition of mineral oil and 3-pentanol by the same amount reduced the yield stress by 72 and 86.67%, respectively.

Interfacial tension measurement

Crude oil contains organic acids and salts, alcohols and other natural surface active agents. When crude oil is brought in contact with brine or water, these natural surfactants accumulate at the interface and form an adsorbed film which lowers the interfacial tension of the crude oil/water interface. For surface active molecules, a slight increase in their concentration produces a high reduction in the interfacial tension. Effect of addition of dilutants and surfactant on interfacial tension at different temperatures is shown in Fig. 3 and the results are depicted in Table 4.

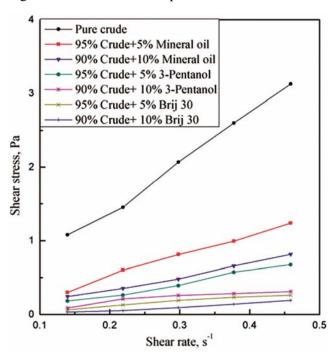


Fig. 2 — Yield stress measurement of crude oil with different additives at 40°C.

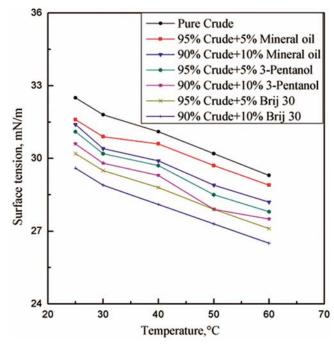


Fig. 3 — Effect of additives on interfacial tension at different temperatures.

| Table 4 — Interfacial Tension of crude oil and its mixture | | | | | | | | |
|--|------------------------|------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--|
| Temperatures (°C) | Surface tension (mN/m) | | | | | | | |
| | Pure Crude | 95% Crude+ 5% mineral oil | 90% Crude+ 10% mineral oil | 95% Crude+ 10% mineral oil | 90% Crude+ 10% mineral oil | 95% Crude+ 10% mineral oil | 90% Crude+ 10% mineral oil | |
| 25 | 32.5 | 31.6 | 31.4 | 31.1 | 30.6 | 30.2 | 29.6 | |
| 30 | 31.8 | 30.9 | 30.4 | 30.2 | 29.8 | 29.5 | 28.9 | |
| 40 | 31.1 | 30.6 | 29.9 | 29.7 | 29.3 | 28.8 | 28.1 | |
| 50 | 30.2 | 29.7 | 28.9 | 28.5 | 27.9 | 27.9 | 27.3 | |
| 60 | 29.3 | 28.9 | 28.2 | 27.8 | 27.5 | 27.1 | 26.5 | |

In case of mineral oil (5% w/w and 10% w/w) addition, interfacial tension decreases because it is adsorbed at the metal surface and form spread films. but the reduction is not substantial. Addition of 3-pentanol to crude oil reduces the interfacial tension of the mixture because of dilution effect²⁵. With an increase in the concentration of 3-pentanol from 5 to 10 %, interfacial tension is further reduced. However, the best result was obtained after using Brij-30. Brij-30 dropped the interfacial tension to up to 10^{-4} mN/m. Interfacial tension can reach ultra-low values at low as well as high surfactant concentration (Table 4). Surfactants molecules tend to align in such a way that the polar end is immersed in oil and the hydrophobic ends align towards the air. As a result, the forces holding the surface together are weakened and surface energy decreases.

As far as the effect of temperature is concerned, interfacial tension decreases with increase in temperature in the crude oil samples, because cohesive forces decrease with increase in molecular thermal activity. So, for every sample of crude oil with surfactant, solvent or mineral oil, there is a linear decrease in interfacial tension from 25 to 60°C²⁶.

Thixotropy behaviour

Thixotropy indicates the amount of energy experienced by a fluid in changing from one state of microstructure to another and back again. The structural change may occur due to the disintegration, build up or non-flow collections. All these activities indicate the intensity of solution viscosity and require time to change from one state to another under the shear force applied²⁶. Figure 4 shows the thixotropic behaviour of crude without and with different additives. Thixotropic behaviour was studied by increasing shear rate from linearly from 0.1 to a maximum value of 800 s⁻¹ followed by decreasing it to 0.1 s⁻¹ at the same rate during a single isothermal rheology experiment. Thixotropic area can be defined as the area enclosed between the up curve and the down curve rheogram of the hysteresis loop. The up

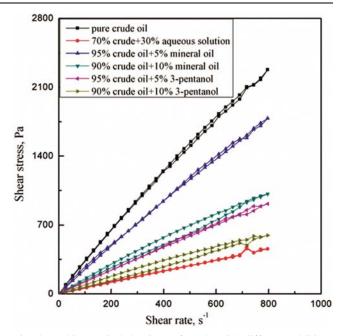


Fig. 4 — Thixotropic behaviour of crude with different additives at 40° C.

and down curve rheogram is identical for non thixotropic materials whereas it is different for thixotropic materials. To make sure that the crude oil sample had completely broken down a number of tests with different running times were carried out for the up cycle and down cycle. Each cycle was run for 150 s, 250 s and 300 s. The test results for the cycle of 300 s confirmed that the crude oil structure was completely disintegrated. A hysteresis loop was formulated for the crude oil sample using 5% and 10% wt/wt Brij-30 at 40°C. The area calculated was compared with the areas obtained with mineral oil and 3-pentanol. The calculated areas are tabulated in Table 5. It is evident from Table 5 that the thixotropic area of pure crude was as high as up to 326 kPa/s. Presence of high amounts of asphaltenes, saturates; resins and aromatics (Table 1) are responsible for this higher value. The addition of 5% mineral oil and 3-pentanol addition reduced the thixotropic area by 43.5 and 85.86% respectively. There was a substantial

decrease (95.98%) in the area of the hysteresis curve compared to original crude after addition of 5% w/w Brij-30. This indicates that lesser energy is required by the crude oil to break the bonds, thereby saving valuable time and power. The addition of 5% w/w of Brij-30 reduced thixotropic area to an extent same as that after addition of 10% w/w of 3-pentanol. Also, as depicted in Table 5 thixotropic area decreases further at 50 and 60°C by a greater amount than at 40°C. This is due to the combined effect of temperature and additives²².

FTIR spectroscopy

Heavy crude and its mixture with different additives have been used to study the correlation between the molecular structural parameters using FTIR spectra. The information obtained from FTIR spectra is important to predict the molecular change in heavy crude which ultimately help in better flowability.

Figure 5 shows the FTIR spectra of heavy crude and its mixture with different additives. The peaks at frequencies 1913.65 and 2907.50 cm⁻¹ corresponds to C=C shift and C-H shift of the carbon-carbon bonds. The peaks at frequencies 1708.03 and 1077.36 cm⁻¹ represent carboxylic acids and thyocarbonyl groups

Table 5 — Thixotropic area at different temperatures for crude oil and its mixture

| Hysteresis area(kPa/s) at | | | | | | | | |
|---------------------------|--------|--------|-------|--|--|--|--|--|
| Composition of sample | 40°C | 50°C | 60°C | | | | | |
| Pure crude | 326.53 | 116.11 | 58.19 | | | | | |
| 95% Crude+5% mineral oil | 184.36 | 82.96 | 50.46 | | | | | |
| 90% Crude+10% mineral oil | 133.65 | 70.74 | 39.81 | | | | | |
| 95% Crude+5% 3-pentanol | 46.160 | 24.63 | 15.09 | | | | | |
| 90% Crude+10% 3-pentanol | 30.46 | 18.68 | 10.01 | | | | | |
| 95% Crude+5% brij 30 | 13.11 | 8.06 | 4.32 | | | | | |
| 90% Crude+10% brij 30 | 9.11 | 4.36 | 1.19 | | | | | |

respectively. On comparing pure crude and its mixture with additives, it was observed that there were shifts in wave number (more than 10 cm⁻¹) of a dominant peak associated with the crude mixture (Table 6)²⁷. From Table 6, it was seen that the interaction of crude oil with Brij-30 surfactant resulted in shifting of the dominant peaks corresponding to alkane and alkene group. It was also noted that after the addition of mineral oil to pure crude the dominant peak corresponding to CH₃ group shifted to a different frequency while Brij-30 totally eliminated the group indicating its better efficiency compared to mineral oil and 3-pentanol. Also, CH₃ group in alkanes and two other functional groups namely carboxylic acids and thiocarbonyls disappear in the crude-Brij-30 mixtures²⁸. This suggests that the interaction between molecules present in the crude oil and Brij-30 eliminates the above mentioned compounds thereby improving the flowability of heavy crude. So, Brij-30 is effective in disintegrating the functional groups responsible for higher viscosities in crude oils much better than 3-pentanol and mineral oil.

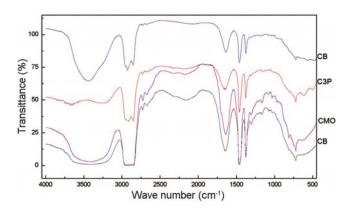


Fig. 5 — FTIR spectra of pure crude (PC), crude + 3- pentanol (C3P), crude + mineral oil (CMO) and crude + brij-30 (CB).

| Bond | Frequency range (cm ⁻¹ |) Attributed to | Pure crude | Crude-Brij30 mixture | Crude-3-pentanol mixture | Crude-mineral oil mixture | |
|---|-----------------------------------|-------------------|--------------|-------------------------|--------------------------|---------------------------|--|
| С-Н | 2850-3000 | Alkanes (stretch) | ✓ | ✓✓ | ✓ | ✓ | |
| СНО | 2700-2900 | Aldehydes | \checkmark | ✓ | ✓ | ✓ | |
| C=H | 1700-2000 | Alkenes | ✓ | $\checkmark\checkmark$ | X | X | |
| COOH | 1700-1725 | Carboxylic acids | ✓ | X | ✓ | ✓ | |
| C=H Bending | 690-900 | Arenes | ✓ | ✓ | ✓ | ✓ | |
| C-H ₂ | 1450-1465 | Alkanes | ✓ | ✓ | ✓ | ✓ | |
| C-H ₃ | 1375-1450 | Alkanes | ✓ | X | ✓ | $\checkmark\checkmark$ | |
| C=S | 1050-1200 | Thiocarbonyl | ✓ | X | ✓ | ✓ | |
| S=O | 1030-1060 | Sulphoxide | ✓ | ✓ | ✓ | ✓ | |
| N-O | 960 <u>+</u> 20 | Aliphatic amines | ✓ | ✓ | ✓ | ✓ | |
| S-OR | 700-900 | Esters | ✓ | ✓ | ✓ | ✓ | |
| \checkmark = Presence of peaks \checkmark \checkmark = Shifting of peaks X = Disappearance of peaks | | | | | | | |

Viscoelastic behaviour

The dynamic studies are very important tool for investigation of the rheological behaviour of heavy crude oil. Complex modulus (G*) is the overall deformation of a material, regardless of the fact whether deformation is recoverable or not. It indicates rigidity of material when stress applied is less than yield stress²⁸. In Fig. 6, complex modulus vs frequency has been plotted for crude oil benefitted with mineral oil, 3-pentanol and Brij-30 at 40°C. As we have seen in Fig. 6, Complex modulus and Frequency exhibit a linear relationship. Also, on increasing the concentration of mineral oil, 3-pentanol and Brij-30 complex modulus decreases at a constant temperature. Non ionic surfactant Brij-30 has a strong influence on G*. This happens because in addition of surfactant rigidity of the system decreases and hence the complex modulus. So the addition of solvents leads to decrease in rigidity of crude oil, which helps it to flow easily due to reduction in complex modulus²⁹. The addition of 5% and 10% w/w, reduced the complex modulus significantly. The addition of Brij-30 is most effective to reduce the complex modulus though a variation of complex modulus between 5% w/w and 10% w/w is very little.

G" also known as storage modulus represents the elastic behaviour of structure and G" (Loss modulus) represents the viscous behaviour of structure. G" and G" are both functions of frequency. The storage modulus measures the stored energy, representing the elastic portion, and loss modulus represents the

energy dissipated as heat, representing the viscous portion. G" and G" for crude oil without and with additives are potted in Fig. 7. This analysis shows that stored energy in crude oil is less than the energy dissipated per cycle as evident in the figures. For heavy crude oil, G" is positioned much lower than G" showing that it exhibits highly viscous behaviour³⁰. The addition of 5% w/w mineral oil to crude oil decreased G" significantly but on increasing

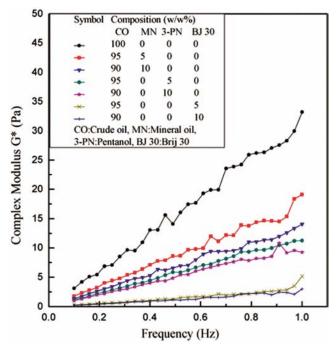


Fig. 6 — Complex modulus of crude oil-additive mixture at 40°C.

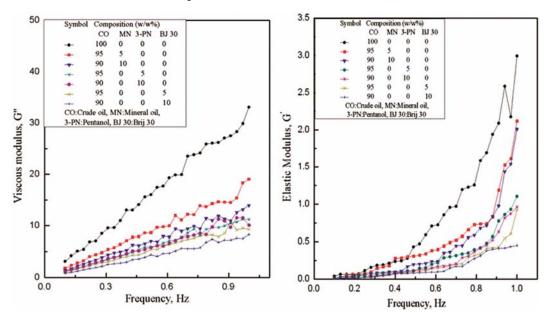


Fig. 7 — Viscous and elastic modulus of crude oil with different additives at 40°C.

concentrations of mineral oil the change in G" was negligible whereas change in G" was significant. This shows the energy dissipated as heat will be greater for 10% Mineral oil. Both G" and G" decreased with the addition of 5% 3-pentanol. 10% w/w 3-pentanol in high concentration decreased G" and G" to a greater extent. This shows that the wax structure is broken on increasing the concentration of solvent and viscous behaviour is lowered³¹. Best results have been obtained in cases of Brij 30. The higher degree of reduction in both elastic and viscous modules was observed with increasing concentration of Brij-30 from 5 to 10%. This shows that non ionic surfactant can reduce the Viscoelastic properties of crude oils which are directly related to its transportation through pipelines.

Conclusion

Effects of addition of mineral oil, 3-Pentanol and Brij-30 have been studied to improve the flowability of heavy crude. The results are summarized as:

Crude oil exhibits a quasi- Newtonian rheological behaviour over increasing shear rate. The viscosity of heavy crude oil decreased over the range of 25-60°C.

The addition of 5% w/w and 10% w/w mineral oil, 3-pentanol and Brij-30 in heavy crude oil reduced the viscosity significantly. But Brij-30 is most effective to reduce the viscosity.

The yield stress of heavy crude oil decreased with temperature. Mineral oil and 3-pentanol are effective to reduce yield stress. Yield stress almost diminished after addition of Brij 30.

On addition of mineral oil, 3-pentanol and Brij 30, thixotropic area of heavy crude decreased by 59.06, 90.67 and 97.21%, respectively. So Brij-30 is most effective to initiate the flow.

The complex modulus of heavy crude oil decreased substantially with increasing temperature. Addition of Brij-30 is most effective to reduce the complex modulus.

Both elastic modulus and viscous modulus decreased with increasing concentrations of 3-pentanol, mineral oil and Brij 30. The highest degree of reduction in viscoelastic properties was obtained in the case of Brij 30.

Brij-30 eliminated some functional groups like carboxylic acids and thiocarbonyls, thereby improving the flow behaviour much better than mineral oil and 3-pentanol.

Brij-30 as natural surfactant can be used extensively for improving rheological properties compared to other additives.

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Nomenclature

- τ applied shear stress
- γ shear rate
- k consistency index
- n flow behaviour index
- τ_0 apparent yield stress
- η apparent viscosity
- N_r viscosity of crude oil at 81.75 s⁻¹ shear rate and 25°C
- N_c viscosity of other samples at 81.75 s⁻¹ shear rate and corresponding temperature
- G* complex modulus
- G' storage modulus
- G" loss modulus

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