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Eco-efficient and green method for the enhanced dissolution of aromatic crude oil sludge using ionic liquids†

Sivabalan Sakthivel,^a Sugirtha Velusamy,^a Ramesh L. Gardas^{*b} and Jitendra S. Sangwai^{*a}

The upstream petroleum industry faces operational and technical problems due to increased deposition of waxes, aromatics and asphaltene from crude oil sludge in oil storage tanks in the form of tank-bottom sludge (TBS). This results in huge production losses, and threatens environmentally safe operation; therefore, safer solutions are needed. In this work, nine aromatic ionic liquids (ILs) are synthesized and tested for the dissolution of TBS with the aid of five solvents, namely, toluene, heptane, decane, ethyl acetate and hexane. The UV absorbance values of the standard solutions (TBS in solvent) are compared with the sample solutions (TBS in solvent + ILs). It is observed that ILs significantly improve the dissolution of TBS in solvents compared with neat solvent alone. Different weight ratios of TBS : ILs (1 : 1, 1 : 0.5 and 1 : 0.1) are considered in this study. Ionic liquids (ILs) based on an imidazolium cation and various anions, such as [Cl]⁻, [Br]⁻, [BF₄]⁻, [H₂PO₄]⁻, [HSO₄]⁻, and [PF₆]⁻, are considered in this investigation. It is observed that the dissolution of TBS in heptane in the presence of [HMIM]⁺[Br]⁻ is efficient to a maximum extent of 66% with other solvents showing similar increased solubility effect with various ILs. In the case of hexane, it should be noted that the efficiency of dissolution of TBS goes on decreasing with increasing concentration of TBS in hexane. A hold-time study is also performed with heptane containing ILs and heptanes without ILs to determine the maximum time required for efficient dissolution of TBS. It is observed that the efficiency is increased beyond 66% in the presence of ILs for the dissolution of TBS in heptane, provided that the mixture of solvent and ILs are in contact with the TBS for a prolonged period of 30 days, or even longer as required. FT-IR and ¹³C-NMR spectral analyses are also performed so as to understand the efficiency of the ILs in the dissolution of TBS in various solvents, and it was observed that there is a decrease in the intensity of the peaks in the spectra of treated TBS with solvents, which is further enhanced by the addition of ILs.

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Introduction

Petroleum is indispensable for industrial growth. Through the last few decades, the petroleum industry has entered into a period of rejuvenation and changeover. Together with industrial growth and development, due care for the environment and sustainability are important concerns for the industry. Due to the increased production of waxy and heavier crude oil from mature reservoirs and heavy oil reservoirs in the recent past, the industry faces operational and technical problems such as deposition of wax, asphaltene and crude oil sludge in storage tanks, production tubing and surface facilities, increased skin

factor near wellbore resisting production, emulsification of crude oil with formation water and oil sludge formation in the crude oil storage tanks. These problems result in huge production losses, increased expenditure due to remedial intervention, involvement of scarce human resources, and threaten the environmentally safe operation. It is, therefore, crucial that intelligent, cost-effective and innovative solutions are identified for these problems.

Crude oil contains higher hydrocarbon contents, particularly waxes and asphaltenes, which remain in the dissolved state as liquid hydrocarbons at the higher pressures and temperatures of the reservoirs. When the crude oil flows from the reservoir to the surface, the drop in the system pressure and temperature causes the waxes and asphaltenes to separate from the bulk stream, resulting in their accumulation and build up in the production tubing and surface facilities in the form of oil sludge. The gradual accumulation of these heavier hydrocarbons is very common in the lower portions of petroleum storage tanks,¹ which is referred as 'tank bottom sludge' (TBS). The composition of TBS differs due to the large diversity in the

^aPetroleum Engineering Program, Department of Ocean Engineering, Indian Institute of Technology Madras, Chennai – 600 036, India. E-mail: jitendrasangwai@iitm.ac.in; Fax: +91-44-2257-4802; Tel: +91-44-2257-4825

^bDepartment of Chemistry, Indian Institute of Technology Madras, Chennai – 600 036, India. E-mail: gardas@iitm.ac.in; Fax: +91-44-2257-4202; Tel: +91-44-2257-4248

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quality of crude oils, variations in the processes used for oil-water separation, leakages during industrial processes, and addition to the existing TBS. Usually, the TBS consists of heavier components of oil such as waxes, asphaltenes, and resins, in addition to water, biomass, and many inorganics (iron-rust, scale, mud, sand), which can induce severe scale and plugging problems. Unless remedial measures are taken, the TBS becomes thicker, gets compactly packed and becomes much more difficult to remove. The presence of water usually aggravates the problem of TBS deposition. It is at this water/crude oil interface that microorganisms grow; moreover, oxidation of the oil results in their accumulation as waste at the bottom of the tank with other dirt and rust to form TBS. On many occasions, such accumulation renders the tank unusable due to its inability to perform suction and dispatch crude oil for delivery through the pipeline. It is customary to use heated oil and water, dispersant formulations and elaborate oil circulation arrangements to make the TBS soluble and pumpable. In absence of such arrangements, time-consuming, manual cleaning becomes necessary.¹ The TBS removed from the storage tanks not only represents lost revenue for petroleum companies, but its disposal is also a serious environmental concern. Chemical treatments of aromatic hydrocarbons such as asphaltenes are typically performed by using cyclic non-polar solvents such as xylene, benzene, and toluene (aromatic), which have the potential to dissolve asphaltenes.^{2,3} However, these aromatic solvents are volatile and hazardous; hence, they are not recommended.² The alternative approach is to use lighter hydrocarbons such as heptane and decane, but they show lower dissolution of aromatic hydrocarbons in TBS; thus they need to be improved. The use of ionic liquids have huge prospective as a good co-solvent along with solvents for TBS and can be used.

Ionic liquids (ILs) generally contain cations, a conjugated aromatic core and anions, which are typically strong hydrogen bond acceptors. ILs are an admirable alternative to substitute volatile organic solvents for green technologies. They possess a combination of unique properties such as high thermal and chemical stability, non-flammability, and negligible vapour pressure, thereby decreasing the risk of a worker's exposure to the hazardous chemicals and the loss of solvent to the atmosphere. When any IL is mixed with any organic solvent for a specific application, it is expected to help reduce the use of hazardous and polluting organic solvents.⁴ Moreover, the ILs used can be recycled by using a small amount of water and both can be readily recovered by distillation⁵ and reused numerous times.^{3,6} ILs also provide help in decreasing the viscosity of the crude oil through catalytic cracking of heavier hydrocarbons. Ionic liquids show very good performance as a novel solvent in the dissolution of asphaltenes.⁷ A fascinating quality of ILs is that any small changes made in the combination of cations and anions or in the nature of the moieties attached to each ion allow physical properties of the ILs to be personalized for definite applications.⁸⁻¹⁰ Asphaltene association could easily be broken by increasing the anionic charge density and decreasing the alkyl chain length of the cationic head ring of the ionic liquids used for dissolution.⁷ Thus, ionic liquids present a potential solution to address the energy and environmental

challenges associated with the handling of tank bottom sludge in the upstream oil and gas industry. The use of ILs for the dissolution of TBS will help to overcome the environmental hazards, eliminate the man-hours and personnel safety issues, facilitate the easy transportation of the crude oil and enhance potential recovery of conditioned fuel. Nowadays, ionic liquids are normally used in mining, desulphurization, and scale removal because of their outstanding solubility and catalytic properties over a wide temperature range.¹¹ In addition to aiding in the removal of oily sludge, this method may also assist in recovering valuable crude oil from oily sludge, which is otherwise lost due to dumping and the common practice of burning of tank-bottom sludge (TBS).

Recently, few studies have shown the use of ILs to address various issues in the upstream oil and gas industry.^{3,7,12,13} Indeed, there is still an ample scope in the area of designing specific ionic liquids that are capable of solubilising and softening crude oil to make it pumpable. The applicability of ionic liquids in the field of petroleum has been investigated by various authors who recognize their peculiar properties. Recently, room temperature ionic liquids such as, $[\text{Et}_3\text{NH}]^+[\text{AlCl}_4]^-$, $[\text{Et}_3\text{N-H}]^+[\text{AlCl}_4]^- \text{Ni}^{2+}$, $[\text{Et}_3\text{NH}]^+[\text{AlCl}_4]^- \text{Fe}^{2+}$ and $[\text{Et}_3\text{NH}]^+[\text{AlCl}_4]^- \text{Cu}^{2+}$, have been used in upgrading heavy oil at reservoir conditions by reducing its viscosity. The results showed significant improvement in the reduction of viscosity at the optimum temperature conditions of the oil reservoir. Among the studied ILs, $[\text{Et}_3\text{N-H}]^+[\text{AlCl}_4]^- \text{Ni}^{2+}$ has shown better viscosity reduction than the rest of the ILs.^{12,14} Chloro-aluminate(III) ionic liquids/ H_3PO_4 systems have been found to be more effective for asphaltic sand degradation.^{12,13} In addition, ionic liquids such as $[\text{EMIM}]^+[\text{BF}_4]^-$ and $[\text{BMIM}]^+[\text{BF}_4]^-$ are found to be more efficient for enhancing the recovery of bitumen from oil sands.⁵ Ionic liquids are also found to work as a new substituent for surfactants in enhanced oil recovery processes.¹⁵

Ionic liquids, such as $[\text{BMIM}]^+[\text{Cl}]^-$ and $[\text{BMIM}]^+[\text{AlCl}_4]^-$, act as better asphaltene dissolution agents.^{16,17} $[\text{BMIM}]^+[\text{BF}_4]^-$ has been found to be very efficient in the field of bitumen recovery from oil sands.³ In the reaction mechanism between ionic liquids and heavy oil, the first step is the reaction of organic sulphur from the heavy oil with transition metal-modified ionic liquids to form the intermediate complex ($\text{S} \rightarrow \text{M}^+$), which help to weaken the C-S bonds and is followed by breakage of the heavy oil molecules. The result of this reaction is that sulphur in the heavy oil escapes as H_2S ; therefore, the content of sulphur gets reduced in the heavy oil.¹⁶ The results show that the separation is easier by using ionic liquids rather than by using water. The interfacial tension and surface tension between bitumen and silica are decreased in the presence of ionic liquids, which facilitate their easy separation.⁶ Adhesion forces between bitumen and silica are significantly smaller in the presence of ILs than in aqueous solution.¹⁷ Similarly, the contact angle between the bitumen oil and water droplets is $\sim 90^\circ$, but in the case of bitumen oil and ionic liquid it is $\sim 73^\circ$.¹⁸ These results show that the separation is easier by using ionic liquids than pure water.

We find that ionic liquids are employed for various kinds of work such as enhanced oil recovery, asphaltene degradation,

bitumen recovery, and desulphurization. Surprisingly, none of the available literature to date addresses the problems associated with the petroleum sludge deposition at the bottom of the petroleum storage tank. This work presents the investigation of dissolution of tank-bottom sludge using nine ionic liquids with five different solvents. The ionic liquids used here are aromatic-based and have been synthesized as per the previous available literature. The choice of using aromatic ILs is due to the fact that the oil sludge being used in the present investigation contains more aromatics. The solvents used are from the classes of paraffinic, aliphatic-polar and aromatic solvents, namely, heptane, hexane and decane from the paraffinic group, ethyl acetate from the aliphatic-polar solvents and toluene from the aromatic solvent group.

2. Experimental section

2.1. Materials

2.1.1 Tank-bottom sludge. For this study, TBS samples were acquired from Oil India Limited (OIL), Assam, India. TBS was found to be more solid and viscous as compared to conventional crude oil. The sample was free of dissolved gas. Saturates (S), aromatics (Ar), resins (R), and asphaltene (A) analysis of the TBS is summarized in Table 1.

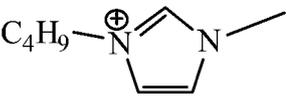
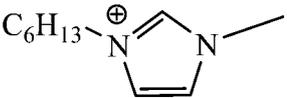
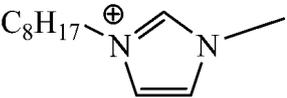
2.1.2 Ionic liquids and solvents. The list of synthesized ILs is given in Table 2 along with their abbreviations. In the present work, nine ILs, namely, [BMIM]⁺[Cl]⁻, [BMIM]⁺[PF₆]⁻, [BMIM]⁺[HSO₄]⁻, [BMIM]⁺[H₂PO₄]⁻, [BMIM]⁺[Br]⁻, [BMIM]⁺[BF₄]⁻,

Table 1 SARA analysis report^a

No. of trials	Composition		
	S (%)	Ar (%)	R + A (%)
1	25.3	63.4	11.3
2	25.2	67.6	7.2
3	28.6	63.5	7.9

^a S: saturates; Ar: aromatics; R: resins; A: asphaltenes.

Table 2 List of synthesized ionic liquids

Cation	Anion	Name	Abbreviation
	Cl [⊖]	1-Butyl-3-methylimidazolium chloride	[BMIM] ⁺ [Cl] ⁻
	Br [⊖]	1-Butyl-3-methylimidazolium bromide	[BMIM] ⁺ [Br] ⁻
	BF ₄ [⊖]	1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM] ⁺ [BF ₄] ⁻
	H ₂ PO ₄ [⊖]	1-Butyl-3-methylimidazolium dihydrogen phosphate	[BMIM] ⁺ [H ₂ PO ₄] ⁻
	HSO ₄ [⊖]	1-Butyl-3-methylimidazolium hydrogen sulfate	[BMIM] ⁺ [HSO ₄] ⁻
	PF ₆ [⊖]	1-Butyl-3-methylimidazolium hexafluorophosphate	[BMIM] ⁺ [PF ₆] ⁻
	Br [⊖]	1-Hexyl-3-methylimidazolium bromide	[HMIM] ⁺ [Br] ⁻
	HSO ₄ [⊖]	1-Hexyl-3-methylimidazolium hydrogen sulfate	[HMIM] ⁺ [HSO ₄] ⁻
	Cl [⊖]	1-Octyl-3-methylimidazolium chloride	[OMIM] ⁺ [Cl] ⁻

[HMIM]⁺[Br]⁻, [HMIM]⁺[HSO₄]⁻, and [OMIM]⁺[Cl]⁻, have been synthesized and purified according to the methods reported in literature^{19–24} and have been confirmed by ¹H nuclear magnetic resonance (¹H NMR). Prior to usage, all the ILs are dried under constant agitation at 353 K under vacuum (0.1 Pa) for a minimum of 48 h to reduce the water content and volatile compounds to negligible values. Table 3 gives the details of the starting materials used for the synthesis of ILs.

2.2 Experimental procedure

2.2.1 Standard solution. The stock standard solution containing 1000 ppm of TBS in pure solvent (50 mg of TBS in 50 mL of the corresponding solvent) is prepared without ILs and further dilutions are then made from it. As a first step in the investigation, standard solutions, *i.e.*, TBS with solvents at different concentrations (dilutions) are prepared and their absorbance is recorded using an ultraviolet (UV)-visible spectrophotometer at a fixed wavelength corresponding to the λ_{max} of the specific solvent being considered as given in Table 4. This is obtained by running a full spectrum scan of an unknown concentration solution containing TBS in the required solvent in the wavelength range of 190–900 nm. For absorbance studies relating to the standard solution of TBS in toluene, the 1000 ppm solution of TBS in the solvent is diluted to concentrations of 10 ppm to 100 ppm (in increments of 10 ppm). For the rest of the solvents (heptane, decane, ethyl acetate and hexane) the concentrations (with respect to TBS) of the solutions used are in the range of 10 ppm to 120 ppm (in increments of 10 ppm). Herein, the term concentration (in ppm) refers to the concentration of TBS in the solvent only and not of the ionic liquid. Absorbance is measured for all of the above concentrations and the corresponding calibration plots are discussed in Section 3.

2.2.2 Sample solution for different weight-ratios of TBS : ILs. Three different weight ratios of TBS to ILs are considered for sample solutions in the dissolution studies, *i.e.*, TBS : ILs = 1 : 1, 1 : 0.5, 1 : 0.1. For TBS : ILs = 1 : 1, a stock solution of 1000 ppm has been prepared by dissolving 50 mg of TBS and 50 mg of IL in 50 mL of the corresponding solvent. For

Table 3 List of chemicals used for the present investigation

S. no.	Chemical name	CAS no.	Source	Purity (%)
1	1-Bromo butane	109-65-9	Spectrochem	98%
2	1-Bromo hexane	111-25-1	Spectrochem	98%
3	Calcium hydride	7789-78-8	Spectrochem	97%
4	1-Chloro butane	109-69-3	Spectrochem	99%
5	1-Chloro octane	111-85-3	Sigma Aldrich	99%
6	Dichloromethane	75-09-2	Rankem	99%
7	1-Methyl imidazole	616-47-7	Spectrochem	99%
8	<i>o</i> -Phosphoric acid	7664-38-2	Merck	85%
9	Potassium bromide	7758-02-3	S D Fine-Chem Ltd	99%
10	Potassium hexafluorophosphate	17084-13-8	Sigma Aldrich	98%
11	Sulphuric acid	7664-93-9	Merck	98%
12	Tetrafluoroboric acid	16872-11-0	Spectrochem	45%

Table 4 λ_{\max} of the TBS in various solvents

S. no.	Solvents	CAS no.	Source	Purity	λ_{\max} (nm)
1	Toluene	108-88-3	Merck	99%	288
2	Heptane	142-82-5	Merck	99%	226
3	Decane	124-18-5	Aldrich	95%	227
4	Ethyl acetate	141-78-6	Rankem	99%	257
5	Hexane	110-54-3	Merck	99%	229

TBS : ILs = 1 : 0.5 and 1 : 0.1, a similar procedure as described above has been followed. The concentrations considered in this work (*i.e.*, 10, 30, 50, and 70 ppm) are made by dilution from the stock solution, except in case of toluene where only three concentrations of 30, 50 and 70 ppm (concentration of TBS in toluene) are considered. As mentioned above, three different weight ratios of TBS to ILs (*i.e.*, TBS : ILs = 1 : 1, 1 : 0.5 and 1 : 0.1) has been studied for all nine ILs considered in this work. Furthermore, for each ratio of TBS to ILs four different concentrations (*i.e.*, 10, 30, 50, and 70 ppm) have been prepared in five different solvents (*i.e.*, toluene, heptane, decane, ethyl acetate and hexane). Thus, a total of 513 sample solutions are prepared for this work, and each of them has been prepared thrice from their respective stock solution for three trial studies. The absorbance values for all of the sample solutions are recorded compared with their respective standard solution and used for TBS dissolution calculations. The schematic of the experimental procedure followed is shown in Fig. 1(a) and (b). It should be noted that only the soluble part (filtrate) is taken for UV-visible analysis, and the standard and sample solutions for this study have been freshly prepared; moreover, their absorbance are recorded on the same day within approximately two hours of solution preparation.

2.2.3 Preparation of sample for FT-IR and ^{13}C -NMR. Samples for Fourier transform-infrared spectroscopy (FT-IR) and ^{13}C -nuclear magnetic resonance (^{13}C -NMR) are prepared by evaporating the solvent from the bottom sediments (obtained from the solutions containing a 1 : 1 ratio of TBS : ILs) left over after sample preparation for UV spectra, and then collecting the dried portion. Note that very little amount of solid is obtained, and a small amount is used for recording the

^{13}C -NMR from that portion. Then, the remaining left-over solid is used for recording the FT-IR spectra by grinding it with potassium bromide (KBr). Similarly, the dissolved portion of TBS is collected and the solvent is evaporated by a rotavapor. The left-over portion of the sample is collected for analysis by FT-IR and ^{13}C -NMR. By using water, ionic liquids used in the

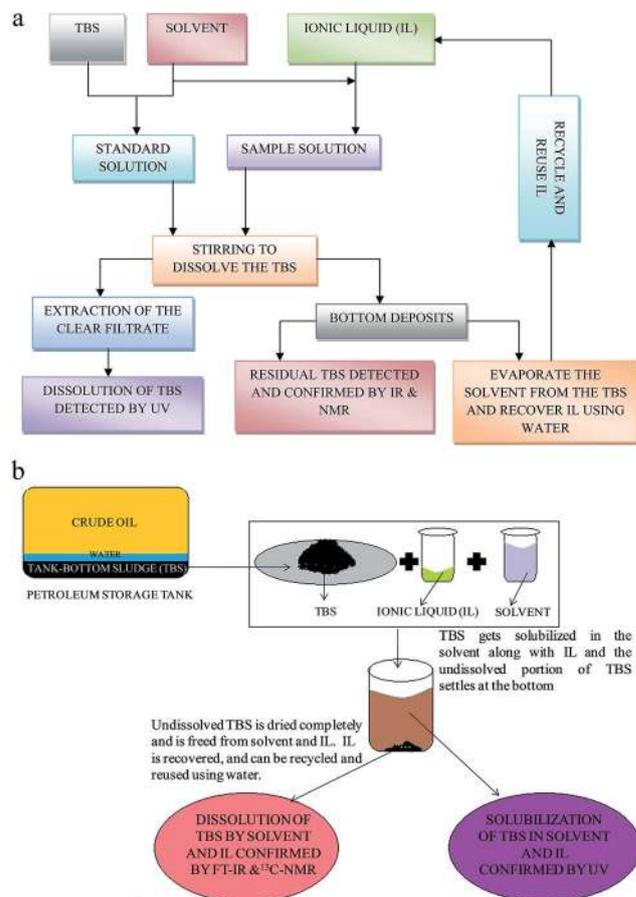


Fig. 1 (a): Flowchart for the experimental procedure followed for the present investigation of dissolution of tank-bottom sludge (TBS). Fig. 1(b): Schematic for the experimental procedure involving the dissolution of tank-bottom petroleum sludge.

sample solutions are recovered and can be recycled and reused. The same procedure is followed for all five of the solvents considered in this study.

2.3 Analytical methods

The water content is measured by an Analab (Micro Aqua Cal100, India) Karl Fischer Titrator using Karl Fischer reagent from Merck. The calibration is performed with distilled water (by weight) with an average titre factor of 5.356. This instrument can detect water content from less than 10 ppm to 100% by conductometric titration with a dual platinum electrode. The purities of the synthesized ionic liquids were determined using $^1\text{H-NMR}$, ^1H and $^{13}\text{C-NMR}$ with a Bruker Avance 500 MHz spectrometer (made in Switzerland) using deuterated DMSO and CDCl_3 , respectively, as solvents. The standard absorbance values of TBS in the presence of the solvents and ILs are recorded using a UV-visible spectrophotometer (JASCO V-650, Japan; accuracy = ± 0.2 nm; wavelength range = 190–900 nm) at a fixed wavelength corresponding to the λ_{max} . FT-IR spectra are recorded on an FT-IR spectrophotometer (JASCO FT-IR-4100, Japan). The device has a maximum resolution of 0.9 cm^{-1} and has a signal-to-noise ratio of 22 000 : 1. $^{13}\text{C-NMR}$ is performed as formerly described,²⁵ except that we employ $^{13}\text{C-NMR}$ for investigating the dissolution of TBS in the presence of solvent and ILs.

3. Results and discussion

This section discuss the quantification of the solubility of TBS without ILs (standard solutions), followed by the studies of the sample solutions containing TBS in solutions of various solvents and ILs. UV-visible spectrophotometry was used,

followed by hold-time studies, to understand the effect of ILs on the dissolution of TBS with time. Detailed results of the FT-IR and $^{13}\text{C-NMR}$ analyses confirm the results obtained.

3.1 Solubility studies of TBS without ILs

The solubility studies of the standard solutions (TBS in various solvents) are carried out by measuring their absorbances using a JASCO UV-visible spectrophotometer at the particular wavelength corresponding to the λ_{max} of the respective solvent (as in Table 4). Fig. 2(a–e) shows the plot of the absorbances of the standard solutions against the concentration (in ppm) of TBS in solvents such as toluene, heptane, decane, ethyl acetate and hexane, respectively. These plots are fitted with linear regression analysis and have a regression coefficient (R^2) greater than 0.99. The values of R^2 obtained for the various standard solutions of TBS in toluene, heptane, decane, ethyl acetate and hexane are 0.9980, 0.9982, 0.9993, 0.9997 and 0.9995, respectively.

3.2 Solubility studies of TBS with ILs

The solubility studies of the sample solutions with nine ionic liquids, five solvents and with three different weight ratios of TBS : ILs were performed by measuring their absorbances at the particular wavelength corresponding to the λ_{max} of the respective solvent (as in Table 4). All the values corresponding to the absorbance runs are consistent between three trials within ± 0.001 and the averages of each set of three trials are considered for further calculations and plots. The absorbances of the sample solutions are compared with the respective concentrations of the standard solutions and the increase in the percentage solubility relative to the standard solution (with absorbance values of the standard solutions as base references)

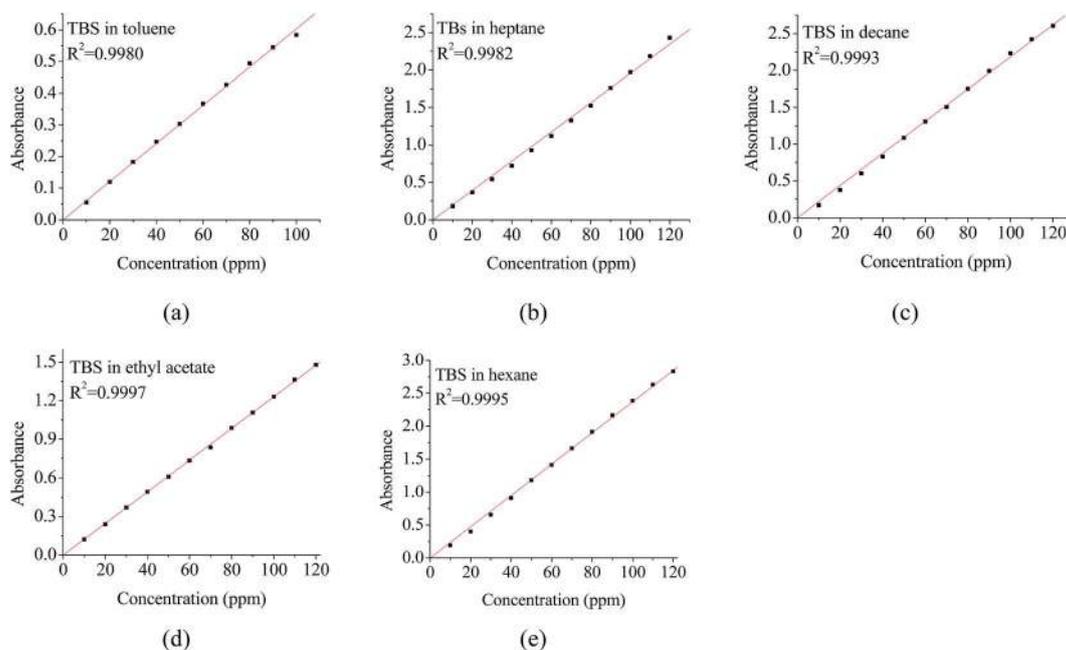


Fig. 2 Standard calibration curve (Linear fit) – UV absorption for the TBS in different solvents such as (a) toluene, (b) heptane, (c) decane, (d) ethyl acetate and (e) hexane at different concentrations (ppm).

are plotted. Fig. 3 shows the UV absorption of the sample solution in comparison with the standard solution prepared in heptane with TBS : ILs = 1 : 1. In Fig. 3, (a)–(i) show the effect of ILs $[\text{BMIM}]^+[\text{Cl}]^-$, $[\text{BMIM}]^+[\text{PF}_6]^-$, $[\text{BMIM}]^+[\text{HSO}_4]^-$, $[\text{BMIM}]^+[\text{H}_2\text{PO}_4]^-$, $[\text{BMIM}]^+[\text{Br}]^-$, $[\text{BMIM}]^+[\text{BF}_4]^-$, $[\text{HMIM}]^+[\text{Br}]^-$, $[\text{HMIM}]^+[\text{HSO}_4]^-$ and $[\text{OMIM}]^+[\text{Cl}]^-$, respectively. Similar observations are made for all other solvents and provided as ESI in Fig. S1–S4.† The percentage increase in solubility ($\pm 0.1\%$) versus the concentration in ppm and the varying proportions of TBS : ILs is represented as bar diagrams in Fig. 4–8, each showing the performance of various ionic liquids. In this investigation, it is observed that the dissolution of TBS in toluene is more efficient in the range from 25% to 66% using ILs, in which $[\text{BMIM}]^+[\text{PF}_6]^-$ is found to cause the maximum dissolution of TBS and the minimum efficiency of less than 20% is shown by the IL $[\text{BMIM}]^+[\text{Br}]^-$. In contrast to their behavior in toluene, it is surprising that the ILs, such as $[\text{BMIM}]^+[\text{Br}]^-$ and $[\text{HMIM}]^+[\text{Br}]^-$ with Br^- as the anion, exhibit very good performance in heptane.

Likewise, in the case of heptane and decane, $[\text{HMIM}]^+[\text{Br}]^-$ and $[\text{BMIM}]^+[\text{H}_2\text{PO}_4]^-$, respectively, show an efficiency to the

maximum limits of 66% and 38%. In the case of ethyl acetate, the dissolution of TBS is increased by the usage of either $[\text{BMIM}]^+[\text{H}_2\text{PO}_4]^-$ or $[\text{BMIM}]^+[\text{Br}]^-$ to the maximum limits of 18% or 19%, respectively. Similar to toluene, $[\text{BMIM}]^+[\text{PF}_6]^-$ shows the maximum dissolution of TBS up to the limit of 68% in hexane. In the case of hexane, it should be noted that the efficiency of the dissolution of TBS decreases with an increase in the concentration of TBS in hexane in all three weight ratios of TBS : ILs used.

In general, with respect to the different weight ratios of TBS : ILs, a meagre 10% of IL content is sufficient to cause successful dissolution of TBS in various solvents. From Fig. 9, which shows the comparison of solvents in the presence of ILs, it can be concluded that toluene and heptane show the highest efficiency in the dissolution of TBS. From the present investigation, with respect to enhanced dissolution of TBS using ionic liquids, it can be seen that, in toluene, ILs that have the same cation but different anions show decreasing solubility for TBS as follows: $[\text{PF}_6]^- > [\text{H}_2\text{PO}_4]^- > [\text{Cl}]^- > [\text{HSO}_4]^- > [\text{BF}_4]^- > [\text{Br}]^-$; however, in heptane, they show decreasing solubility as follows: $[\text{Br}]^- > [\text{Cl}]^- > [\text{HSO}_4]^- > [\text{BF}_4]^- > [\text{PF}_6]^- > [\text{H}_2\text{PO}_4]^-$. Similarly,

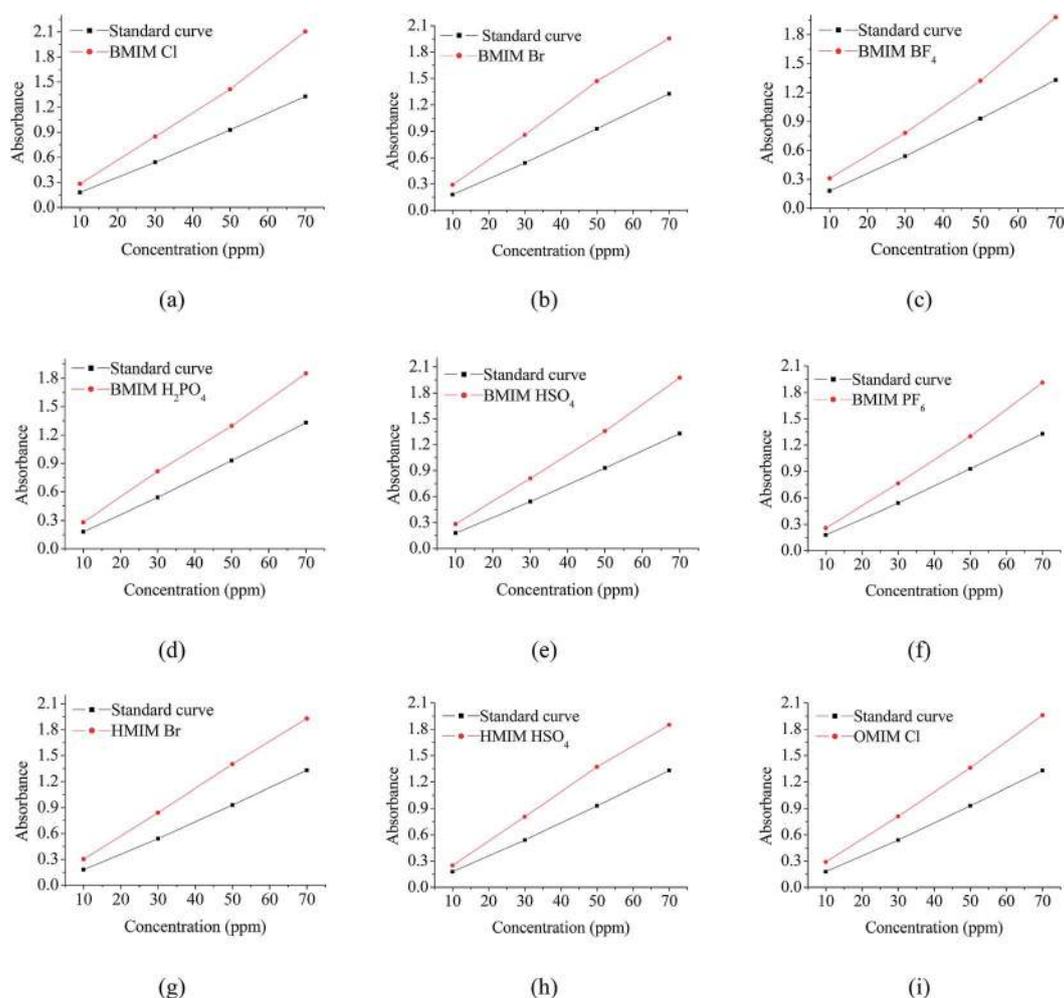


Fig. 3 UV absorption showing the effect of ionic liquids on TBS in heptane (TBS : ILs = 1 : 1). (a) Effect of $[\text{BMIM}]^+[\text{Cl}]^-$, (b) Effect of $[\text{BMIM}]^+[\text{Br}]^-$, (c) Effect of $[\text{BMIM}]^+[\text{BF}_4]^-$, (d) Effect of $[\text{BMIM}]^+[\text{H}_2\text{PO}_4]^-$, (e) Effect of $[\text{BMIM}]^+[\text{HSO}_4]^-$, (f) Effect of $[\text{BMIM}]^+[\text{PF}_6]^-$, (g) Effect of $[\text{HMIM}]^+[\text{Br}]^-$, (h) Effect of $[\text{HMIM}]^+[\text{HSO}_4]^-$, (i) Effect of $[\text{OMIM}]^+[\text{Cl}]^-$.

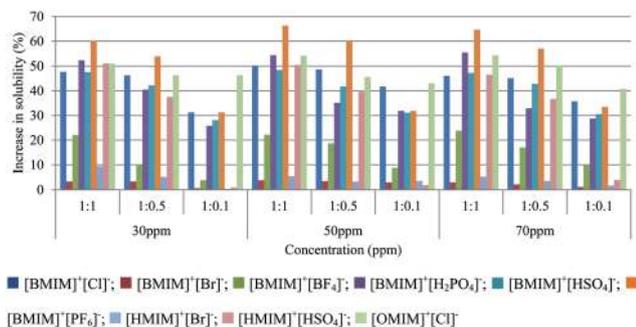


Fig. 4 Comparison of the efficiency of the said ILs in terms of increase in solubility of TBS in toluene for solutions containing varying ratio of TBS:ILs at three different concentrations (concentration (in ppm) of TBS in toluene). Base line of 0 % solubility is for standard solution.

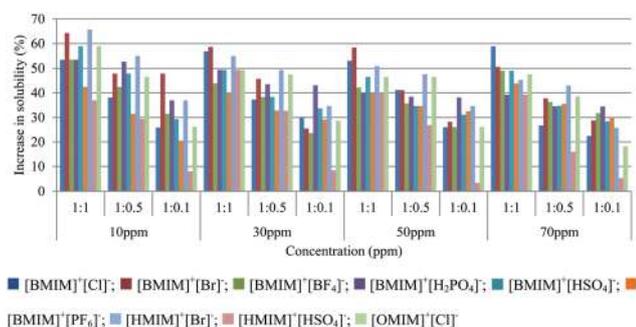


Fig. 5 Comparison of the efficiency of the ILs in terms of increase in solubility of TBS in heptane for solutions containing varying ratio of TBS:ILs at three different concentrations (concentration (in ppm) of TBS in heptane). Base line of 0 % solubility is for standard solution.

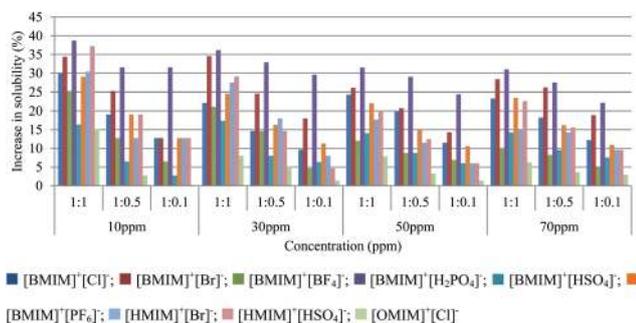


Fig. 6 Comparison of the efficiency of the said ILs in terms of increase in solubility of TBS in decane for solutions containing varying ratio of TBS:ILs at three different concentrations (concentration (in ppm) of TBS in decane). Base line of 0 % solubility is for standard solution.

the ionic liquids that have the same anion but different cations show the solubility order as $[BMIM]^+ > [HMIM]^+ > [OMIM]^+$ in all of the solvents considered, and may vary slightly but follow a similar trend.

We also present a few of the full scan spectra of TBS in heptane and toluene, both in the absence and presence of the IL $[BMIM]^+[PF_6]^-$ at different concentrations as given below, and this is included in Fig. S5 of the ESI.† From Fig. S5(i) and (ii),† it

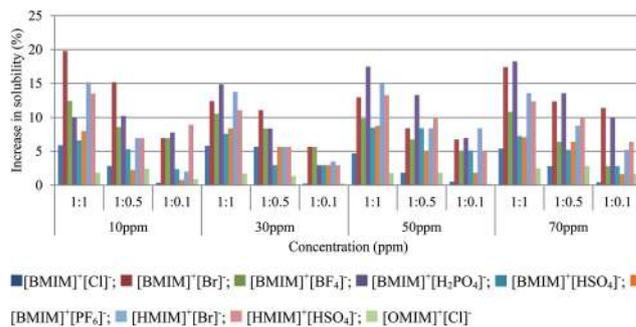


Fig. 7 Comparison of the efficiency of the said ILs in terms of increase in solubility of TBS in ethyl acetate for solutions containing varying ratio of TBS:ILs at three different concentrations (concentration (in ppm) of TBS in ethyl acetate). Base line of 0 % solubility is for standard solution.

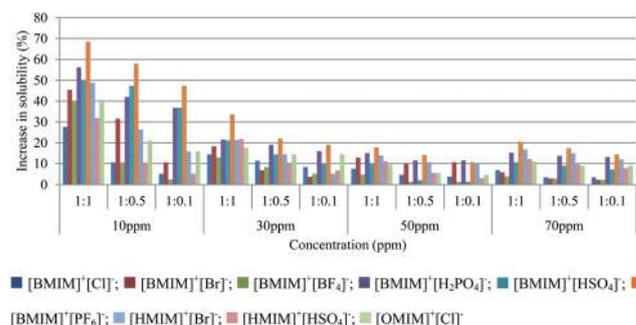


Fig. 8 Comparison of the efficiency of the said ILs in terms of increase in solubility of TBS in hexane for solutions containing varying ratio of TBS:ILs at three different concentrations (concentration (in ppm) of TBS in hexane). Base line of 0 % solubility is for standard solution.

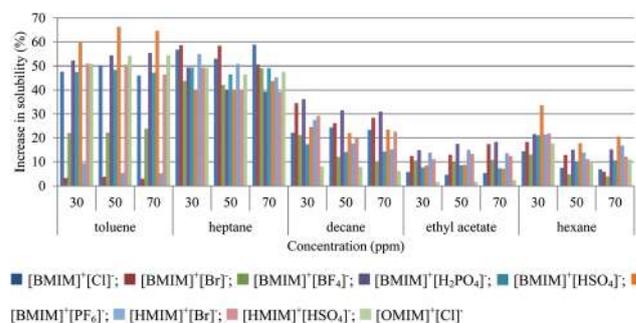


Fig. 9 Comparison of the efficiency of all the said ILs in terms of increase in solubility of TBS in all of the mentioned solvents involved in the present investigation containing varying ratio of 1:1 (TBS:ILs) at three different concentrations. Base line of 0 % solubility is for standard solution.

is evident that there is significant improvement in the absorbance value of TBS in a given solvent (heptane or toluene) as a result of the addition of the IL as compared to TBS in neat solvent alone. This is because of the fact that ILs do not dissolve in the solvent, which is evident as there is no peak that corresponds to the added IL.

3.3 Hold-time study

A hold-time study helps with the understanding of the trend of degradation/dissolution of TBS in any solvent with or without ILs. Hold-time study data of TBS in a solvent with and without ILs will provide knowledge of the maximum allowable time that is suitable to hold the mixture (either TBS with solvent alone or with the addition of ILs) inside the storage tank before progressing to the next stage. In other words, a hold-time study allows for the time required for maximum and efficient dissolution of TBS in the solvent with or without ILs to be determined. This knowledge could further be applied for practical applications on a large-scale in oil and gas industries, considering the fact that these industries typically require more than a month of manual cleaning to render the petroleum storage tank free from sludge.

The hold-time study is carried out for a sample case for the dissolution of TBS in heptane with and without ILs using the UV-visible spectrophotometric technique. The absorbance values are given in Table 5. The results obtained for the sample solutions are convincingly and significantly better as compared with the standard solutions. Fig. 10 and 13 represent the hold-time study for the different concentrations of the standard and sample solutions of heptane respectively, for days 1, 2, 4, 10 and 30. From Fig. 10 and 11, the increase in the dissolution of TBS is observed to be in the range of 11–16% and 66–154% for the standard (TBS in heptane without ILs) and sample solutions (TBS in heptane with the addition of various ILs), respectively. The above increase in percentage is calculated by considering the absorbance of the respective concentration of standard solutions as the base reference.

3.4 FT-IR Spectral analysis

Fig. 12(a–e) shows the FT-IR spectral analysis for the crude TBS and the TBS treated with solvents and ionic liquids. The solvents used are toluene, heptane, decane, ethyl acetate and hexane in Fig. 12(a) to (e), respectively. The results are consistent with the results from UV studies. For the FT-IR study for TBS with different solvents, the ILs used are those that dissolve a higher percent of the TBS with an accuracy of ± 0.1 . Similarly, spectra of the soluble parts of TBS in heptane in the absence and presence of $[\text{HMIM}]^+[\text{Br}]^-$ are shown in Fig. 12(f). The results indicate that the soluble parts of the TBS (filtrate) show more purity as compared to the TBS residue. For both the crude

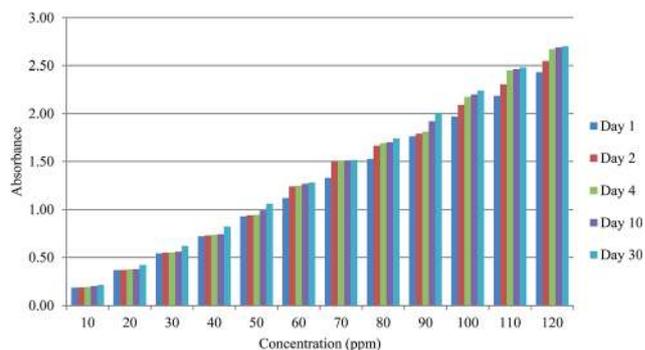


Fig. 10 Representation of the hold-time study for the standard solution (TBS in heptane) at different concentrations.

TBS and the treated TBS (residue TBS), mineral bands (predominantly clay and sand) around 1100 cm^{-1} , 800 cm^{-1} and 500 cm^{-1} absorb very strongly in the infrared region. The absorption modes seen around 1450 cm^{-1} correspond to C–H bending frequency, the peak at 2950 cm^{-1} corresponds to C–H stretching frequency and the peak around 3500 cm^{-1} corresponds to O–H/ H_2O . The highest absorbance is noted between 2900 and 3000 cm^{-1} , where the methylene groups (*e.g.*, alkanes) corresponding to the crude oil in TBS appear. For the TBS (residue TBS) treated with different solvents such as toluene, heptane, decane, ethyl acetate and hexane, a significant reduction in the intensity of the peaks is observed. The decrease in the intensity of the peaks, which shows the proportion of crude oil present in the TBS, is considerable and is more pronounced in the case of the TBS treated with both solvent and ionic liquid than with the solvent alone. In the spectrum of the crude TBS, intense bands can be noticed as a sharp doublet near 1010 cm^{-1} , which are due to kaolinite (a clay mineral), and these modes are superimposed over absorbances due to other clays.^{26,27} A characteristic doublet near 800 cm^{-1} corresponds to the silicates.

3.5 ^{13}C -NMR spectral analysis

In Fig. 13, (a) shows the ^{13}C NMR spectrum of the crude TBS, (b) shows the ^{13}C NMR spectrum of the TBS bottom sediments treated with solvent and (c) shows the ^{13}C NMR spectrum of TBS in solvent with ILs. The solvent and IL considered for this analysis is TBS in heptane with $[\text{HMIM}]^+[\text{Br}]^-$, based on the increased solubility observed for this combination in the UV

Table 5 Absorbance of the standard solutions of TBS in heptane at various concentrations taken on day 1, day 2, day 4, day 10 and day 30 of the sample preparation

Days	Absorbance												
	Std. Concn	10 ppm	20 ppm	30 ppm	40 ppm	50 ppm	60 ppm	70 ppm	80 ppm	90 ppm	100 ppm	110 ppm	120 ppm
1		0.18	0.37	0.54	0.72	0.93	1.12	1.33	1.53	1.76	1.97	2.19	2.43
2		0.19	0.37	0.55	0.73	0.94	1.24	1.51	1.66	1.79	2.09	2.31	2.55
4		0.19	0.37	0.55	0.74	0.95	1.25	1.51	1.69	1.81	2.18	2.45	2.67
10		0.20	0.38	0.56	0.74	0.99	1.27	1.51	1.70	1.92	2.20	2.46	2.69
30		0.21	0.42	0.62	0.82	1.06	1.28	1.52	1.74	2.01	2.24	2.48	2.70

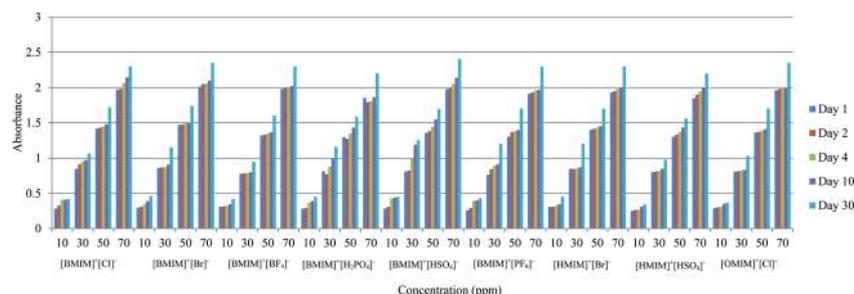


Fig. 11 Representation of the day- hold study for the sample solution (TBS in heptane with ILs) at different concentrations.

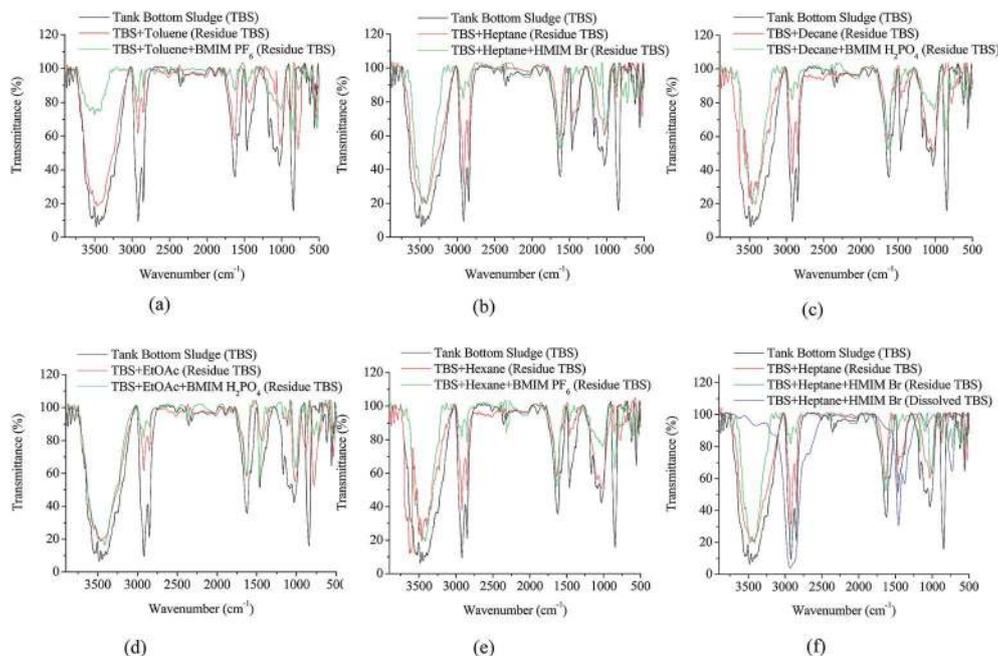


Fig. 12 FT-IR spectra of the crude TBS, solvent treated TBS and TBS treated with solvent along with the best ionic liquid, which gave the highest percentage increase in solubility. (a) TBS, TBS + Toluene (residue TBS) and TBS + Toluene + [BMIM]⁺[PF₆]⁻ (residue TBS); (b) TBS, TBS + Heptane (residue TBS) and TBS + Heptane + [HMIM]⁺[Br]⁻ (residue TBS); (c) TBS, TBS + Decane (residue TBS) and TBS + Decane + [BMIM]⁺[H₂PO₄]⁻ (residue TBS); (d) TBS, TBS + EtOAc (residue TBS) and TBS + [BMIM]⁺[H₂PO₄]⁻ (residue TBS); (e) TBS, TBS + Hexane (residue TBS) and TBS + Hexane + [BMIM]⁺[PF₆]⁻ (residue TBS); (f) TBS, TBS + Heptane (residue TBS), TBS + Heptane + [HMIM]⁺[Br]⁻ (residue TBS), TBS + Heptane + [HMIM]⁺[Br]⁻ (dissolved TBS).

and FT-IR studies. In the case of crude TBS, there are numerous peaks in the region between 10 and 55 ppm, which corresponds to the presence of aliphatic methyl and methylene carbon atoms. These peaks get diminished in the case of heptane treated TBS and nearly vanish in the spectrum for the heptane treated TBS with ILs. Similar to the FT-IR results, these ¹³C-NMR results are consistent with the results discussed earlier.

In Fig. 13(a), a peak around 170 ppm is present for the crude TBS, which is an indication of a >C=O group present in the TBS. The peaks in the region of 120–140 ppm indicate the presence of aromatics in the crude TBS. It is observed from Fig. 13(b) that these peaks do not completely vanish, indicating that there is oily sludge still present in the sample. In Fig. 13(c), the peaks due to the aromatics disappear, which signifies the absence of oily sludge after the treatment of TBS with heptane and the IL [HMIM]⁺[Br]⁻. Fig. 13(d) and (e) show the ¹³C-NMR

spectra of the soluble parts of TBS in heptane in the absence and presence of [HMIM]⁺[Br]⁻, respectively. The results indicate that the soluble parts of the TBS (filtrate) show more purity as compared to the TBS residue. This indicates that the addition of ILs helps in the removal of impurities from the crude oily sludge sample.

The reason for the efficient dissolution of TBS in solvents containing aromatic ILs could be due to the fact that there is an interaction between the cationic part of the ILs and the heteroatomic groups (S, N and O) of TBS, *i.e.*, the asphaltenes present in the TBS contain heteroatoms such as N, S and O, each possessing at least one lone pair of electrons, which are susceptible to interactions. Fig. 14 shows a schematic of the mechanism proposed for the enhancement in the dissolution of TBS in solvents containing aromatic ILs. The model of asphaltene is from the previous literature.²⁸ At high concentrations of ILs, the

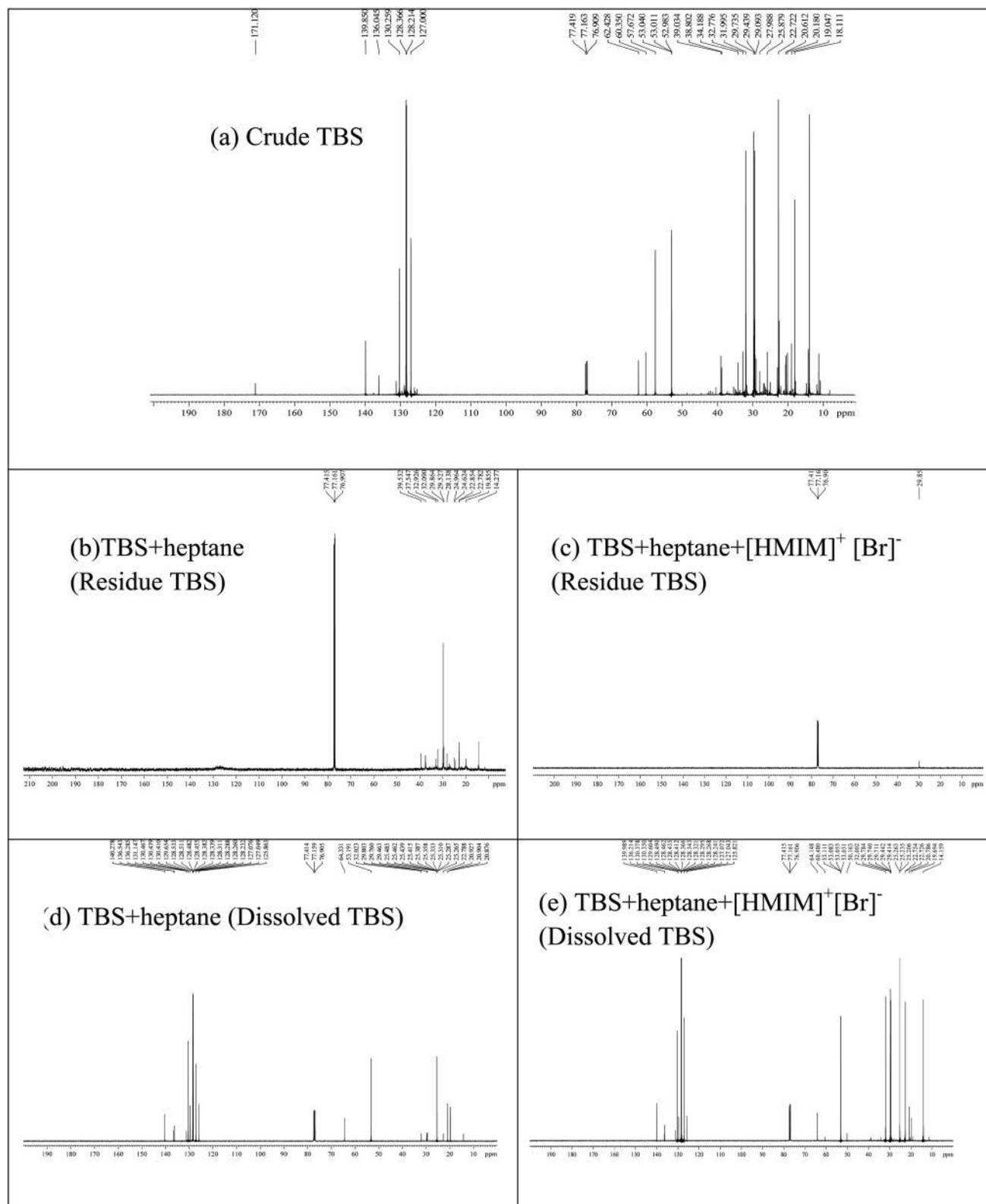


Fig. 13 ¹³C-NMR spectra of the (a) crude TBS, (b) heptane-treated TBS (residue TBS), (c) TBS treated with heptane along with [HMIM]⁺[Br]⁻ (residue TBS) (d) treated TBS (dissolved TBS) and (e) TBS treated with heptane along with [HMIM]⁺[Br]⁻ (dissolved TBS).



Fig. 14 Proposed mechanism for the enhancement in the dissolution of aromatic TBS in solvents containing aromatic ILs. Blue color dotted lines indicate the interaction between ILs and heteroatoms of asphaltene present in the TBS; Green color represents the aromatic ILs; Brown color is the asphaltene/resin moiety of the TBS.

degree of interactions increases and improves the dissolution process. Eventually, at high enough concentration of ILs, asphaltene molecules are effectively surrounded by ILs and solvated by the interaction forces. It is assumed that the ionic liquids, as well as the heteroatoms of the asphaltene/resin units, separate from the rest of the asphaltene/resin moiety. The asphaltene/resin moiety without the heteroatoms is merely hydrocarbons, which get easily dissolved in the organic solvent. The aromatic ILs and heteroatoms from the asphaltene/resin units may be present in the aqueous phase as a salt.

4. Conclusion

This study presents the investigation of the enhanced dissolution of tank-bottom sludge with solvents such as toluene, heptane, decane, ethyl acetate and hexane, as well as nine aromatic-based ionic liquids. From the experiments carried out in this work using the UV-visible spectrophotometric technique, it is observed that the absorbance values with respect to a particular IL are in similar range (0.3 to 2.1) for the solutions in the concentration range of TBS (10 to 70 ppm) in a given solvent with mixed weight ratios of TBS : ILs. It is also noted that an IL content of about 10% is adequate for nearly complete dissolution of TBS. Henceforth, it is marked that a small quantity of ionic liquid is enough to dissolve the tank-bottom sludge (TBS) efficiently, thereby providing room for environmentally friendly atmosphere. In dissolution studies of TBS in the presence of ILs in different solvents, [BMIM]⁺[PF₆]⁻ gives a better performance in toluene and hexane, whereas [HMIM]⁺[Br]⁻ in heptane; [BMIM]⁺[H₂PO₄]⁻ in decane, and both [BMIM]⁺[H₂PO₄]⁻ and [BMIM]⁺[Br]⁻ ILs give better dissolution TBS in ethyl acetate, irrespective of the weight ratio of TBS : ILs. From the studied solvents, toluene is the best solvent for the dissolution of TBS, followed by heptane, decane, hexane and ethyl acetate. Considering the toxicity of toluene, it is wise to incorporate heptane as a solvent for TBS. The results of the FT-IR and

¹³C-NMR also prove to be consistent with the above findings from the UV studies. A hold-time study of the dissolution of TBS in heptane, with and without addition of ILs, reveals that contact of TBS with heptane for a prolonged period (30 days) dissolves about 16% of the TBS while that is increased up to 154% in presence of ILs. Results obtained in the present work suggest that a small amount of ionic liquids (green solvents) are sufficient for the dissolution of tank-bottom sludge, and its exploitation at a large scale for petroleum industries will provide room for an economically and environmentally friendly atmosphere.

Acknowledgements

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