

Study of synergetic effect of green chemicals on dissolution of tank bottom sludge

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The present paper discusses the study on dissolution dispersion efficiency of tank bottom sludge (TBS) in the presence of new series of green chemical additives i.e., Ionic Liquids (ILs). This work highlights the synthesis of series of six imidazolium based ILs ([BMIm]Br, [BMIm]BF₄, [PMIm]Br, [PMIm]BF₄, [HMIm]Br, and [HMIm]BF₄) along with their influence on dissolution of the TBS. Dissolution–dispersion efficiency of the TBS is evaluated by calculating the residue and absorbance data of the standard solutions along with TBS solution in the presence of solvents independently followed by treatment with synthesized ILs by UV spectroscopy. Dissolution of TBS in heptane is found to be 40%, however it increases to 88% when employed along with 800 ppm of [BMIm]BF₄. Similarly [PMIm]Br shows extreme dissolution efficiency at 800 ppm up to 80% and 82% in the presence of toluene and heptane, respectively. ILs work by softening the TBS which is accumulated at the bottom of the tank. It also helps in diminishing the use of toxic organic solvents. Interaction of IL product with the suitable solvent can directly influence the dissolution efficiency of TBS. ILs have the potential to replace toxic organic solvents used in oil and gas industry.

Keywords: Dissolution-dispersion efficiency, Green chemical additive, Ionic liquids, Tank bottom sludge

Discovery of major oil field is becoming rare and most of the onshore & offshore discoveries are small in size. Even in deep water the fields are not long lasting. Issues of wax deposition and scales have created serious threats due to uneconomical intervention techniques. However, consumption of the hydrocarbons is increasing day by day since industrial revolution. Humans are directly or indirectly dependent on hydrocarbon sources for the fulfillment of their livelihood. In hydrocarbon resources available worldwide, the quantity of heavy crude oil resources are more than double in comparison to the conventional light oil reserves¹. Crude oil contains paraffin waxes, aromatics, asphaltenes, resins, inorganics, etc. Heavy crude oil contains waxes, asphaltene and resins in higher amount which affects the rate of viscosity. The constituents in the crude oil are in soluble form under the reservoir conditions. As soon as the crude oil reaches the surface it starts congealing from liquid state into gel like state due to wide temperature and pressure gradient². The transportation via pipeline needs prior reduction in viscosity. The high viscosity leads to high pressure drop which requires several technologies which adds financial stress to the industry. Also, the overall cost of transportation increases which becomes

economically unfeasible³. The deposition of higher hydrocarbons in production facilities leads to fatigue in equipment. The maximum accumulation of the heavier components of oil is observed in the bottom of the petroleum storage tanks. The deposition in the tanks is due to the density difference of the constituents present. This deposition is known as tank bottom sludge (TBS)⁴.

Petroleum refineries generate solid waste pollutants such as TBS or oily sludge. Unlike sewage sludge, TBS contains varying amounts of total petroleum hydrocarbons (TPH) and other toxic components that are the main culprits of environmental pollution⁵. It contains water and inorganics which forms a tough emulsion with other constituents. Long term storage of crude oil in a stagnant position result in the deterioration in turn leads to photo-oxidation and air-oxidation of crude oil. The deterioration at room temperature results in formation of polymeric polar substances which are in the form of tough emulsion. The hydrocarbons in the crude oil starts precipitating from the homogenous phase to form emulsion with the other components which results in difficulty in transferring the crude oil from one body to the other. In this process, a significant number of valuable hydrocarbons are lost during the storage in the form of the TBS.

The mechanism of the sludge formation includes separation or precipitation of asphaltene and paraffin fractions in the crude oil. The other mechanism includes oxidative polymerization, agglomeration and precipitation of hetero-atoms (nitrogen, sulphur and oxygen in asphaltene and resin) along with inorganic contaminants (sand, silt, clay, scale and rust) present in the crude oil tank⁴. Micelle formation occurs within the constituents leads to decrease in the homogeneity of the crude oil, results into adsorption of inorganic contaminants on the body of micelle complexes, thus leads to solid insoluble deposits at the bottom of the tank body. Along with the inorganics, organic constituents are also present. During photo or air oxidation the oxides produced form the core of the sludge. The polar hydrocarbons are strongly adsorbed on the oxide contaminants at their polar positions which makes them tough emulsion which hard to be separated. The hydrocarbon chain comprises of independent paraffin chains as well as chains with aromatic moiety attached to it. Some of the polar substances may coordinate to ferric or calcium ions at their polar positions⁶. Water molecules are also adsorbed on the oxides which results in the reduction of the solubility of polar hydrocarbons in the crude. The long hydrocarbon chain with alkyl groups is directed away from the hydrophilic atmosphere at the core of the sludge because of their non-polar nature. Micelles produced during this phenomenon precipitates at the bottom of the tank due to their poor solubility and density difference with the other components of the crude. Thus, the TBS shows poor dissolution even in typical solvents like benzene, hexane or THF. A variation in the types of sludge is observed depending upon the type of crude oil it has been originated from. For that physico-chemical studies to identify the ratio of the constituents present in the sludge are taken into consideration.

According to Waste Management norms the '3R' procedure (Reduce, Reuse and Recycle) should be adopted for waste management⁷. Methods like incineration, stabilization, bio-composting, biodegradation, oxidation treatment, etc. are used for oil sludge disposal. For oil sludge recovery, methods like solvent extraction, surfactant enhanced oil recovery, froth floatation, sludge pyrolysis, etc. are implemented⁸. Washing the sludge with additives like surfactants and polymers along with co-solvent is one of the most commonly used recovery processes. The

surfactants act best for water in oil (W/O) emulsions by working on the interfacial phase of oil and water. The constant washing creates agitation resulting in breaking of the emulsion. Surfactants like Triton X-100, Triton X-114, Tween 80, sodium dodecyl sulphate (SDS), biosurfactants, etc. have been extensively used for this purpose. Along with the additives, co-solvents like Pentane, Hexane, Toluene, etc. are also used for the treatment for enhancement of the miscibility of oil in solvent⁹. A new category of chemicals called Ionic Liquids (ILs) has been developed with low toxicity features. ILs have inquisitive features like high thermal stability and negligible pressure at room temperature which makes them non-volatile therefore preventing the release of ILs into the atmosphere¹⁰. These are green chemicals as these can be recovered from the system by water wash and reused. These stable salts at ambient temperature are loosely secured by less coordination of organic cation and anion, which has drawn the focus of researchers as a substitute chemical for upstream oil industry because of their distinct characteristics of adapting anions and cations. They are prevalent in bitumen recovery, asphaltene degradation, desulphurization, biomass conversion, EOR and water treatment¹¹. They are gaining popularity due to their exceptional attributes such as low melting point, nonflammability, and negligible vapor pressure. They can be potential substitutes for surfactants and chemicals and are also known as Green chemicals because they can be recycled, recovered, and reused^{12,13}.

Ionic liquids are crystalline compounds that contain only ions at room temperature, and these have melting point that ranges from -100°C to 200°C. These have a functional group that can incorporate specific physical or chemical aspects such as melting point, solubility, hydrophobicity, viscosity and reactivity. These properties can be amended by altering the structure of the anion, the cationic core, or the substituents on the anion or cation. The type of anions and cations used determines the trait of the IL product, and they can be synthesized by metathesis reaction.^{14,11}

The petroleum sludge or TBS consists of asphaltene moieties which are crucial to handle. Asphaltene are N, S and O containing complex compounds present in the crude oil. They are highly polar so they can easily get precipitated in the bottom of the tank resulting in deposition¹⁵. ILs contains alkyl tails are effective on the asphaltene present in

sludge since they interact with asphaltene and form steric stabilization layers around the asphaltene molecule which results in hindering asphaltene aggregation and destabilizes the emulsion¹⁶.

Experimental Section

Scheme 1 shows the flowchart of the steps conducted during the experimental procedure.

Collection of TBS sample

TBS sample used in this study was obtained from Oil and Natural Gas Corporation, Western onshore region of India. The sludge was analyzed by ASTM methods for determination of physico-chemical properties of TBS. The appearance of sludge was black viscous solid.

Synthesis of Ionic Liquids (ILs)

All the chemicals and reagents were of analytical grade and used directly without purification. Chemicals used were 1-methylimidazole, 1-bromobutane, 1-bromopentane, 1-bromohexane and sodium hexa-fluoroborate. ethyl acetate, acetone and dichloromethane. The synthesis was done in two steps. In the first step, the cations were synthesized by quaternization of amine with a haloalkane or by protonation of amine by acid and heating the mixture. In the second step, anion exchange was carried out by treatment of halide salts with Lewis acids to form Lewis acid-based ionic liquids or by anion metathesis¹⁷.

Synthesis of [BMIm]Br

To synthesize the product, 1-methylimidazole and bromobutane were taken in (1:1.1 ratio).

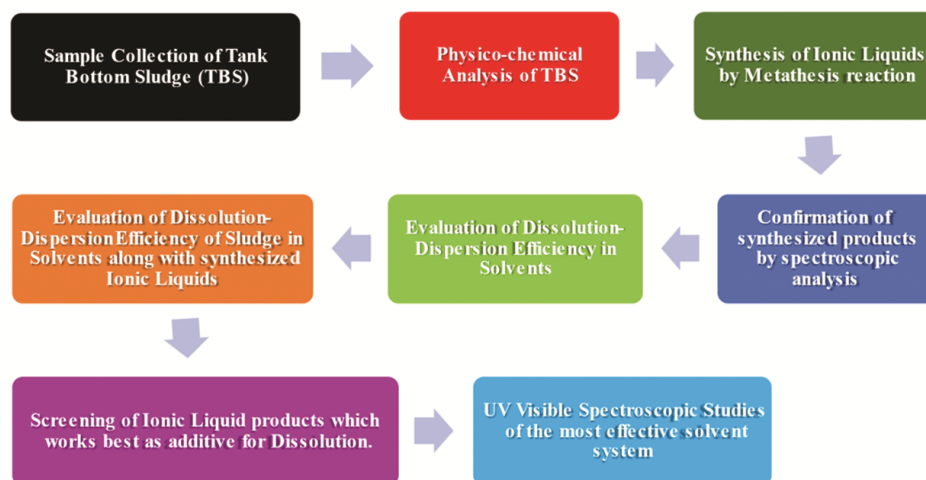
1-methylimidazole was heated to 70°C in a three-necked flask with a reflux condenser. Once the desired temperature was reached, slow addition of bromobutane was started and reaction temperature was maintained for 48 h at 70°C until two phases appeared. The unreacted material in the top layer was decanted and the bottom layer was treated with ethyl acetate to remove any unreacted material. Any solvent traces were removed by heating the pale-yellow solid product [BMIm]Br at 70°C^{18,19}.

Synthesis of [BMIm]BF₄

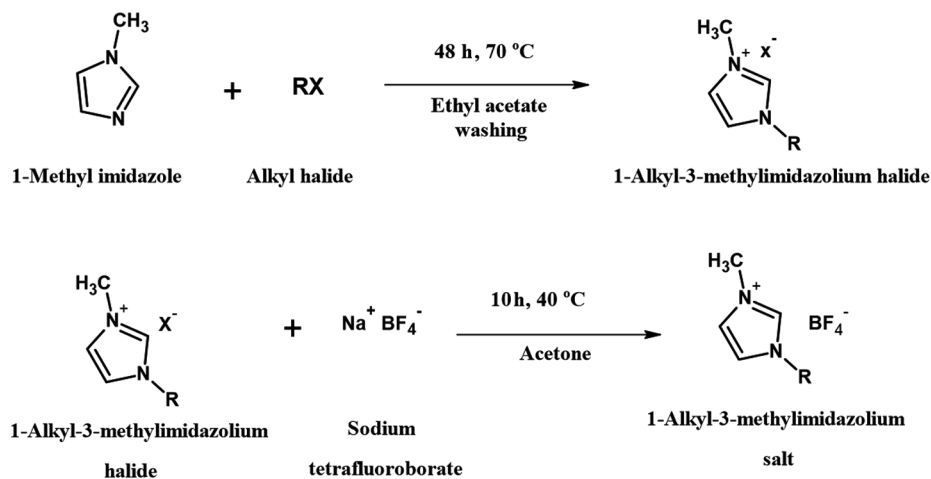
To synthesize the final product, [BMIm]Br and NaBF₄ were added to a single-mouthed flask with acetone as the solvent and heated at 40°C for 10 h under vigorous stirring. The reaction mixture was filtered. Dichloromethane was added to the residue until the appearance of white solid precipitates of [BMIm]BF₄. The product was dried at 80°C for 2 h to remove any traces of dichloromethane¹⁸⁻²⁰. Both [BMIm]Br and [BMIm]BF₄ works as IL. Scheme 2 shows the steps followed for the synthesis. The same procedure was followed for synthesizing [PMIm]Br, [PMIm]BF₄, [HMIm]Br and [HMIm]BF₄ with different alkyl halides. Table 1 comprises of the list series of 1-alkyl 3-methyl imidazolium derivatives which were synthesized. The alkyl halides used during the syntheses were bromobutane, bromopentane and bromohexane.

Dissolution-dispersion studies of TBS

An aliquot quantity of TBS was added to known amount of solvent, 100 shakes were given and left for 24 h. Number of solvents viz, hexane, heptane, methanol, toluene and ethyl acetate were used during



Scheme 1 — Flowchart of the experimental steps



Scheme 2 — Steps followed for the syntheses of ILs

Table 1 — List of Synthesized ILs				
Cation	Anion	Molecular formula	Abbreviation	Molecular weight (g mol ⁻¹)
	Br ⁻	C ₈ H ₁₅ BrN ₂	[BMIm] Br	219.12
	BF ₄ ⁻	C ₈ H ₁₅ BF ₄ N ₂	[BMIm] BF ₄	226.03
	Br ⁻	C ₉ H ₁₇ BrN ₂	[PMIm] Br	233.14
	BF ₄ ⁻	C ₉ H ₁₇ BF ₄ N ₂	[PMIm] BF ₄	240.05
	Br ⁻	C ₁₀ H ₁₉ BrN ₂	[HMIm] Br	247.18
	BF ₄ ⁻	C ₁₀ H ₁₉ BF ₄ N ₂	[HMIm] BF ₄	254.08

the dissolution studies. The portion of TBS which was soluble in solvent was solubilised and the remaining portion was settled down at the bottom. After 24 h, it was filtered and the residue obtained was dried and weighed to get an idea about the dissolution efficiency of the TBS in the solvent. Further, the same procedure was repeated with TBS and solvent in the presence of IL products [BMIm]Br, [BMIm]BF₄, [PMIm]Br, [PMIm]BF₄, [HMIm]Br, and [HMIm]BF₄ at doses in the range of 100-800 ppm and the dissolution of sludge was checked. The residue which remained undissolved in the solvent system was completely dried and evaluated. The IL product was recycled from the solvent system using water.

Preparation of standard solution (TBS + Solvent)

To investigate TBS, a standard stock solution was prepared containing 1000 ppm of TBS in solvent (0.05 g of TBS in 50 mL of the respective solvent). The absorbance of TBS with different solvents at different concentrations was recorded using a UV-visible spectrophotometer (UV1800 Shimadzu) at a predefined λ_{\max} of the respective solvent system. A full spectrum scan was taken of the unknown concentration of TBS in the range of 200-800 nm. The 1000 ppm solution of TBS in respective solvents was diluted to concentrations of 10 ppm, 30 ppm, 50 ppm, 70 ppm, and 90 ppm. The experiment was repeated three times to ensure

accuracy and to establish λ_{\max} . The same task was repeated for all the solvents, and the regression co-efficient (R^2) for the solvent data was established.

Preparation of sample solution (TBS + ILs + Solvent)

The concentration of IL products added in the TBS and solvent systems were in the range of 100 – 800 ppm, subjected for absorbance evaluation through UV-visible spectrophotometer. The value of absorbance obtained for all the samples were compared with the standard solution. The supernatant portion was taken into consideration for the absorbance studies which were carried out after the completion of 24 h. Scheme 3 shows the schematic representation of the experimental procedure.

Results and Discussion

Physico-chemical characteristics of the TBS

Physico-chemical analysis of the TBS was performed and the results are shown in Table 2. Wax content, asphaltene content, melting point and congealing point of waxes and SARA (saturates, aromatics, resins and asphaltene) analysis was performed. Further the dissolution of the sludge in different solvent system (with and without IL product) was also tested.

FT-IR studies of IL products

The confirmation of the synthesized product was done by FT-IR spectroscopy. Fig. 1 and Fig. 2 shows the FT-IR spectra of IL [BMIm]Br and [BMIm]BF₄,

respectively. The results confirmed the synthesized product [BMIm]BF₄ with peaks of wavenumbers at 757.38 and 620.01 cm⁻¹ depicts C–N stretching vibration, a peak in the range of 3145 cm⁻¹ shows the formation of quaternary amine salt along tetrafluoroborate. The vibrations at 2941 and 2871 cm⁻¹ shows aliphatic asymmetric and symmetric (C–H) and strong in-plane bending vibrations. The vibrations at 1168 cm⁻¹ are due to methyl groups²⁰.

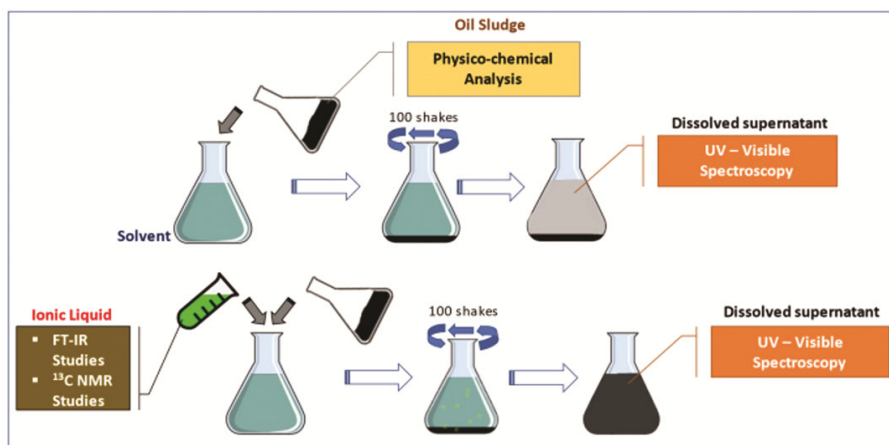
¹³C NMR studies of IL

The product was analysed with the help of NMR spectroscopy and the spectra is shown in Fig. 3. The NMR peaks can be assigned as follows.

¹³C NMR (76 MHz, CDCl₃): d (ppm) 135.99 (C2), 123.80 (C4, d), 126.5 (C5, d), 49.57 (C6, d), 31.86 (C7), 19.25 (C8), 13.27 (C9), 36.04 (C10).

Dissolution studies of TBS with IL products

The dissolution efficiency of TBS was carried out in solvent system without IL and in the presence of IL. According to the evaluation of the first slot, dissolution of TBS in hexane, heptane, methanol, toluene and ethyl acetate as 25%, 40%, 20%, 43% and 30%, respectively. Further ppm doses ranging from 100-800 ppm of IL products [BMIm]Br, [BMIm]BF₄, [PMIm]Br, [PMIm]BF₄, [HMIm]Br, and [HMIm]BF⁻ was employed. For [BMIm]Br, maximum dissolution was observed in hexane which was up-to 68%. [BMIm]BF₄ showed tremendous efficiency in heptane and hexane solvent up to 88% and 70%, respectively, at 800 ppm dosage. 80% and 82% dissolution of TBS



Scheme 3 — Schematic representation of experimental procedure

Table 2 — Physico-chemical parameters of TBS

Appearance	Wax content	Asphaltene content	Saturates	Aromatics	Resins	M.P. of wax	Congealing point of wax
Semi solid	46.53%	9.74%	49.38%	18.50%	32.12%	69°C	64°C

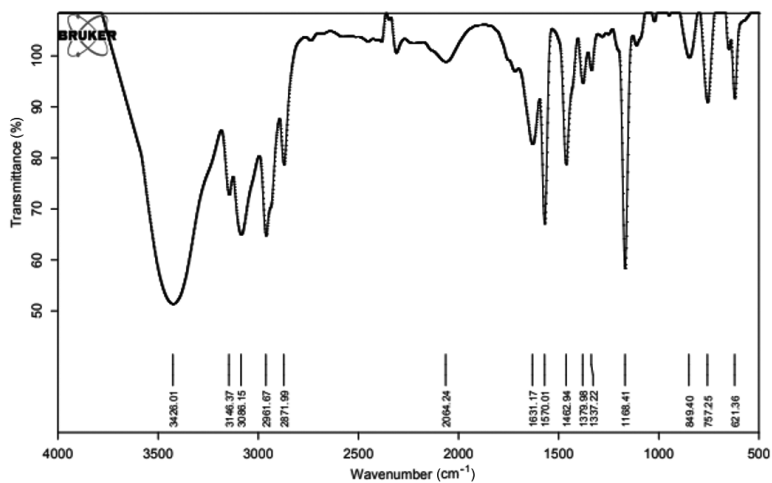


Fig. 1 — IR spectrum of [BMIm]Br

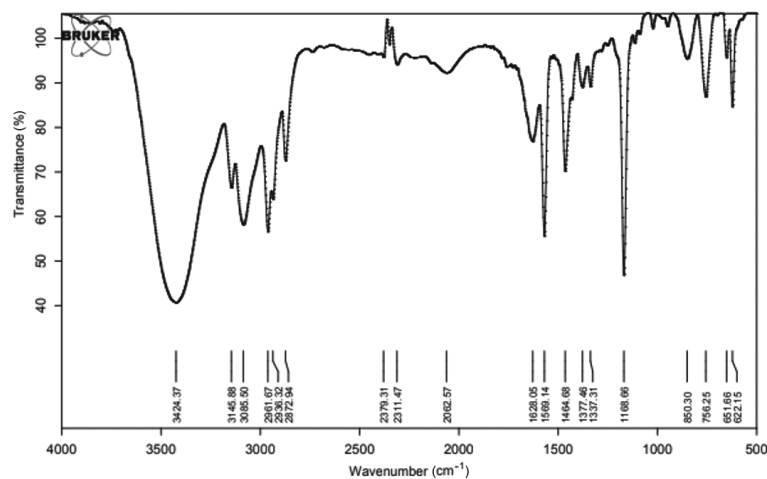


Fig. 2 — IR of [BMIm]BF₄

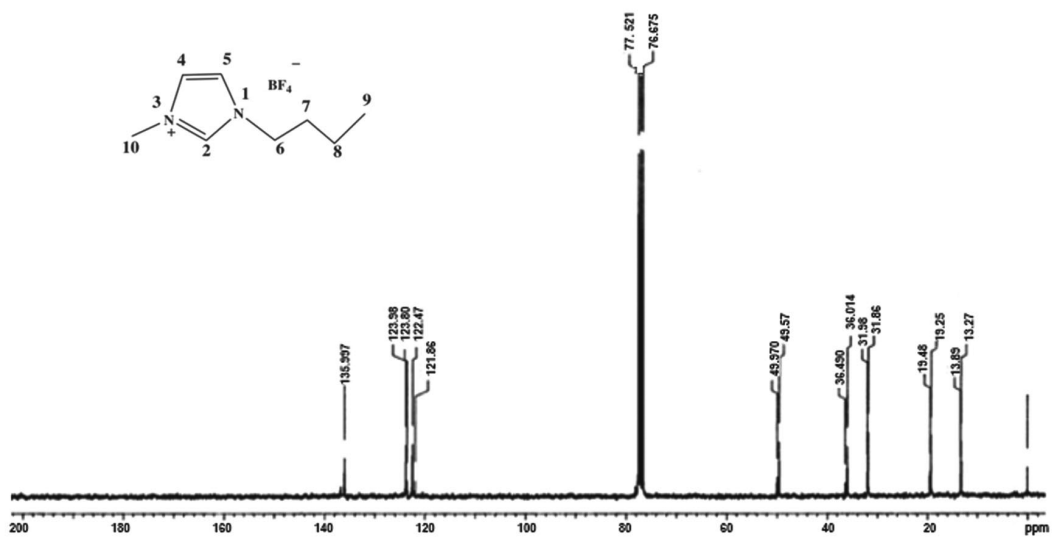


Fig. 3 — ¹³C NMR spectrum of [BMIM]BF₄

was observed in toluene and heptanes, respectively, in the presence of [PMIm]Br. [PMIm]BF₄ shows excellent results in heptane and hexane solvent up to 78% and 74%, respectively. 84% and 82% dissolution were evaluated in toluene along with [HMIm]Br, and [HMIm]BF₄, respectively. A decrease in the trend of dissolution efficiency of TBS in the presence of [PMIm]Br was recorded in ethyl acetate solvent. [HMIm]Br worked best for ethyl acetate solvent which showed dissolution efficiency results up to

65%. For better understanding in dissolution efficiency the samples were investigated by UV-visible spectroscopy. A comparative study of the absorbance of sample solution and standard solution was performed. The detailed trends of dissolution are shown in Figs 4-6. The UV absorbance studies are shown in Fig. 7.

The efficient dissolution of TBS in solvents containing aromatic ILs could be attributed to the interaction between the cationic part of the ILs and

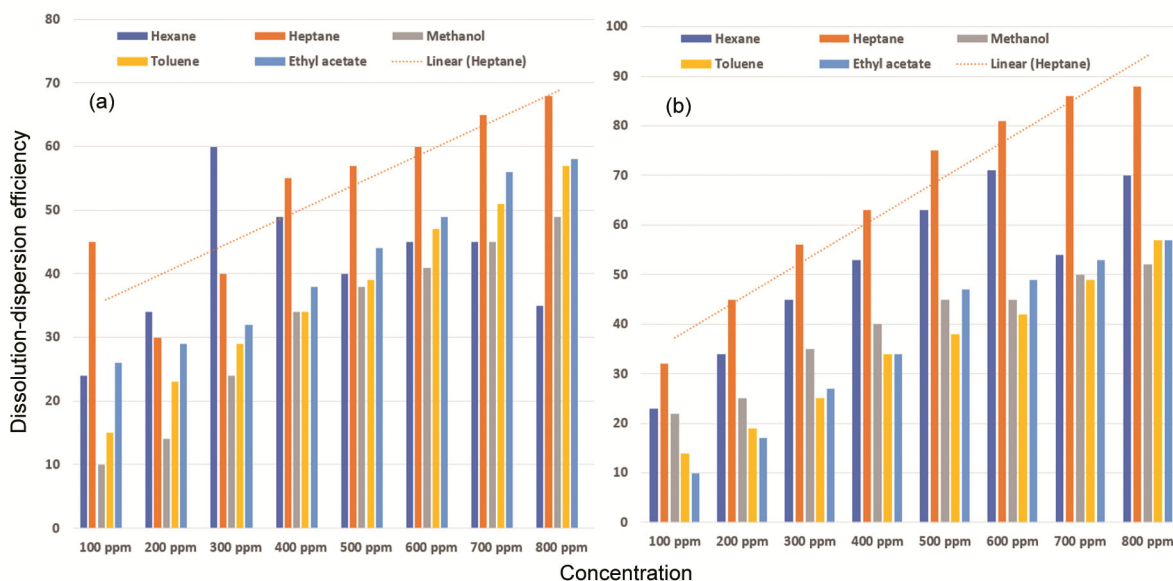


Fig. 4 — Dissolution-dispersion efficiency of TBS in the presence of (a) [BMIm]Br and (b) [BMIm]BF₄

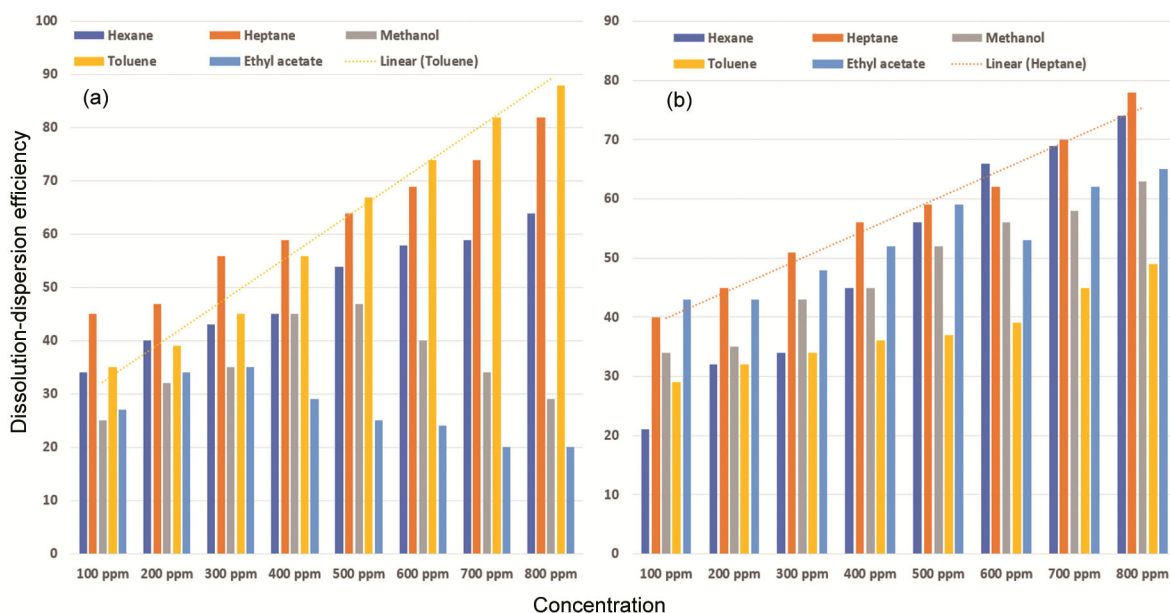


Fig. 5 — Dissolution-dispersion efficiency of TBS in the presence of (a) [PMIm]Br and (b) [PMIm]BF₄

the heteroatomic groups of TBS. Asphaltenes present in the TBS contain heteroatoms such as N, S and O, each having at least one lone pair of electrons that are susceptible to interactions⁴. It's important to comprehend the chemical aspect of asphaltene and examine its stability in crude oil. Asphaltenes exhibit different behaviour based on the conditions present in the reservoir and surface. Solvents like toluene, benzene, xylene, etc. are capable of solubilizing asphaltenes in TBS but they are usually not recommended due to their carcinogenic nature. In an

alternative, lower hydrocarbons like Hexane, Heptane, etc. can be utilized but their ability to dissolve asphaltene is less as compared to aromatic hydrocarbons which needs to be improved^{21,22}. Additives like ILs have a huge role in improving the efficiency of the existing solvent system. The association of asphaltenes can be disrupted by lowering the alkyl chain length of the cationic head ring utilized for dissolution and increasing the anionic charge density. As ILs are eco-friendly in nature, by improving the efficiency of the solvent they indirectly

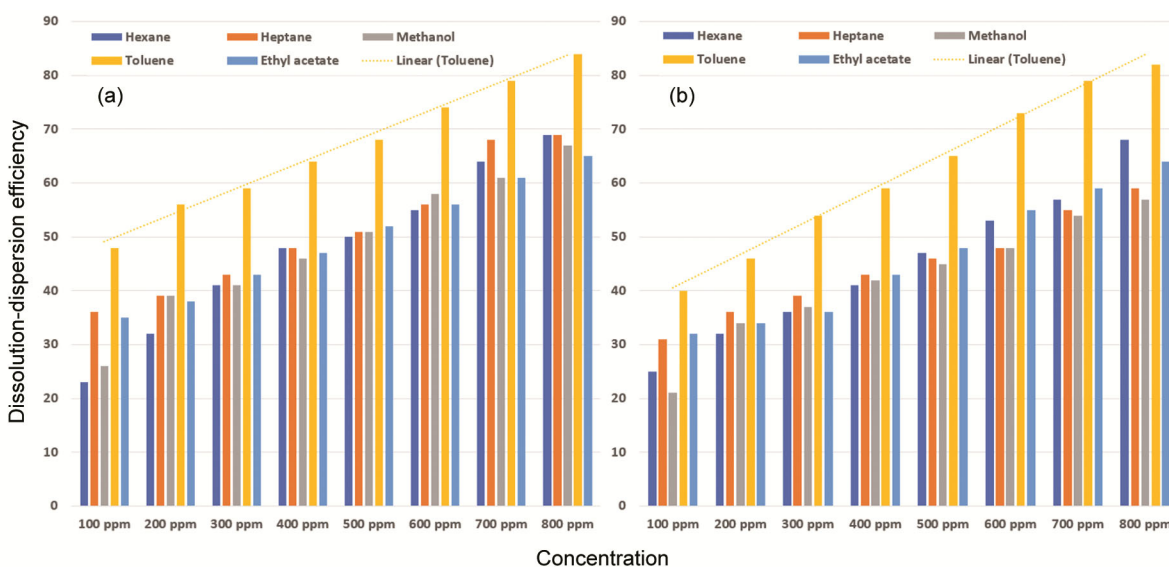


Fig. 6 — Dissolution-Dispersion efficiency of TBS in the presence of (a) [HMIm]Br and (b) [HMIm]BF₄

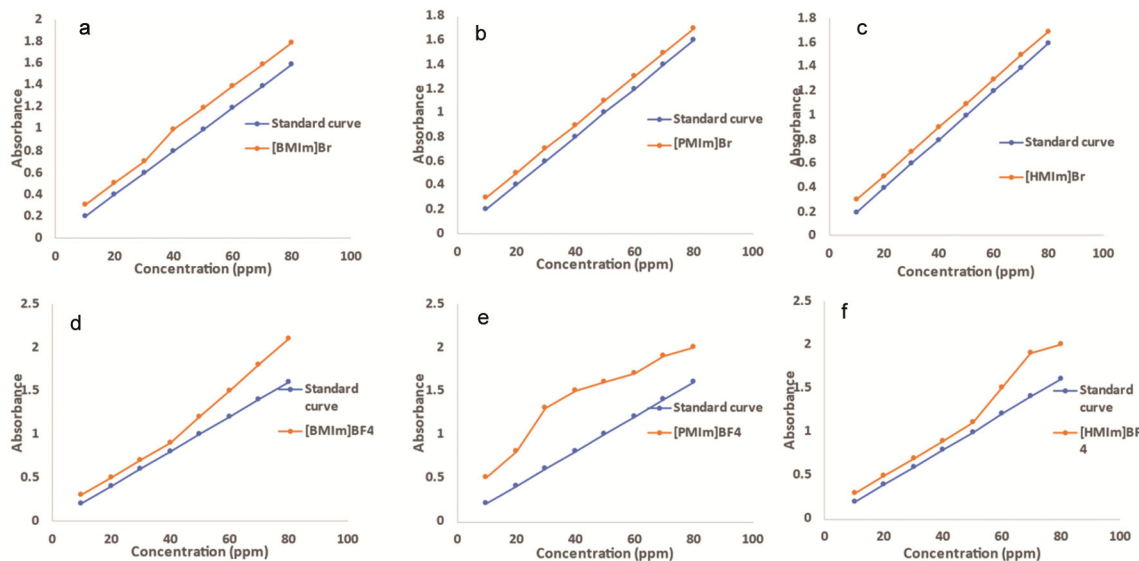


Fig. 7 — UV absorbance studies showing the effect of synthesized ILs at 800 ppm on TBS in heptane: (a) Effect of [BMIm]Br, (b) Effect of [BMIm]BF₄, (c) Effect of [PMIm]Br, (d) Effect of [PMIm]BF₄, (e) Effect of [HMIm]Br and (f) Effect of [HMIm]BF₄

decrease the necessity of utilizing hazardous solvents²³. The beauty of these products is they can be extracted again from the system by dissolving it in small amount of water or by distillation and re-used²⁴.

Conclusion

The dissolution pattern of TBS in solvent systems (TBS + Solvent) and along with the six synthesized ILs; [BMIm]Br, [BMIm]BF₄, [PMIm]Br, [PMIm]BF₄, [HMIm]Br and [HMIm]BF₄ (TBS + Solvent + IL) were studied. The role of these ILs in enhancing the dissolution performance was better than that of solvent independently. Dissolution - dispersion efficiency of solvent heptane was found to be 40%, however it increased to 88% when employed along with 800 ppm of [BMIm]BF₄. Similarly [PMIm]Br shows extreme dissolution efficiency at 800 ppm up to 80% and 82% in the presence of toluene and heptanes, respectively. It is also observed collectively that IL possessing tetrafluoroborate anion with 1-butyl 3-methyl imidazolium cation [BMIm]BF₄ showed better results in terms of dissolution. It is noted that even small amount of IL is effective in increasing the dissolution efficiency of the solvents thus serves as an environmental-friendly alternative. ILs work by softening the TBS which is accumulated in the bottoms of tank so that risks involved in manual cleaning can be avoided. This method can be utilized in minimizing the use of toxic organic solvents. It can be said that the interaction of IL product with the suitable solvent can directly influence the dissolution efficiency of TBS. From the present work, it can be stated that ILs can become potential substitute for toxic solvents and additives utilized in the petroleum industry.

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