INTRODUCTION

Transportation of viscous crude oil through pipelines is one of the most tedious practices in petroleum industry. The mobility of such oils in reservoirs is inferior, which leads to the restriction in production [1]. This creates economical rift for the industries to carry out production and transportation operations efficiently. To increase the movement of such viscous oils, deployment of viscosity reducers is inevitable. Viscosity reduction can be attained either by thermal methods, light oil blending or by addition of chemicals as viscosity reducers which can increase the flowability [2]. Using thermal method requires ample amount of heat energy and utilizing lighter crude oil can add economic burden to the concerns [3]. Thus, it is necessary to tailor chemical additives, which can give desirable reduction in viscosity.

Crude oil consists of complex mixture of hydrocarbons, mainly polar and non-polar moieties such as asphaltenes, resins, saturates and aromatics. Paraffin and asphaltenes are the prime reason for deposition and viscosity issues. Other components include polycondensate aromatic moiety along with alkyl components of different dimensions and functional groups formed by O, N and S as well as metals like iron, nickel and vanadium [4]. Asphaltene is the bulkiest and the most tedious attribute in terms of its mechanism and structure in crude oil. Resins are slightly different from asphaltenes in the electrical charges [5]. They attract asphaltene molecules and connect to the alkyl tails, which helps the asphaltene particles dispersed and flowing smoothly within the oil. This forms a steric stabilization layer beyond petroleum asphaltenes which acts as barriers amongst polar moieties of asphaltene and non-polar components of oil [6]. Thus, they act as natural asphaltene-stabilizing agents. The asphaltene precipitation progresses along with the exceeding of asphaltene constituents from the critical value [7]. The factors encouraging the asphaltene precipitation includes the temperature-pressure gradient, phase separation, association of oil from different source and composition, etc. [8]. The intermolecular arrangements of the constituents present in asphal-
tene reflects a wide range of complexity. The exhibition of π-π* interactive bonds associated with long alkyl chains connected with each other along with different heteroatoms (O, N, S); presence of functional groups such as carbonyl and hydroxyl interacted with each other through hydrogen bonding and interaction of metal ions via charge transfer makes asphaltene an intricate component. The presence of these interactions leads to self-association in asphaltene [9]. Asphaltene precipitation is one of the most interfering issues in petroleum industry and creates rifts during production, transportation, refining and recovery of crude oil. From wellbores and pipes to storage tanks at refineries, the sticky deposits clog equipment and disrupt operations [10].

Ionic liquids (ILs) possess an array of unique characteristics like low vapour pressure, high surface activity, thermal stability, low melting point, etc. [11]. They are made up of amphiphilic cationic moieties such as ammonium, imidazolium, pyridinium, pyrrolidinium, sulfonium/phosphonium, inorganic/organic anions, halides, phosphates, sulfates, borates, etc. [12] and can be classified on the basis of their solubility depending upon the presence of anion. Ionic liquids having PF6 and NTf2 are hydrophobic and water-insoluble (hydrophobic) ILs whereas others are water-soluble. However, increase in the alkyl chain length of ILs cation could increase their hydrophobic character. A wide range of ILs’ applications in the petroleum field have been recognized for demulsification, viscosity reduction, desulfurization of fuels, denitrogenation of gasoline, selective gas separation, biofuel synthesis, for EOR techniques, as wax and asphaltene inhibitors, etc. [13].

The formation of microstructures of component present in oil due to temperature-pressure gradient, creates a resistance to flow during pipeline production and transportation [14]. For treating this type of network methods like heating, solvent dilution and blending of light oil is widely applied. For dilution of extra heavy oils, less viscous crude oil is blended along with lighter hydrocarbon fractions like condensates, kerosene, diesel or naphtha [3]. The blending is economically stringent due to high prices of lighter hydrocarbon. One major difficulty is the incompatibility of crude oil with its lighter components, which can manifest the precipitation of solid phases, leading to the formation of undesirable plugs within the production infrastructure. These constraints prompted more studies which can be economically and environmentally efficient.

Studies of using ILs as viscosity reducers is in light due to its eco-friendly nature. Some initial works include studies of using new class of green ionic liquids (ILs) to increase the flowability of viscous oil instead of hazardous solvents is the main objective of this study. This study involves the synthesis and characterization of a series of ILs derived from alkyl imidazolium cations with a high degree of aromaticity. Fourier-transform infrared (FTIR) and NMR spectroscopies were employed for the structural elucidation. The synthesized ILs were also evaluated as pour point depressants and viscosity reducers through rheology on viscous crude oil.

**EXPERIMENTAL**

The chemicals and reagents procured were of analytical grade and used directly without purification. Imidazole (≥ 99%), 1-bromoethane (≥ 99%), 1-bromobutane (≥ 99%), 1-bromohexane (≥ 99%), 1-bromoheptane (≥ 99%), potassium hydroxide (≥ 98%), acetonitrile (> 99%) and dodecyl benzene sulfonic acid (DBSA) (≥ 99%). Crude oil was collected from Western onshore field of Oil and Natural Gas Corporation (ONGC) Limited.

Alkyl imidazoles were synthesized by treating imidazole along with alkyl halide (1:1) in the presence of KOH and acetonitrile. Firstly, imidazole was mixed with KOH with vigorous stirring in acetonitrile until the dissolution of the reactants in the solvent. After the complete miscibility, dropwise addition of alkyl halide was done to the mixture for 3 h until a white
precipitation was observed and filtered to obtain 1-alkyl imidazole products. The product derivatives were refluxed and stirred overnight with dodecyl benzene sulphonic acid (DBSA) at 70-80 °C for obtaining the designated product (1-alkyl-1H-imidazolium-dodecylbenzenesulphonate) [20-22]. Alkyl halides viz. C₆H₅Br, C₄H₉Br, C₆H₁₃Br and C₇H₁₅Br were used to synthesize DIL1, DIL2, DIL3 and DIL4, respectively where RX resembles to C₆H₅Br, C₄H₉Br, C₆H₁₃Br, C₇H₁₅Br are shown in Scheme-I.

RESULTS AND DISCUSSION

FT-IR studies: FTIR analysis successfully verified the chemical structures of the synthesized DILs. The presence of aliphatic C-H bonds was identified by peaks around 2960 and 2844 cm⁻¹. Additionally, aromatic C-H bonds were observed in the range of 3150-3130 cm⁻¹. The imidazole ring structure was confirmed by C-C vibrations between 1590 and 1570 cm⁻¹, along with aromatic C=C stretching bands at 1462-1460 cm⁻¹. Furthermore, C-N stretching vibrations in the imidazole ring were evident between 1410 and 1400 cm⁻¹. Lastly, the peaks at 1380-1370 cm⁻¹ indicate the presence of S=O bonds, while the symmetric stretching of the −SO₂ group was assigned to the peak at 1040-1034 cm⁻¹ [22].

Physico-chemical, pour point and rheological studies of crude oil in the presence of synthesized products: It is evitable to investigate the physico-chemical and rheological behaviour of crude oil to understand the complex nature of crude oil. The nature of crude oil depends on the relationship between the components and their crystallization mechanism. The adherence of the crystallization of the microstructures directly affects the deposition and flow behaviour of crude oil to assure smooth transportation [3]. With the temperature and pressure drop these components forms tough emulsion which are quite stable and contributes in high viscosity of crude oil [4]. During the production crude oil and water phase emulisify and results into water-in-oil emulsion which affects the pipeline systems. The adsorption of water molecules on oxide surfaces impacts the dissolution of polar hydrocarbons within crude oil [23]. Crude oil consists of waxy substances called paraffins. These paraffins are essentially long, straight-chain hydrocarbons made up of n-alkanes linked by simple single bonds. The bulk of any wax deposits in crude oil are dominated by the high-molecular-weight paraffins. Firstly, the water content of the crude oil sample was determined by Dean-Stark apparatus. The physico-chemical components of crude oil were determined from the maltene obtained from 210+ residue of the crude oil after distillation process. An aliquot amount of residue is refluxed with n-hexane solvent and filtered. The residue contains asphaltene is soluble in hot toluene and the filtrate obtained is known as maltene. Further, maltene was divided into two parts; one for determining wax content and other for saturate, aromatic, resin and asphaltene compounds (SARA) analysis. One part of maltene was subjected to hot bed of silica and washed with hot n-hexane. Acetone was added to the fraction and kept at -23 °C for wax precipitation. The SARA fractions consist of a preliminary separation of asphaltenes from maltene and further subjected to silica column for column chromatography where saturates, aromatics and resins are eluted with petroleum ether, toluene and methanol through column [5]. Further, the pour point analysis of the crude oil was performed using ASTM method, which was obtained by heating the crude upto 60 °C, then cooled down till 45 °C and kept in pour point apparatus. The pour point test determines the lowest temperature at which the crude oil remains fluid. To find this point, the temperature of a sample in pour point tube was gradually lowered. After every 3 °C lowering, the tube was inclined to observe the flow of oil. The physico-chemical properties and SARA composition of crude oil are listed in Table-1.

The value of API gravity shows that the crude oil is viscous in nature having a pour point of 30 °C, 10.08% and 1.56% of wax and asphaltene content, respectively. Waxes and asphaltenes are generally higher molecular weight hydrocarbons which remain in dissolved form at reservoir conditions, where temperatures range from 70 to 150 °C and pressures ranges between 50 and 100 MPa, crude oil acts like a flowable fluid (Newtonian fluid). However, as these conditions changes, when

![Scheme-I](image-url)
it gets cooler and the pressure drops, components in the oil start to solidify and come out of the solution, forming precipitates of macro and micro-structure deposits on the cooler surfaces of the pipeline during crude oil transportation. The agglomerates give the complexity to the crude oil and impart non-Newtonian characteristics to the rheological properties of the crude oil. The pour point studies of the crude sample were determined followed by treating the crude sample with DIL1, DIL2, DIL3 and DIL4 additives at 500 and 1000 ppm. The pour point studies of the crude are shown in Table-2.

<table>
<thead>
<tr>
<th>Products</th>
<th>Untreated crude oil (°C)</th>
<th>500 ppm (°C)</th>
<th>1000 ppm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIL1</td>
<td>30</td>
<td>30</td>
<td>27</td>
</tr>
<tr>
<td>DIL2</td>
<td>30</td>
<td>30</td>
<td>27</td>
</tr>
<tr>
<td>DIL3</td>
<td>30</td>
<td>27</td>
<td>24</td>
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<tr>
<td>DIL4</td>
<td>30</td>
<td>24</td>
<td>24</td>
</tr>
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</table>

DIL1, DIL2, DIL3 and DIL4 at different temperature and shear rates were done through rheometer. There is a need of evaluation of rheological properties of crude oil because the flow properties of crude drastically change when the temperature of crude oil is lowered to near pour point and below [24].

Fig. 1a investigates the impact of temperature on the flow characteristics (viscosity) of crude oil. The untreated crude oil showed the greatest change in viscosity when heated between 35 °C and 50 °C. In this range, there is a significant decrease in the viscosity suggesting that the crude oil’s clumps (agglomerates) begin to break apart as the temperature increases above 35 °C. Interestingly, when the crude oil was treated with the newly developed compounds DIL1, DIL2, DIL3 and DIL4, the rate of viscosity decrease becomes even more pronounced. Compared to untreated oil, the viscosity reduction with these additives was 46%, 55%, 64% and 78%, respectively. Fig. 1b shows the effect of shear rate of crude oil at 30 °C, 40 °C and 50 °C, whereas Fig. 2 illustrates the relationship between shear rate (the rate at which the oil layers are forced to move past each other) and viscosity at different temperatures (30 °C, 40 °C and 50 °C).

Crude oil viscosity also exhibits a strong temperature dependence. Elevated temperatures induce significant alterations in
the rheological properties of viscous crude oil. High viscosity of crude oil can be attributed to the careful arrangement of the constituents at low temperature. The involvement of chemical additives which directly affects the agglomeration of the chemical components helps in dissolution of agglomerates and results in the drop of viscosity [4]. The resistance crude oil offers to flow (viscosity) is also influenced by the amount of stress applied (shear rate). When the amount of stress is high, the oil flows more smoothly. At high shear rates, these chains get untangled and line up in the direction of flow, reducing the overall resistance and making the heavy crude oil flow more smoothly. Crude oil exhibits a shear-thinning behaviour at constant temperature and moreover, its viscosity inversely correlates with temperature [3].

The high viscosity of crude oil creates difficulty in the transportation due less flowability. Extra thermal treatment is necessary for such types of oil which creates economic rift. Thus, lowering the viscosity by use of chemical additives reduces the friction by lowering the viscosity of the crude [25]. Studies suggest that addition of DILs enhances the ability of crude oil to dissolve the solid clumps (agglomerates) present within it and improved solubility allows the crude oil to flow more easily, even at lower temperatures.

The synthesized ionic liquids (DIL1, DIL2, DIL3 and DIL4) underwent rheological analysis to determine their impact on the behaviour of viscous crude oil. An effective additive interacts or bind with the chemical functional groups present in it. The selection of this type of ILs is done due to its structural property which can mimic the effect of resin [19]. They consist polar aromatic components comprising alkyl chains with electron donor–acceptor tendencies. The polar head with aromatic character interacts with the other aromatic moieties in asphaltene through π–π* stacking, hydrogen and van der Waal’s interactions. The other alkyl chains dissolves in the oil along with naphthene and saturates. Also, DBSA alone was used as a surfactant during enhanced oil recovery operations. Thus, DBSA based ILs can be effective on the surface of asphaltene present in crude. According to the literature, longer alkyl chains (more than 16 carbons) undergo self-association and crystallization in the crude system. After that they start behaving like wax and causes deposition [26]. It is reported that with the addition of optimum concentration of an IL additive, change in the viscosity of crude oil is observed. The synthesized products possess good solubility in crude oil, solvents (in the viscosity of crude oil is observed. The synthesized products addition of optimum concentration of an IL additive, change through interactions. The other alkyl chains dissolves in the oil along and line up in the direction of flow, reducing the overall resistance and making the heavy crude oil flow more smoothly. Crude oil exhibits a shear-thinning behaviour at constant temperature and moreover, its viscosity inversely correlates with temperature [3].

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Further the effectiveness of the synthesized DILs for the prevention of asphaltene clumping (asphaltene dispersion) was investigated. Heptane and toluene mixtures containing varying DIL concentrations were used. To pinpoint the asphaltene onset precipitation (the point when asphaltene molecules start clumping together), the absorption within a wavelength range of 200-800 nm was measured. By analyzing this light absorption along with the amount of n-heptane present the dispersion studies were done. The precipitation of the extracted asphaltene in solvent mixture was minimal for DIL1 at 20% whereas it was around 50% and 60% for DIL3 and DIL4, respectively (Fig. 3). It gives impetus to the theory that compounds containing long chains are more likely to interact with the asphaltene molecules due to their high surface activity.

![Fig. 3. Dispersion studies of asphaltene in the presence of additives](image)

**Conclusion**

The synthesis of four ionic liquids (DIL1, DIL2, DIL3 and DIL4) was done by reacting alkyl imidazoles with dodecylbenzene sulfonic acid and characterized by FT-IR and 1H NMR. A crude oil having API gravity of 28.57, pour point of 30 °C, wax and asphaltene content of 10.08% and 1.56% was utilized for the studies. The evaluation of ionic liquids as pour point depressants was assessed as per ASTM procedure and also evaluated as viscosity reducers on viscous oil sample through rheology. The pour point studies shows DIL4 depresses the Pour point of crude oil from 30°C to 24°C at 500 ppm dose. Studies indicate that DIL1, DIL2, DIL3 and DIL4 showed decrease in viscosity upto 46%, 55%, 64% and 78%, respectively. Furthermore, the interaction of ionic liquids with asphaltene was analyzed through UV-Visible spectroscopic method, which further confirmed that the synthesized products were effective on asphaltene. Overall results confirmed that the excellent viscosity reduction was observed for synthesized products DIL3 and DIL4 due to the structural property of interacting with the complex asphaltene components present in the crude oil.

**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.
REFERENCES

7. A.I. Ismail, A.M. Atta, M. El-Newehy and M.E. El-Hefnawy, Polymers, 12, 1273 (2020); https://doi.org/10.3390/polym12061273
11. I. Ganesh, J. Carbon Res., 6, 47 (2020); https://doi.org/10.3390/c6030047
22. A. Ghanem, R.D. Alharthy, S.M. Desouky and R.A. El-Nagar, Materials, 15, 1600 (2022); https://doi.org/10.3390/ma15041600