RSC Advances

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Research Article

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

Sivabalan Sakthivel[1], Sugirtha Velusamy[1], Ramesh Gardas[2,#], Jitendra S. Sangwai[1,*]

[1]Petroleum Engineering Program, Department of Ocean Engineering, Indian Institute of Technology Madras, Chennai – 600 036, India

[2]Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600 036, India

Corresponding Author:

*Jitendra Sangwai: jitendrasangwai@iitm.ac.in; Phone: +91-44-2257-4825 (Office); Fax: +91-44-2257-4802

#Additional Corresponding Author: Ramesh Gardas: gardas@iitm.ac.in; Phone: +91-44-2257-4248 (Office); Fax: +91-44-2257-4202

Abstract

The upstream petroleum industry faces operational and technical problems due to increased waxes, aromatics and asphaltene contents, such as deposition of crude oil sludge in oil storage tanks in the form of tank-bottom sludge (TBS). This results in huge production losses, and threatening the environmentally safe operation, thus needing safer solutions. 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 improves the dissolution of TBS in solvents than 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 imidazolium cation and various anions such as $[Cl]^-$,$[Br]^-$, $[BF_4]^-$, $[H_2PO_4]^-$, $[HSO_4]^-$, and $[PF_6]^-$ 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 is to be noted that the efficiency of dissolution of TBS goes on decreasing on increasing the concentration of TBS in hexane. Hold-time study is also performed with the solvent heptane containing ILs and without ILs to know 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 the mixture of solvent and IL are in contact with the TBS for a prolonged period of 30 days or even longer as required. FT-IR and ^{13}C-NMR spectral analysis are also performed so as to understand the efficiency of the ILs in the dissolution of TBS in various solvents and it was observed to be evident that there is decrease in the intensity of the peaks in the spectra of treated TBS with solvent, which is further enhanced by the addition of ILs.

Key words: aromatic ionic liquids; dissolution; FT-IR;^{13}C-NMR; tank-bottom sludge; solvents; Ultraviolet-visible spectrophotometric technique.

Broader context:

The deposition of crude oil sludge in various production and surfaces facilities, such as, oil storage tanks in the form of tank-bottom sludge (TBS), invites several operational challenges resulting in huge production losses, involvement of scarce human resources, and threatening the environmentally safe operation, thus needing safer solutions.An environmental-friendly method for the dissolution of TBS with the use of ionic liquids (ILs) along with solvents has been developed which is considered to be a novel application of the ILs. These ILs work efficiently in softening the crude oil sludge settled at the bottom of any petroleum storage tank and hence sludge can be easily pumpable, thereby reducing the risk of manual cleaning and consumption of time and overcomes other hazards as well, unlike classical methods of cleaning. This method helps in minimizing the use of organic solvents (e.g. toluene) which is customarily used to soften the TBS. Moreover, the ILs used could be recovered and can be recycled and reused several times. This method, therefore represents a greener-environmentally friendly method for the dissolution of TBS which has always been a major menace to oil and gas industries.

Introduction

Petroleum is indispensable for industrial growth. Through the last few decades, this 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 recent past, the industry faces operational and technical problems, such as wax, asphaltene and crude oil sludge deposition in storage tanks, production tubing and surface facilities, increased skin factor near well-bore resisting production, emulsification of crude oil with formation water and oil sludge formation in the crude oil storage tanks, etc., which result in huge production losses, increased expenditure on remedial intervention, involvement of scarce human resources, and threatening the environmentally safe operation. It is, therefore, crucial that these problems require intelligent, cost-effective and innovative solutions.

Crude oil contains higher hydrocarbon, particularly waxes and asphaltenes which remain in the dissolved state in the liquid hydrocarbon at the higher pressure and temperatures of the reservoir. When the crude oil flows from the reservoir to the surface condition, the drop in the system pressure and temperature makes waxes and asphaltenes separate from the bulk stream resulting in the 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 portion of the petroleum storage tanks.[1] This is referred as 'tank bottom sludge' (TBS). The composition of TBS differs due to the large diversity in the quality of crude oils, variations in the processes used for oil-water separation, leakages during industrial processes, and also addition with the existing TBS. Usually, the TBS consists of heavier components of oil such as waxes and asphaltenes, resins, etc. apart from water, biomass, and many inorganics (iron-rust, scale, mud, sand etc.)

that 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; oxidizing the oil resulting in their accumulation as waste at the bottom of the tank with other dirt and rust forming TBS. On many occasions, such accumulation renders the tank unusable due to inability to take suction and dispatch crude oil for delivery through pipeline. It is customary to use heated oil and water, dispersant formulations and elaborate oil circulation arrangement 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 the petroleum companies, but its disposal is also a serious environmental concern. Chemical treatments of aromatic hydrocarbons such as asphaltenes, etc., are typically done by using cyclic non-polar solvents such as xylene, benzene, and toluene (aromatic) which has potentiality to dissolve asphaltenes.[2,3] However, these aromatic based solvents are volatile and hazardous, and hence not recommended.[2] The alternative approach is to use lighter hydrocarbons such as heptane, decane, etc., which however, shows lower dissolution with aromatic hydrocarbons of TBS and need improvement. 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) are the combination of cation, generally containing a conjugated aromatic core and anion, typically which are strong hydrogen bond acceptors. ILs are an admirable alternative to substitute volatile organic solvents for green technologies as 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 worker's exposure and the loss of solvent to the atmosphere. When any IL is mixed with any organic solvent for specific application, it is expected to help reduce the use of hazardous and polluting organic solvent.[4] Moreover the ILs used can be recycled by using small amount of water and both can be readily recovered by distillation[5]and can also be reused numerous times.[3,6] They also provide help in decreasing the viscosity of the crude oil through catalytic cracking of heavier hydrocarbons as contacted. Ionic liquids show very good performance in the dissolution of asphaltenes as novel solvents.[7] A fascinating quality of ILs is that any small changes made in its combination of cation and anion or in the nature of its moieties that are attached to each ion allows its physical properties to be personalized for explicit applications.[8-10] Asphaltene association could easily be broken by increasing the charge density of the anionic part and decreasing the alkyl chain length of the cationic head ring of ionic liquids.[7] Ionic liquids thus shows potential solution to address the energy and environmental challenges associated with the handling of tank bottom sludge in an upstream oil and gas industry. The use of ILs for the dissolution of TBS will help to overcome the environmental hazards, to eliminate man-hours and personnel safety issue, help to facilitate the easy transportation of the crude oil and to 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 in a wide temperature range.[11] In addition to the aiding of removing the oily sludge easily, this method may also assists in recovering valuable crude oil from the oily sludge which is otherwise lost due to dumping and burning of tank-bottom sludge (TBS), which is usually performed.

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 which are capable to solubilise crude oil sludge by softening and making them pumpable. The applicability of ionic liquids in the field of petroleum has been investigated by various authors recognizing their peculiar properties. Recently, room temperature ionic liquids such as, $[Et_3NH]^+[AlCl_4]^-$, $[Et_3NH]^+[AlCl_4]^-Ni^{2+}$,$[Et_3NH]^+[AlCl_4]^-Fe^{2+}$ and $[Et_3NH]^+[AlCl_4]^-Cu^{2+}$ have been used in the upgrading of heavy oil at the reservoir conditions by reducing the viscosity. The results showed significant improvement in the reduction of viscosity at optimum temperature conditions of the oil reservoir. Among the studied ILs, $[Et_3NH]^+[AlCl_4]^-Ni^{2+}$ has showed better viscosity reduction than the rest ILs.[12,14] Chloro-aluminate (III) ionic liquids/H_3PO_4 systems have been found to work more effectively on asphaltic sand degradation.[12-13] In addition, ionic liquids such as $[EMIM]^+[BF_4]^-$and $[BMIM]^+[BF_4]^-$are found to be more efficient to enhance the recovery of bitumen from oil sands.[5] Ionic liquids are also found to be working as a new substituent for surfactants in enhanced oil recovery processes.[15]

Ionic liquids such as $[BMIM]^+[Cl]^-$ and $[BMIM]^+[AlCl_4]^-$ act as a better asphaltene dissoluting agent.[16-17] $[BMIM]^+[BF_4]^-$ has been found to be very efficient in the field of bitumen recovery from oil sand.[3] In the reaction mechanism between ionic liquids and heavy oil, first step is the reaction of organic sulphur from heavy oil with transition metal modified ionic liquids to form the intermediate complex ($S \longrightarrow M^+$), which help to weaken the C-S bonds followed by breakage of the heavy oil molecules. The result of this reaction is that sulphur in the heavy oil escapes as H_2S and thus, the content of the 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 force 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 ~90°, but in the case of bitumen oil and ionic liquid it is ~73°.[18] These results show that the separation is easier by using ionic liquids than pure water.

We find that several ionic liquids are employed for various kinds of work such as enhanced oil recovery, asphaltene degradation, bitumen recovery, desulphurization, etc. Surprisingly, so far, none of the available literature addresses the problem 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. 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 present investigation contains more aromatics. The solvents used are from the class of paraffinic, aliphatic-polar and aromatic solvents namely heptane, hexane and decane from the paraffinic group and ethyl acetate from the aliphatic-polar solvents and toluene from the aromatic solvents.

2. Experimental Section

2.1. Materials

2.1.1 Tank-Bottom Sludge

For this study, TBS samples are acquired from Oil India Limited (OIL), Assam, India. TBS is found to be more of a solid and viscous as compared to conventional crude oil. The sample is free of dissolved gas. Saturates (S), aromatics (A), 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 $[BMIM]^+[Cl]^-$, $[BMIM]^+[PF_6]^-$, $[BMIM]^+[HSO_4]^-$, $[BMIM]^+[H_2PO_4]^-$, $[BMIM]^+[Br]^-$, $[BMIM]^+[BF_4]^-$, $[HMIM]^+[Br]^-$, $[HMIM]^+[HSO_4]^-$, $[OMIM]^+[Cl]^-$ have been synthesized and purified according to the methods reported in literature[19-24] and have been confirmed by ^{1}H Nuclear Magnetic Resonance (^{1}H NMR). Prior to usage, all the ILs are dried under constant agitation at 353K under vacuum (0.1 Pa) for a minimum of 48 h to remove 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 solutions 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 Ultraviolet (UV) -Visible spectrophotometer at fixed wavelength corresponding to the λ_{max} of specific solvent considered as given in Table 4, which is obtained by running full scan spectra of unknown concentration of solution containing TBS in the required solvent in the wavelength range of 190-900 nm. For absorbance studies relating to standard solution of TBS in toluene, the 1000 ppm solutions of TBS in solvent is diluted for 10 ppm to 100 ppm (with an increment of 10 ppm). For the rest of the solvents (heptane, decane, ethyl acetate and hexane) the concentrations of the solutions (with respect to TBS) used are in the range of 10 ppm to 120 ppm (with an increment of 10 ppm). The term concentration (in ppm) further referred herein refers to the concentration of the TBS in the solvent only and not of the ionic liquid. Absorbance is measured for all 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 making sample solution for the dissolution studies, viz., TBS:ILs =1:1, 1:0.5, 1:0.1. For TBS:ILs = 1:1, stock solution of 1000 ppm has been prepared by dissolving 50mg of TBS and 50mg of IL in 50mL of the corresponding solvent. For TBS:ILs =1:0.5 and 1:0.1, similar procedure as described above has been followed. The concentrations considered in this work (i.e., 10, 30, 50, 70 ppm) are made by dilution from 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. Further for each ratio of TBS to ILs, four different concentrations (i.e., 10, 30, 50, 70 ppm) have been prepared in five different solvents (i.e., toluene, heptane, decane, ethyl acetate and hexane). Thus total of 513 sample solutions are prepared for this work, moreover 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 and are compared with their respective standard solution and used for dissolution of TBS calculations. The schematic of the experimental procedure followed is shown in Figure 1 (a) and (b). It is to be noted that only the soluble part (filtrate) is taken for UV-Visible analysis and that the standard and sample solutions for this study have been freshly prepared and their absorbance are recorded on the same day approximately within 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 off from the bottom sediments (obtained from the solutions containing 1:1 of TBS:ILs) left after sample preparation for UV spectra, and then collecting the dried portion. Only very little solid is obtained and from that portion, a small amount is used for recording the ^{13}C-NMR and the rest of the left-over solid is then used for recording the FT-IR spectra by grinding it with potassium bromide (KBr). Similarly, the dissolved portion of TBS is collected and solvent evaporated by rota-vapor. The left-over portion of the sample is collected for analysis of FT-IR and ^{13}C-NMR. By using water, ionic liquids used in the sample solutions are recovered which can be recycled and reused. The same procedure is followed for all the five solvents considered in this study.

2.3 Analytical Methods

The water content is measured by Analab (Micro Aqua Cal100, India) Karl Fischer Titrator and Karl Fischer reagent from Merck. 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 dual platinum electrode. The purity of the synthesized ionic liquids is determined using ^{1}H-NMR. ^{1}H and ^{13}C-NMR are recorded on Brukar Avance 500 MHz spectrometer (made in Switzerland) using deuterated DMSO and $CDCl_3$ as solvents respectively. The standard absorbance values of TBS in the presence of solvent and ILs are recorded using UV-Visible spectrophotometer (JASCO V-650, Japan; accuracy= ±0.2nm; wavelength range= 190 to 900 nm) at fixed wavelength corresponding to the λ_{max}. FT-IR spectra are recorded on FT-IR spectrophotometer (JASCO FT-IR-4100, Japan). The device has a maximum resolution of 0.9 cm^{-1} and have 22,000:1 signal to noise ratio.^{13}C-NMR is performed as formerly described,[25] with the exception of employing ILs for ^{13}C NMR analysis.

3. Results and Discussion:

This section discuss in detail the quantification of the solubility of TBS without ILs (standard solutions) followed by the studies on the sample solutions containing TBS in solvents along with various ILs using UV -Visible spectrophotometric followed by hold-time studies to understand the effect of ILs on dissolution of TBS with time. Detailed results on the FT-IR and ^{13}C-NMR analysis to 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 absorbance using JASCO UV-Visible spectrophotometer at the particular wavelength corresponding to the λ_{max} of the respective solvent concerned (as in Table 4). Figure 2 (a-e) shows the plot of absorbance of standard solutions against the concentration (in ppm) of the TBS in solvents such as toluene, heptane, decane, ethyl acetate and hexane, respectively. These plots are fitted with linear regression analysis with regression coefficient (R^2) to be greater than 0.99. The values of R^2 obtained for various standard solutions of TBS in pure solvents (without ILs) 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 are done by measuring their absorbance at the particular wavelength corresponding to the λ_{max} of the respective solvent concerned (as in Table 4). All the values corresponding to the absorbance runs are consistent for three trials, within ± 0.001 and average of these three trials are considered for further calculations and plots. The absorbances of the sample solutions are compared with the respective concentration of the standard solutions and the increase in the percentage solubility over standard solution (with absorbance values of standard solution as base reference) are plotted. Figure 3 shows the UV absorption of the sample solution in comparison with the standard solution in the solvent heptane with TBS:ILs= 1:1. In the Figure 3, (a)-(i) show the effect of ILs in the order $[BMIM]^+[Cl]^-$, $[BMIM]^+[PF_6]^-$, $[BMIM]^+[HSO_4]^-$, $[BMIM]^+[H_2PO_4]^-$, $[BMIM]^+[Br]^-$, $[BMIM]^+[BF_4]^-$, $[HMIM]^+[Br]^-$, $[HMIM]^+[HSO_4]^-$and $[OMIM]^+[Cl]^-$ respectively. Similar observations are made for all other solvents and provided as supplementary information in Figures S1-S4. The percentage increase in solubility (±0.1%) versus the concentration in ppm and the varying proportion of TBS:ILs is represented as bar diagrams in Figures 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 of 25% to 66% using ILs where $[BMIM]^+[PF_6]^-$ is found to cause the maximum dissolution of TBS and the minimum efficiency shown by the IL,$[BMIM]^+$ $[Br]^-$ of less than 20%. It is surprising that the ILs with Br- as the anion such as $[BMIM]^+[Br]^-$ and $[HMIM]^+$ $[Br]^-$ exhibit very good performance in the solvent heptane where as in the case of toluene it is just the contradictory.

Likewise, in the case of heptane and decane, $[HMIM]^+[Br]^-$ and $[BMIM]^+[H_2PO_4]^-$, respectively, show an efficiency to the maximum limit of 66% and 38% in the said solvents. In the case of ethyl acetate, the dissolution of TBS is greater by the usage of either $[BMIM]^+[H_2PO_4]^-$ or $[BMIM]^+$ $[Br]^-$ to the maximum limit of 18% or 19% respectively. Similar to toluene, $[BMIM]^+[PF_6]^-$ shows the maximum dissolution of TBS upto the limit of 68% in hexane. In the case of hexane, it is to be noted that the efficiency of dissolution of TBS goes on decreasing with 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 is sufficient to cause proficient dissolution of TBS in various solvents. From Figure 9, showing the comparison of solvents in the presence of ILs, it can be concluded that the performance of toluene and heptane shows highest efficiency in the dissolution of TBS in the said solvents. From the present investigations with respect to enhancement of dissolution of TBS using ionic liquids, those ILs which have the same cation with different anions, shows the solubility order in the order in the corresponding solvents, for toluene: $[PF_6]^-$ > $[H_2PO_4]^-$ > $[Cl]^-$ > $[HSO_4]^-$ > $[BF_4]^-$ > $[Br]^-$; Heptane: $[Br]^-$ > $[Cl]^-$ > $[HSO_4]^-$ > $[BF_4]^-$ > $[PF_6]^-$ > $[H_2PO_4]^-$. Similarly the ionic liquids which has the same anion with different cations, show the solubility order as $[BMIM]^+$ > $[HMIM]^+$ > $[OMIM]^+$ with respect to all the solvents considered, and may slightly vary but follows similar trends.

We also present *a few* full scan spectra of TBS with heptane and toluene, both in the absence and presence of IL, BMIM PF_6 at different concentrations as given below and this is included in Figure S5 of the supplementary information. From the Figure S5 (i) and (ii), it is evident that there is significant improvement in the absorbance value of TBS in solvent (heptane and toluene) as a result of addition of IL as compared to TBS in neat solvent alone. This is because the fact that ILs do not dissolve in the solvent which is evidently convincing as there is no peak appearance due to the added IL.

3.3 Hold-time study

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

Hold-time study is carried out for a sample case for the dissolution of TBS in heptane as solvent with and without ILs using UV-Visible spectrophotometric technique. The absorbance values are given in Table 5. The results are found compromising as compared with the standard solution. Figure 10 and 13 represent the hold-time study for the different concentrations of the standard and sample solutions of heptane respectively, for day 1, 2, 4, 10 and 30. From the two figures (Figure 10 and 11) the increase in the dissolution of the TBS is observed to be in the range of 11 to 16% and 66 to 154% for the standard (TBS in heptane without ILs) and sample solutions (TBS in heptane with 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

Figure 12 (a-e) shows FT- IR spectral analysis determined for the crude TBS, the treated TBS with solvents along with ionic liquids. The solvents used follow the order as toluene, heptane, decane, ethyl acetate and hexane in Figure 12 (a) to (e), respectively. The results are in consistent with the results from UV studies. For the FT-IR study for TBS with solvents, the ILs used are the ones giving higher dissolution of TBS in percentage with an accuracy of ± 0.1. Similarly spectra of the soluble parts of TBS in heptane in the absence and presence of HMIM Br are shown in Figure 12 (f). The results indicate that the dissoluble parts of TBS (filtrate) show more purity as compared to the residue TBS. For the crude TBS and both the treated TBS (Residue TBS), mineral bands (predominantly clay and sands) 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} corresponds to C-H bending frequency, 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 methylene groups, (e.g., alkanes) corresponding to the crude oil in TBS appear. For the treated TBS (Residue TBS) with different solvents such as toluene, heptane, decane, ethyl acetate and hexane, a significant reduction in the intensity of the peaks are observed. The decrement in the intensity of the peaks, which shows the proportion of crude oil present in the TBS, has decreased considerably, and is evidently more convincing in the case of the TBS treated with solvent and ionic liquid together than with the solvent alone. In the spectrum of the crude TBS, intense bands are noticed as a sharp doublet near 1010 cm^{-1} which are due to kaolinite (a clay mineral) and these modes are superimposed on 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 Figure 13, (a) displays the ^{13}C NMR spectra of the crude TBS and (b) the ^{13}C NMR spectra of treated bottom sediments of the TBS with solvent and (c) the ^{13}C NMR spectra of TBS in solvent with ILs. The solvent and IL considered for analysis is TBS in heptane along with $[HMIM]^+[Br]^-$ based on the better solubility performance observed in UV and FT-IR studies. In the case of crude TBS, there are numerous peaks in the region between 10-55 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. Like the FT-IR results, these ^{13}C-NMR results are also consistent with the results discussed earlier.

In Figure13 (a), a peak around 170 ppm is present for the crude TBS, which is an indication of >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 Figure 13(b) these peaks do not get completely vanished, indicating that there is oily sludge still present in the sample. In the Figure 13 (c), the peaks due to the aromatics get disappeared signifying the absence of oily sludge after the treatment of TBS in heptane with the IL, $[\mathrm{HMIM}]^+[\mathrm{Br}]^-$. Figures 13 (d) and (e) show the ^{13}C-NMR spectra of the soluble parts of TBS in heptane in the absence and presence of $[\mathrm{HMIM}]^+[\mathrm{Br}]^-$, respectively. The results indicate that the dissoluble parts of TBS (filtrate) show more purity as compared to the residue TBS which shows more impurity. This indicate that the use of ILs help in the removal of impurity from the crude oily sludge sample.

The reason for the efficient dissolution of TBS in solvents in the presence of aromatic ILs could be due to the fact that, there is an interaction between the cationic part of 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 atleast one lone pair of electrons which are susceptible to interaction. Figure 14 shows a schematic of the shows a schematic of the mechanism proposed for the enhancement in the dissolution of TBS in solvents in the presence of aromatic ILs. Resource of the model of asphaltene is from the previous literature.[28] At high concentration of ILs, the degree of interaction increases and improves the dissolution process. Eventually, at high concentration of ILs, asphaltene molecules are effectively surrounded by ILs and solvated by its interaction force. It is assumed that the ionic liquids along with the heteroatoms of the asphaltene/resin units separate from the rest of the asphaltene/resin moiety. The asphaltene/resin moiety without heteroatoms is now merely hydrocarbons which get easily dissolved in the organic solvent. The aromatic ILs along with 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 along with 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 solvent with mixed weight-ratios of TBS:ILs. It is also noted that about 10% of IL is adequate for nearly complete dissolution of TBS. Henceforth, it is marked that small quantity of ionic liquid is enough to dissolve the Tank-Bottom Sludge (TBS) efficiently, thereby providing space for greater friendly environment by its usage and minimizing the expenditure incurred by following other methods. Dissolution study of TBS in presence of ILsin varied solvents, $[BMIM]^+$ $[PF_6]^-$ gives better performance in toluene and hexane, whereas $[HMIM]^+$ $[Br]^-$ in heptane; $[BMIM]^+$ $[H_2PO_4]^-$ in decane, and both $[BMIM]^+$ $[H_2PO_4]^-$ and $[BMIM]^+[Br]^-$ ILs give better dissolution of 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 always wise to incorporate the use of heptane as solvent for TBS. The results of the FT-IR and ^{13}C-NMR also prove to be in consistence to the above. Hold-time study of 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 TBS while that is increased upto 154% in presence of ILs. Results obtained in present work suggest that small amount of ionic liquids (green solvents) is sufficient for dissolution of tank-bottom sludge, and its exploitation in large scale for petroleum industries will provide room for economically and environmentally friendly atmosphere.

Acknowledgment

Financial support from Oil India Limited through grant CONT/HC/C-5/0931/2012 is highly appreciated and acknowledged. We also thank Dr. Srinivasan V. Raju, General Manager (R&D) and Mr. Prashant Dhodapkar, Chief Research Scientist, Research and Development/Oil India Limited for technical support relating to the studies of oily sludge (crude TBS).

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Table 1: SARA analysis report

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

$^+$S: Saturates; Ar: Aromatics; R: Resins; A: Asphaltenes

Table 2: List of synthesized Ionic Liquids

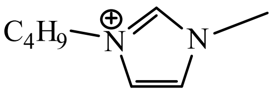
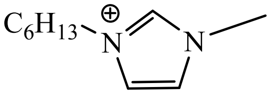
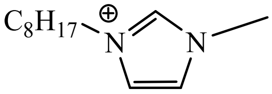
Cation	Anion	Name	Abbreviation
	$Cl^{\ominus}$	1-butyl-3-methyl imidazolium chloride	$[BMIM]^+ [Cl]^-$
	$Br^{\ominus}$	l-butyl-3-methylimidazolium bromide	$[BMIM]^+ [Br]^-$
	$BF_4^{\ominus}$	l-butyl-3-methylimidazolium tetrafluoroborate	$[BMIM]^+ [BF_4]^-$
	$H_2PO_4^{\ominus}$	l-butyl-3-methylimidazolium dihydrogen phosphate	$[BMIM]^+[H_2PO_4]^-$
	$HSO_4^{\ominus}$	1-butyl-3-methylimidazolium hydrogen sulfate	$[BMIM]^+ [HSO_4]^-$
	$PF_6^{\ominus}$	1-butyl-3-methyl imidazoliumhexafluorophosphate	$[BMIM]^+ [PF_6]^-$
	$Br^{\ominus}$	l-hexyl-3-methylimidazolium bromide	$[HMIM]^+ [Br]^-$
	$HSO_4^{\ominus}$	l-hexyl-3-methylimidazolium hydrogen sulfate	$[HMIM]^+ [HSO_4]^-$
	$Cl^{\ominus}$	1- octyl-3-methylimidazolium chloride	$[OMIM]^+ [Cl]^-$

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	Dichloro methane	75-09-2	Rankem	99%
7	1- methyl imidazole	616-47-7	Spectrochem	99%
8	o-phosphoric acid	7664-38-2	Merck	85%
9	Potassium bromide	7758-02-3	S D Fine-Chem Ltd	99%
10	Potassium hexafluoro phosphate	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

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

Figure Captions:

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

Figure 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).

Figure 3: UV absorption showing the effect of ionic liquids on TBS in heptane (TBS:ILs=1:1). (a)Effect of $[BMIM]^+[Cl]^-$ (b) Effect of $[BMIM]^+[Br]^-$ (c) Effect of $[BMIM]^+[BF_4]^-$ (d) Effect of $[BMIM]^+[H_2PO_4]^-$ (e) Effect of $[BMIM]^+[HSO_4]^-$ (f) Effect of $[BMIM]^+[PF_6]^-$ (g) Effect of $[HMIM]^+[Br]^-$ (h) Effect of $[HMIM]^+[HSO_4]^-$ (i) Effect of $[OMIM]^+[Cl]^-$.

Figure 4: Comparison of the efficiency of the said ILs interms 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.

Figure 5: Comparison of the efficiency of the ILs interms 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.

Figure 6: Comparison of the efficiency of the said ILs interms 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.

Figure 7: Comparison of the efficiency of the said ILs interms 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.

Figure 8: Comparison of the efficiency of the said ILs interms 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.

Figure 9: Comparison of the efficiency of all the said ILs interms 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.

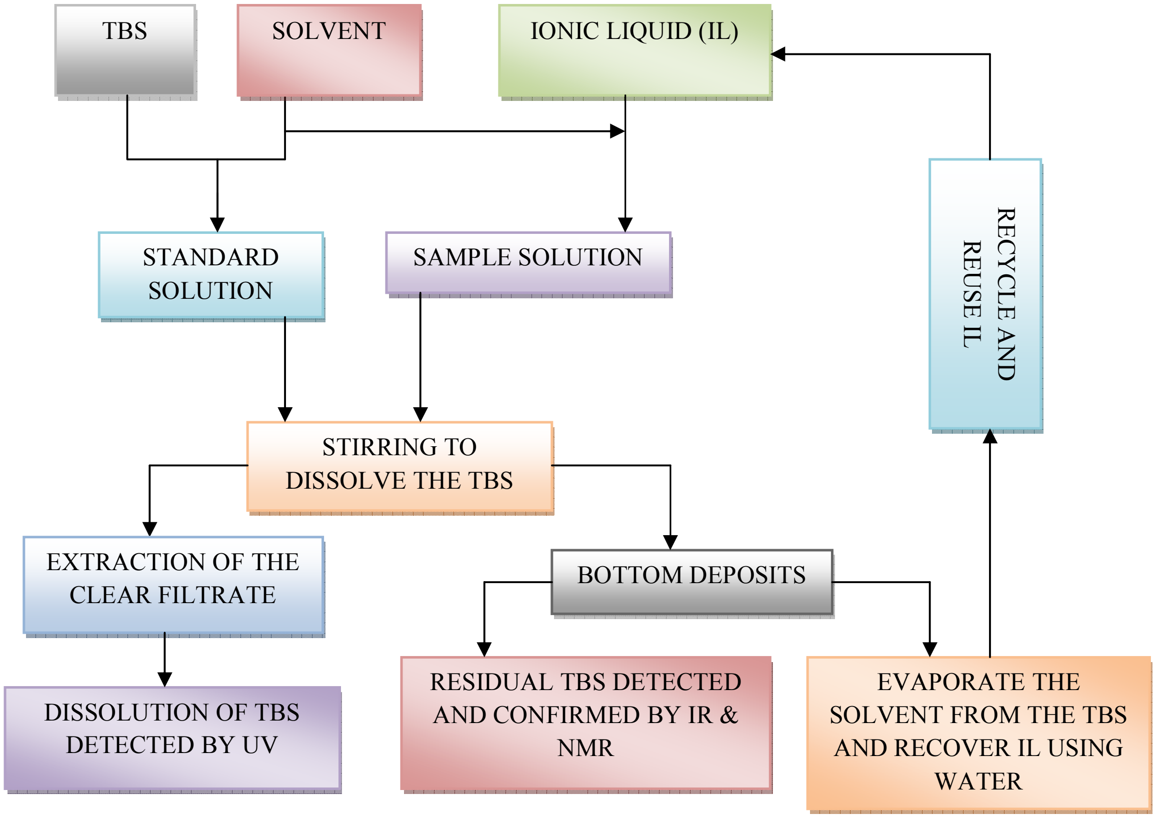
Figure 10: Representation of the day- hold study for the standard solution (TBS in heptane) at different concentrations.

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

Figure 12: FT-IR spectra of the crude TBS, solvent treated TBS and TBS treated with solvent along with one best ionic liquid which gave the highest percentage increase in solubility.(a) TBS, TBS+Toluene (residue TBS) and TBS+Toluene+$[BMIM]^+[PF_6]^-$ (residue TBS); (b) TBS, TBS+Heptane (residue TBS) and TBS+Heptane+$[HMIM]^+[Br]^-$ (residue TBS); (c) TBS, TBS+Decane (residue TBS) and TBS+Decane+$[BMIM]^+$ $[H_2PO_4]^-$ (residue TBS); (d) TBS, TBS+EtOAc (residue TBS) and TBS+$[BMIM]^+$ $[H_2PO_4]^-$ (residue TBS); (e) TBS, TBS+Hexane (residue TBS) and TBS+Hexane+$[BMIM]^+$ $[PF_6]^-$ (residue TBS); (f) TBS, TBS+Heptane (residue TBS), TBS+Heptane+$[HMIM]^+[Br]^-$ (residue TBS), TBS+Heptane +$[HMIM]^+[Br]^-$ (dissolved TBS).

Figure: ^{13}C-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).

Figure 14: Proposed mechanism for the enhancement in the dissolution of aromatic TBS in solvents in the presence of 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.



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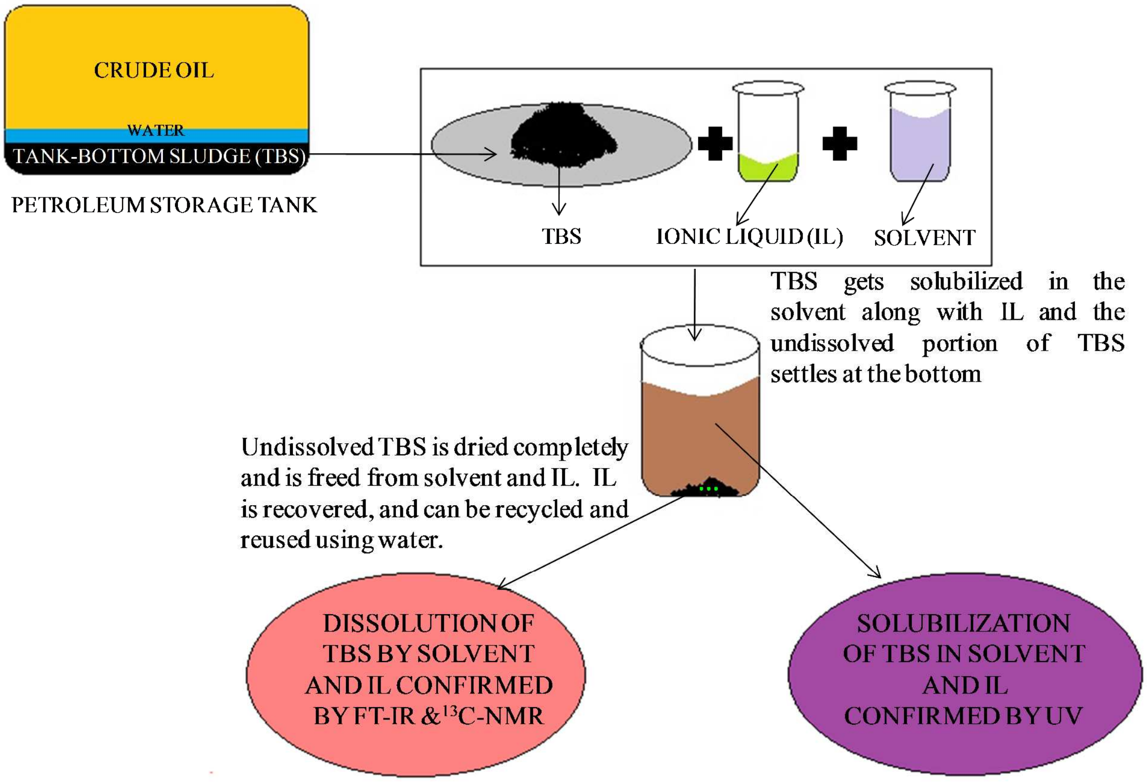
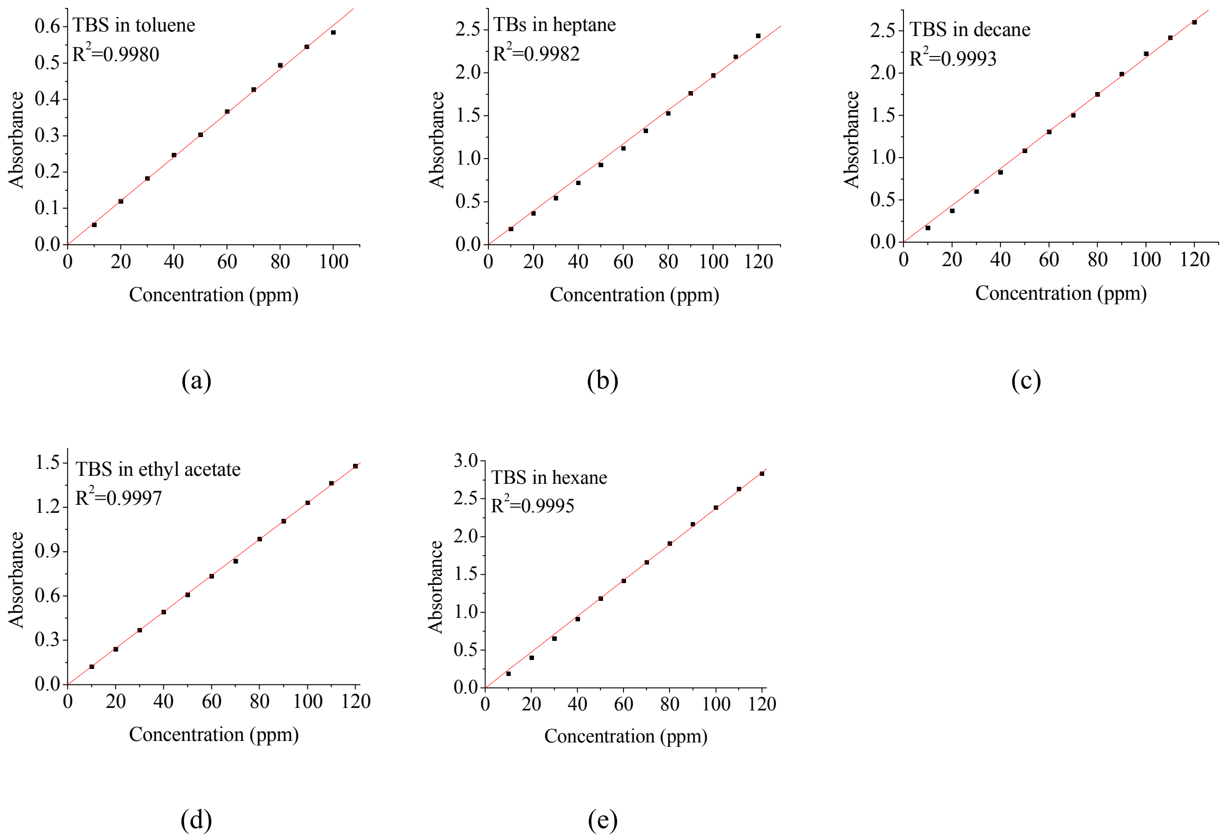


Figure 1 (b): Schematic for the experimental procedure involving the dissolution of tank-bottom petroleum sludge



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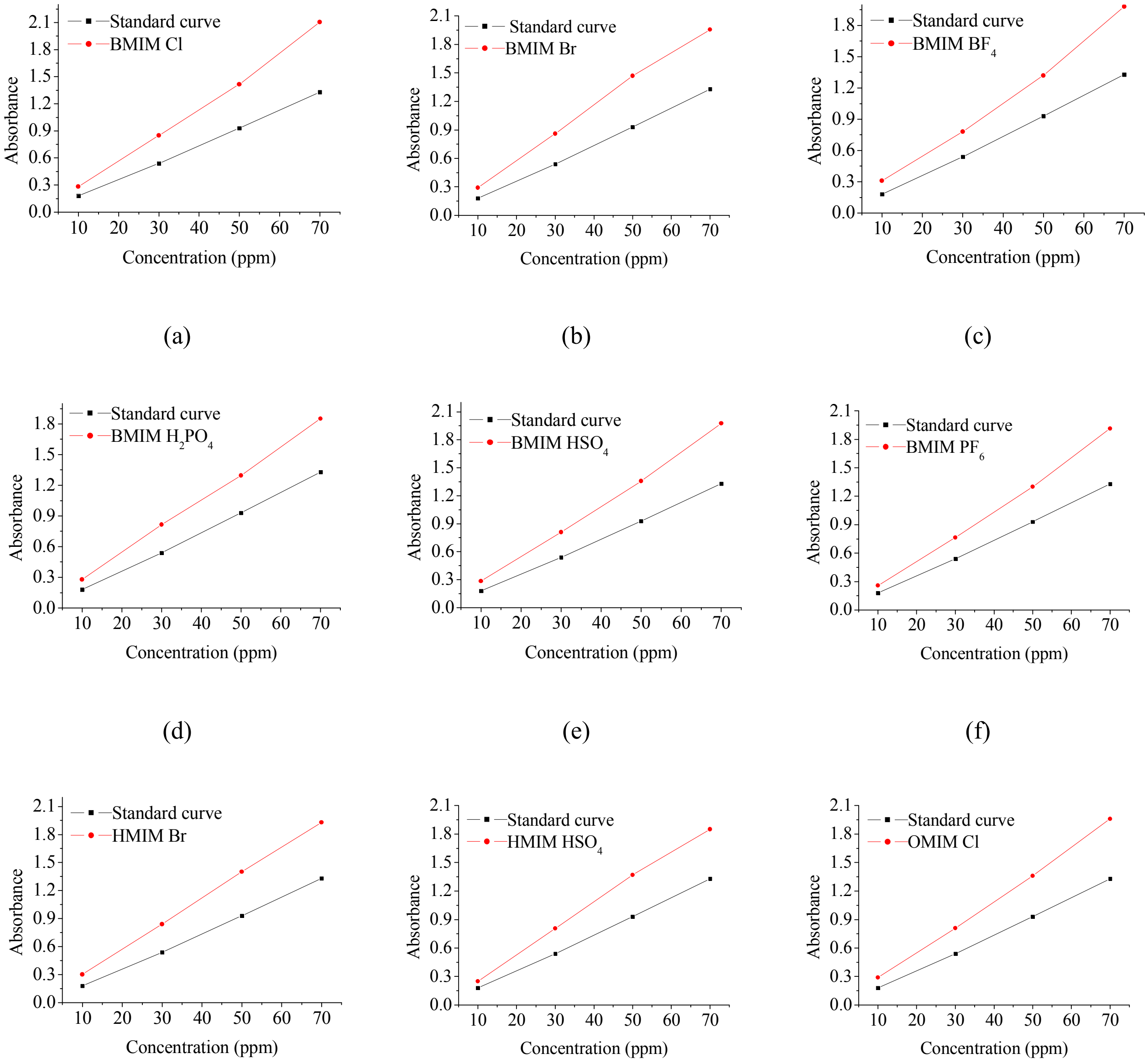

(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

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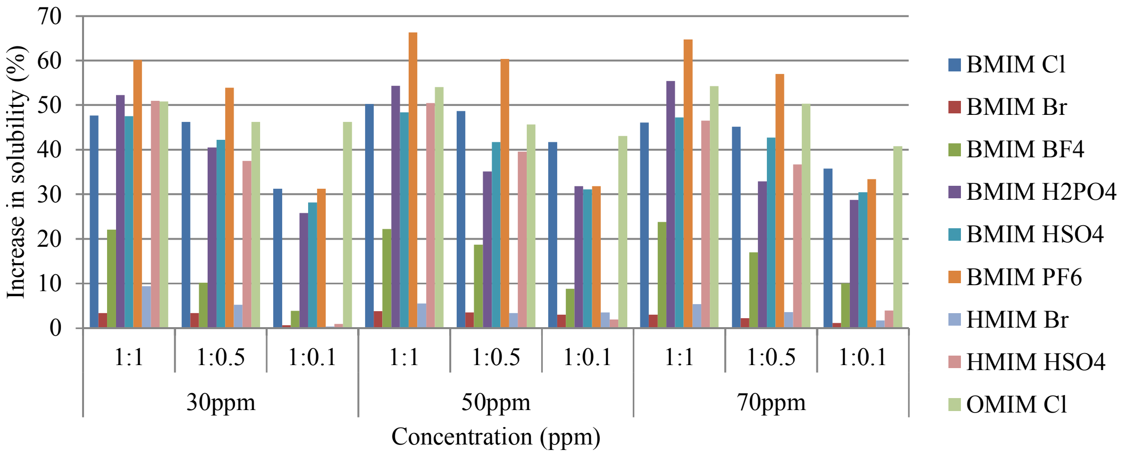

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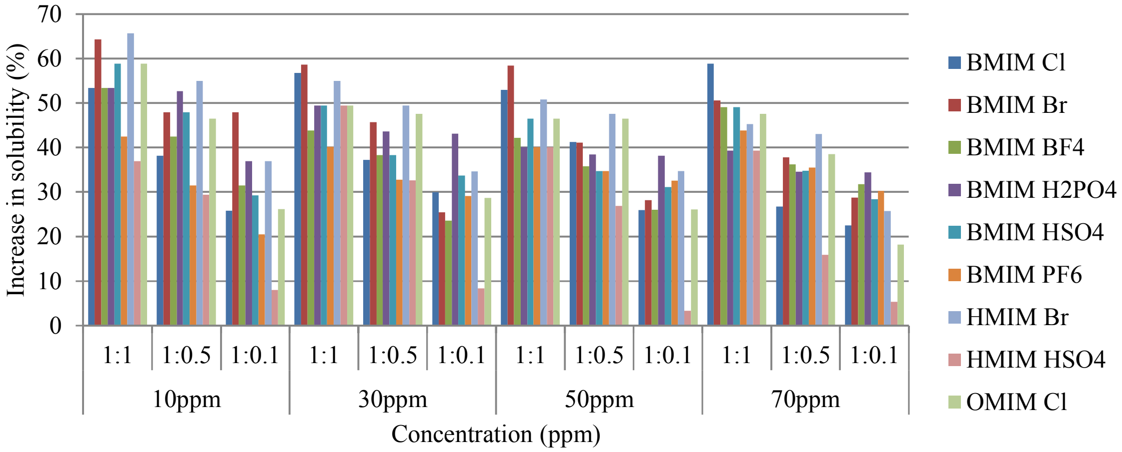

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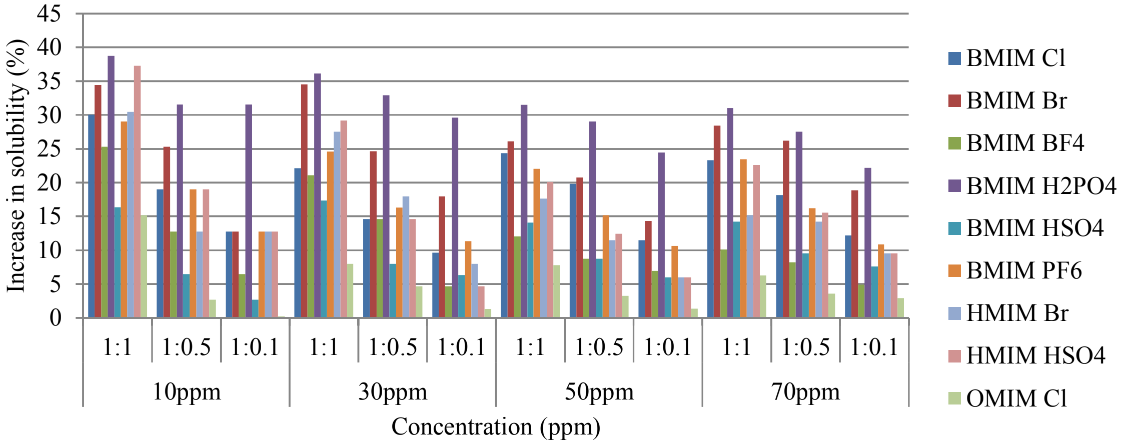

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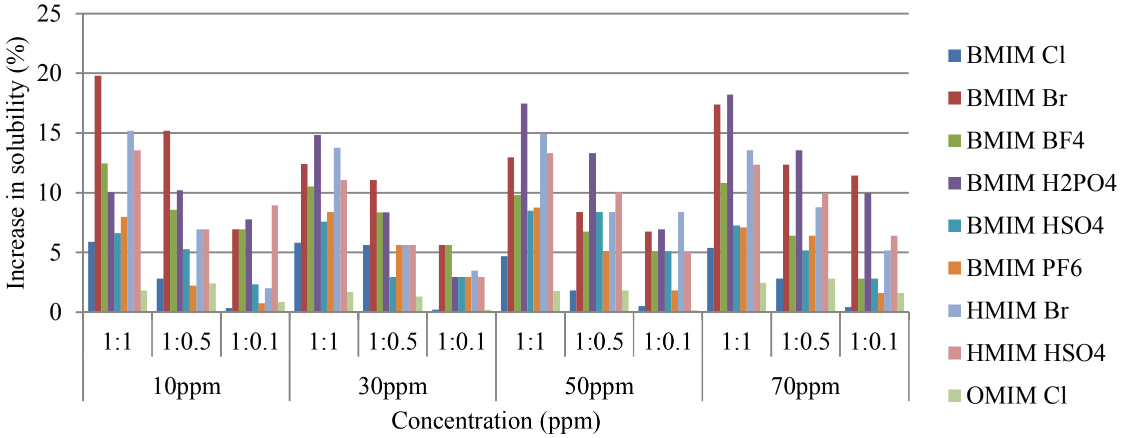

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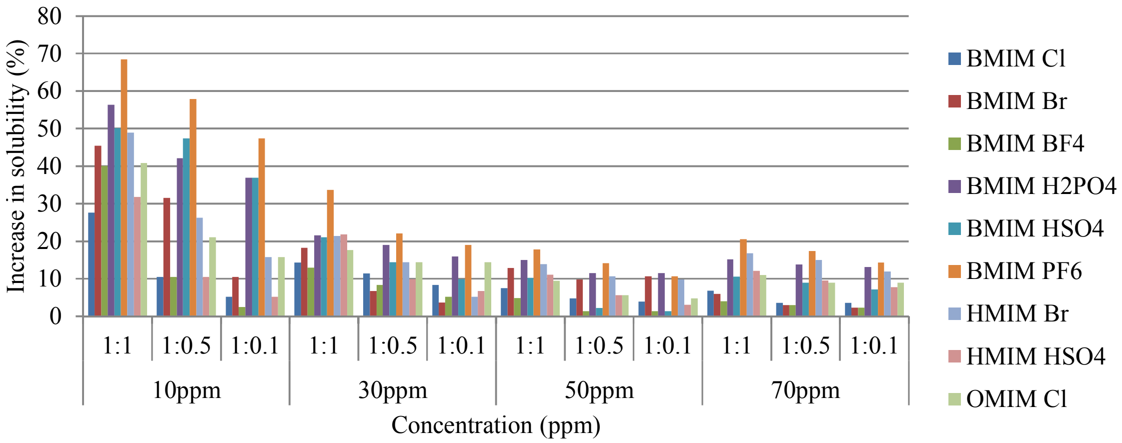

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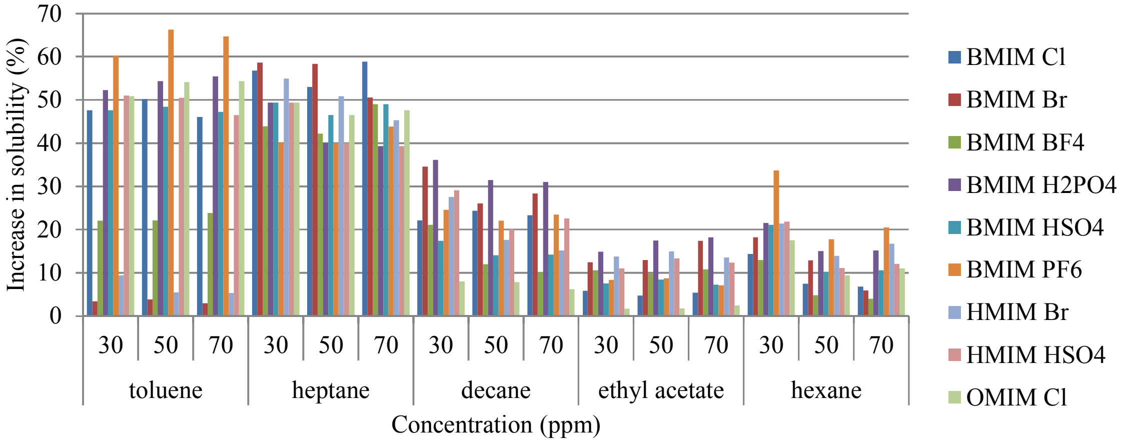

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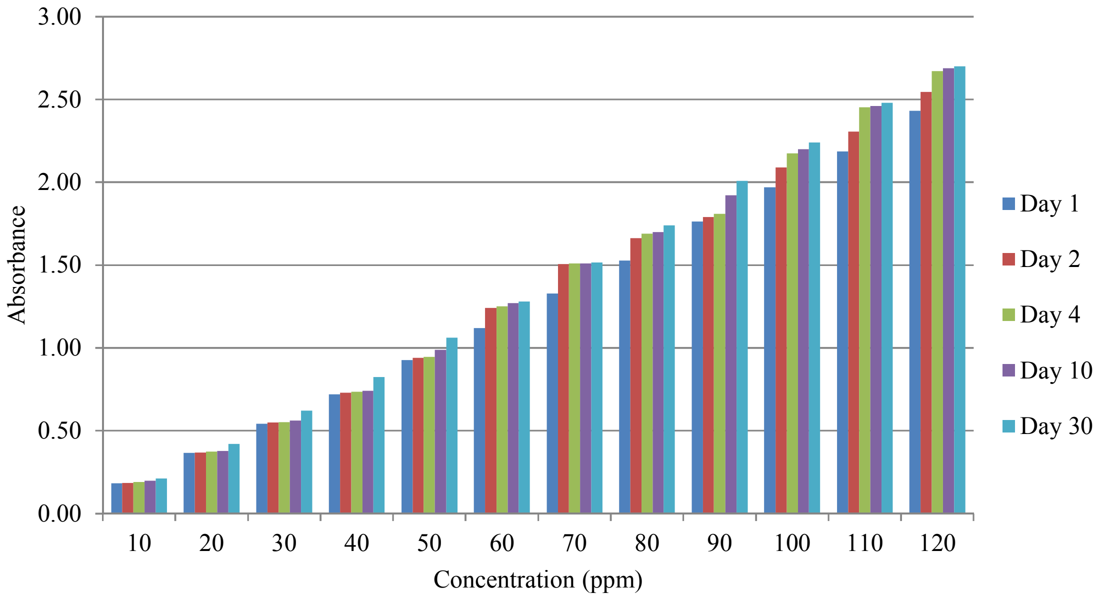
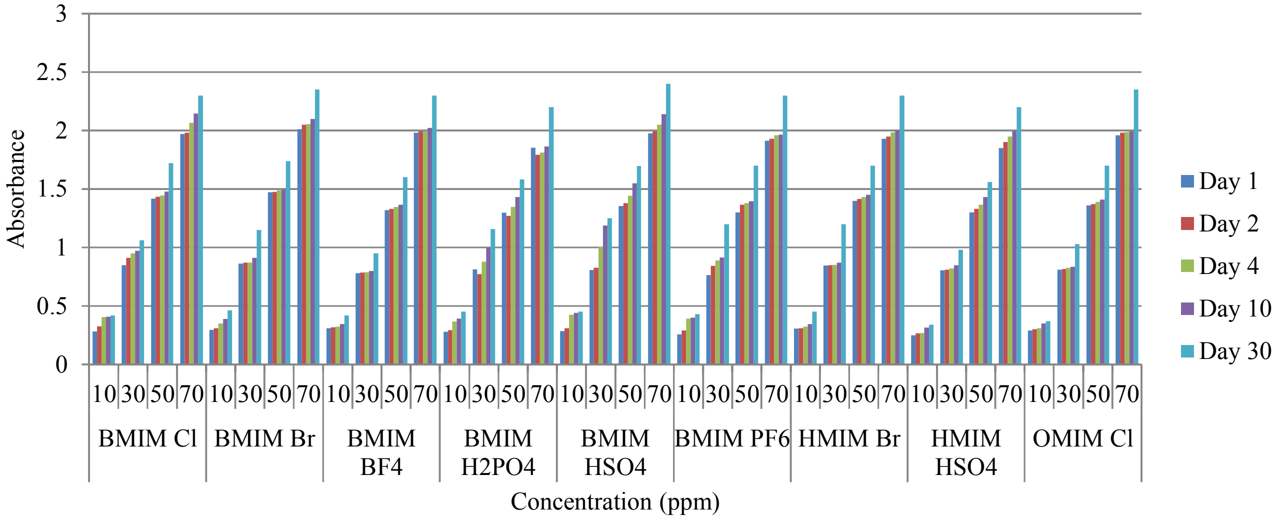


Figure 10: Representation of the day- hold study for the standard solution (TBS in heptane) at different concentrations.



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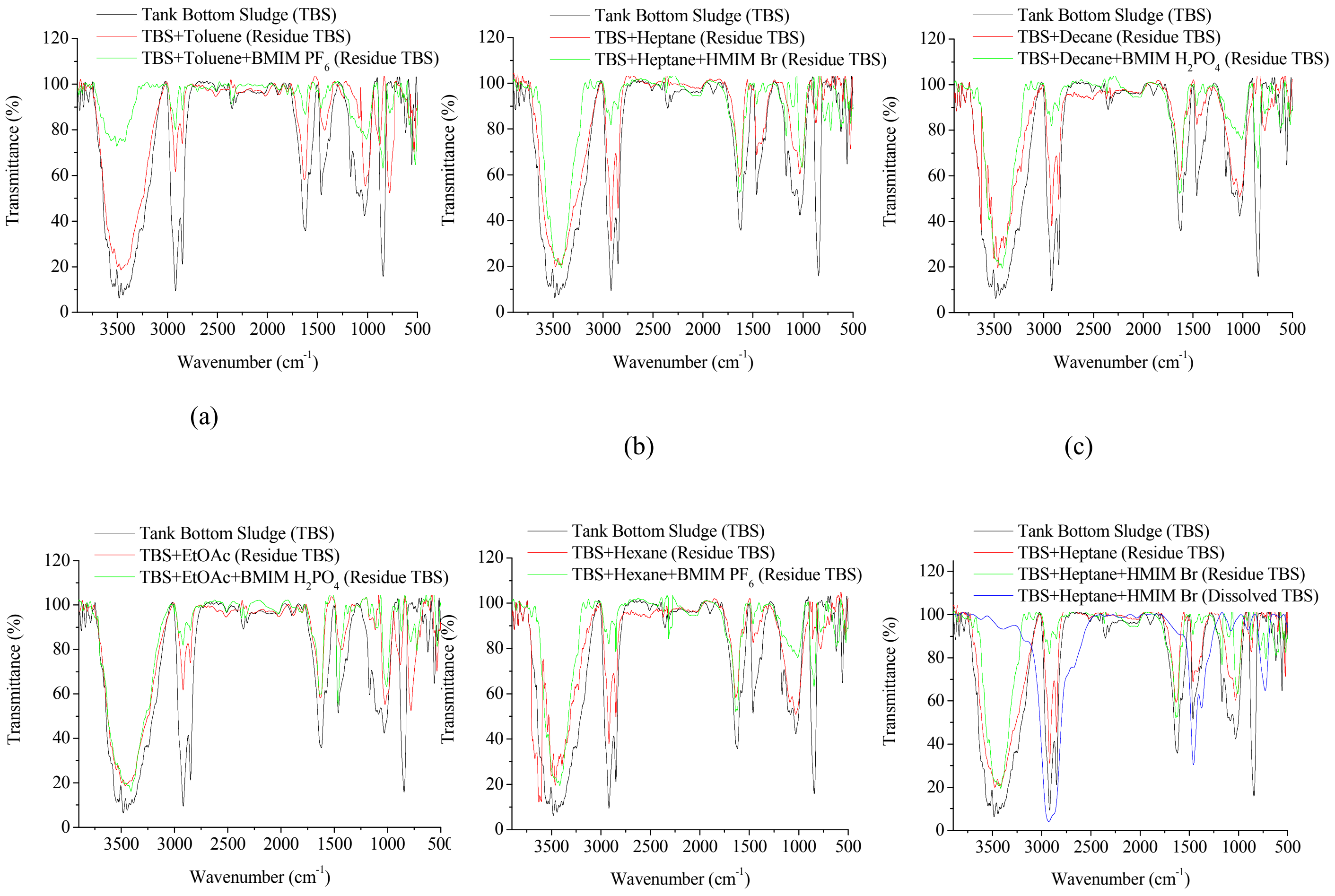

(a) (b) (c)

(d) (e) (f)

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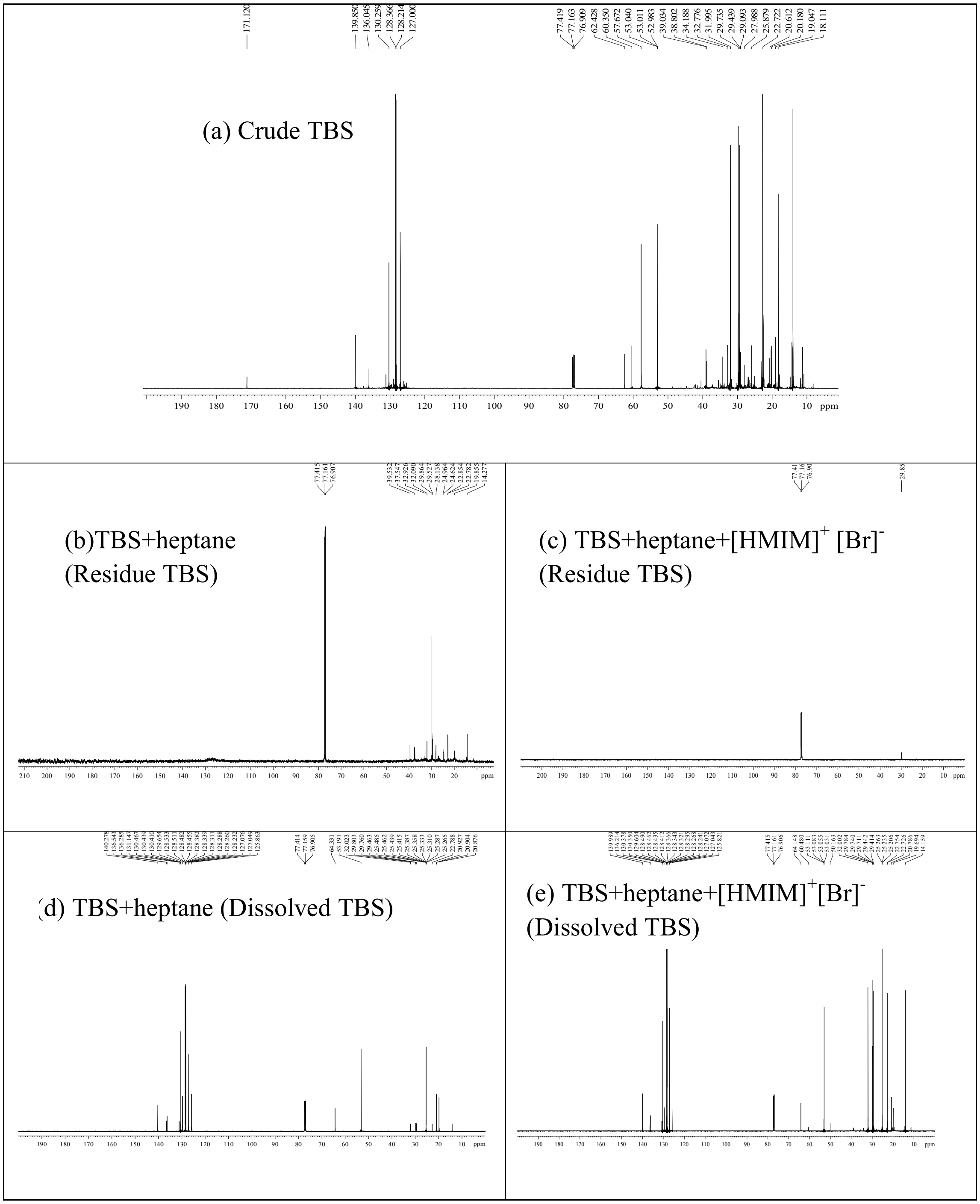

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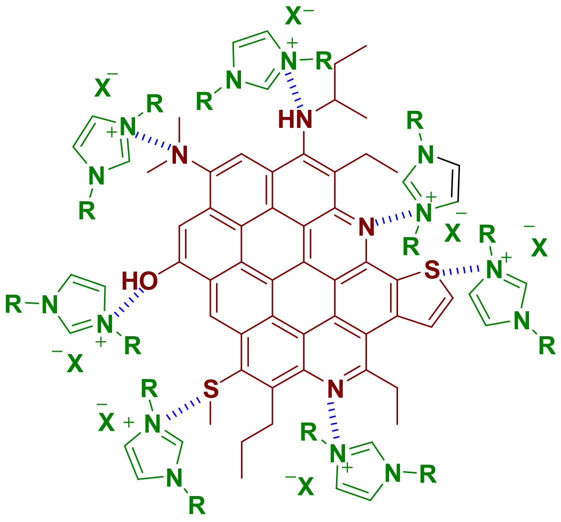

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