

Application of Ionic Liquids in the Upstream oil Industry-A Review

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Abstract

Ionic liquids are gaining much attention as green chemicals due to their unique properties such as extremely low vapor pressure, high thermal and chemical stability, low toxicity and possibility of tuning their cation and anion moieties to make them task-specific. In the chemical industry, they are well established for innumerable processes and applications and several review articles are available. Contrary to this the applications of ionic liquids in the upstream petroleum industry is relatively new and not enough review articles are available. This article discusses the applications of ionic liquids in areas such as CO₂ capture and separation which could be used for enhanced oil recovery and sequestration, heavy crude oil upgradation and viscosity reduction, interfacial tension and surface tension reduction in order to supplement surfactants in chemical enhanced oil recovery and asphaltene dispersion and inhibition during crude oil production and surface transportation. It aims to highlight the wide range of application possibilities of ionic liquids in the upstream sector of the petroleum industry and to encourage further research into some of these areas in order to develop environmentally friendly alternatives to current processes.

Keywords: Upstream; electrochemistry; catalysis; Spectroscopy

Introduction

Ionic liquids (ILs) are compounds of ionic-covalent crystalline structures containing only ions at room temperature [1]. They are mainly salts but differ from molten salts as they have a melting point ranging from -100°C to 200°C [2] [3], whereas molten salts generally have higher melting points. ILs display unique properties originating from a complex interplay of columbic, hydrogen bonding, and van-der-Waals interactions of their ions in liquid state [4].

ILs contain a functional group either as an anion or a cation, or both which incorporate a specific property, either physical or chemical viz. melting point, solubility, hydrophobicity, viscosity, reactivity etc. The desired properties can be achieved through structural modifications of either the anion, the cationic core, or the substituent's on the anion or cation. If needed there exists the possibility of fine-tuning the ions which provides the means of diverse applications of ILs [5] [6]. Their physical and thermal properties strongly depend on the cation and anion species as well as on the alkyl chain length on the cation [7].

In recent years, many room temperature ILs or RTILs (ILs which are liquid at or below room temperature) are developed and got tremendous attention as potential "green" solvents due to their environment friendly and renewable characteristics, though not all ionic liquids are environmental friendly [8].

Due to these wide range of advantages, ILs are preferred for applications in organic synthesis, catalysis, electrochemistry, electro catalysts, chemical separation, solid support, chemical fixation of CO₂, nanoparticle formation, and metal extraction, in addition to their electrochemical stability and high ionic conductivity at room temperature [9].

Ionic liquids can be synthesized in an endless number of ways such as metathesis of a halide salt with ammonium salt of the desired anion, combining halide salt with a halide metal and using nitric acid to neutralize aqueous solution of the amine. The Figure 1 below shows a typical process for preparation of ILs.

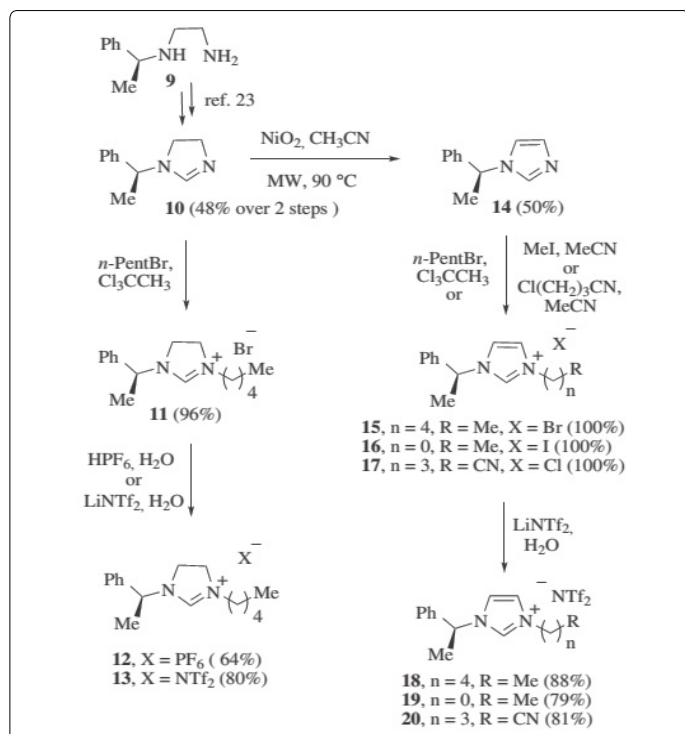


Figure 1. Typical process for preparing ionic liquids [10].

Properties of Ionic Liquids

The various eccentric properties of ILs make them very attractive for use in different applications. The density of ILs is generally more than water and increases with increasing molecular weight of its anion. Furthermore, this property decreases with increasing alkyl chain length in the cation, thus density can be modulated as per requirement.

ILs are generally more viscous than other solvents and show an increase in viscosity as the length of the alkyl chain increases. In addition, ILs have low melting points due to the contribution from both cations and anions present. As the size of anion or cation increases the melting point decreases.

ILs are considered thermally stable as most of them can sustain up to 500°C temperature for a short period of time. Some others may decompose at this temperature. Also, the surface tension of ILs is lower than water but generally higher than other organic solvents. The surface tension of ILs is affected by the size of their alkyl chain length, as the alkyl chain length increases the surface tension decreases.

Another very important property of the ILs is their negligible vapor pressure. This causes them not to evaporate as they are exposed to higher temperature, particularly in solvent extraction processes. Additionally, this low vapor pressure is sustained even at high temperature. Another interesting property of ILs is their large electrochemical window (5-6 V) in comparison with water (1.23 V) [11]. This is shown in Figure 2 below.

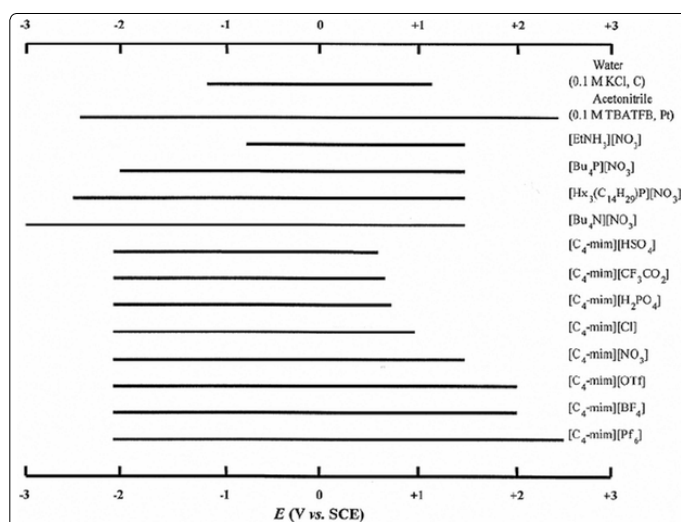


Figure 2. Electrochemical window for ILs [11]

Not enough studies are conducted on the toxicity of ILs, however due to many of their favorable attributes they are considered as green solvents. Table-1 below shows comparison between aqueous amine solvents and ionic liquids and Table-2 compares the solvent properties of ionic liquids with common organic solvents [12] [13] [14].

Table 1. Comparison between different properties of ILs and Aqueous amines [12]

Property	Aqueous amines	Ionic liquids
Molecular weight	60–250	70–800
Density (g/cm ³)	0.65–1.20	0.80–2.10
Viscosity (mPa·s)	<7–460	7–1800
Boiling Point (°C)	111–350	>250
Flash Point (°C)	14–380	50–400
Melting Point (°C)	–65 to 25	–100 to 113
Freezing point (°C)	–46 to 110	–140 to 180
Vapor pressure (mmHg)	<0.001–11	0.000001
Water solubility (1%)	<10–100	Variable
Thermal stability (°C)	100–251	>500
Physical state	Liquid	Liquid, semi-solid and solid
Tunability	No	Highly Tunable
CO ₂ solubility (m ³ /m ³)	<50–85	>2.51
CO ₂ /CH ₄ selectivity	n/a	8–35
H ₂ S/CO ₂ selectivity	1–13	2–15
CO ₂ /H ₂ selectivity	n/a	50–100
CO ₂ /N ₂ selectivity	n/a	30–100
Δ _{vap} H (kJ/mol)	<50–528	>120
Δ _{vap} H (kJ/mol CO ₂)	–36 to 100	–10 to –20
Type of absorption	Physical/chemical	Physical
Nature	Basic	Basic/neutral/acidic

Table 2: Comparison of organic solvents with Ionic liquid [11]

Property	Organic solvents	Ionic liquids
Number of solvents	>1000	>1,000,000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tunable
Chirality	Rare	Common and tunable
Vapor pressure	Obeys the Clausius – Clapeyronequation	Negligible vapor pressure under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Polarity	Conventional polarity concepts apply	Polarity concept questionable

Tunability	Limited range of solvents available	Virtually unlimited range means "designer solvents"
Cost	Normally cheap	Typically between 2 and 100 times of the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity (cP)	0.2–100	22–40,000
Density (g/cm ³)	0.6–1.7	0.8–3.3
Refractive Index	1.3–1.6	1.5–2.2

Applications of ILs

With the aforementioned properties, there have been extensive studies on different applications for ILs. These applications include:

- Use as a catalyst - The main advantage in using ILs as catalysis is that they are considered green catalysts.
- Chromatographic applications- ILs has shown potential benefits in separation science¹⁵
- Solvent extraction - Some room temperature ILs are used as extractors for separation of metal ions
- Sensing using ionic liquids –Chemo-sensing is studied using ILs by observing the rapid decrease in viscosity.
- Spectroscopy - The use of ILs in mass spectroscopy is rapidly increasing after being established by Armstrong's group.

These are a few of the general uses of ILs. Other uses that are related to oil and gas industry include:

- Desulfurization of fuels
- Extraction of naphthenic acids
- Denitrogenation of gasoline
- Use as demulsifiers
- Contaminants removal
- Selective gas separation and mercury removal in natural gas
- Biofuel synthesis or production
- Potential use in Enhanced Oil Recovery (EOR)
- CO₂ Capturing and sequestration
- Use as wax and asphaltene inhibitors
- Extraction of heavy oil or bitumen with ILs
- Applications of Deep Eutectic solvents (DES)s in oil fields

Use of Ionic Liquids in the Petroleum Industry

Ionic Liquids for CO₂ Capture

The global increase in energy demands due to increasing population and industrialization are being met by fossil fuels such as natural gas, coal, oil which make up 85% of energy demand. Simultaneously, there is an exponential increase in carbon dioxide emissions into the atmosphere from the combustion of fossil fuels and therefore the need to reduce anthropogenic emissions of CO₂ the associated greenhouse effect. Thus initiatives taken to capture CO₂ from natural gas based plants are important not only to mitigate the effects of global warming but also to be used as efficient injection fluid for enhance oil recovery (EOR) in the petroleum reservoirs. CO₂-EOR is a tertiary recovery method which has been used in

the oil and gas industry for over 40 years. It has been successfully implemented in oilfields in countries such as the United States and in the North Sea in Norway. There is also a growing interest in using CO₂ for enhanced coal bed methane production (ECBM) and also CO₂ sequestration.

The first step in obtaining CO₂ for the processes mentioned above is to capture and separation. The three main processes which are considered for the capture of CO₂ are, postcombustion, precombustion, oxyfuel combustion and natural gas sweetening as well as amine-capturing technology. Some CO₂ capture processes are already being developed on a laboratory scale or demonstrated in industrial pilot scale, that require various processes involving physisorption/chemisorption, membrane separation or molecular sieves, carbamation, amine dry scrubbing, mineral carbonation etc [3] [16]. Conventional technologies used for CO₂ capture during postcombustion process are solvent-based chemical absorbers such as aqueous amines. CO₂ is captured by chemical absorption process when flue gas streams are passed through a chamber containing aqueous amines [17]. Some commonly used aqueous amines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA) and methyldiethanolamine (MDEA) are used for CO₂ capture through carbamate/carbonate formation. Amines are referred to as "conventional absorbers" because they have been used for decades¹⁸.

The effectiveness of amines to capture CO₂ may be attributed to their properties such as high reactivity, high absorbing capacity (in terms of mass of CO₂), CO₂ selectivity and thermal stability [19]. Nonetheless, some disadvantages that may be associated with the use of amines for CO₂ capture may be attributed to their high vapor pressure, corrosive nature and high-energy requirement for regeneration. The high vapor pressure of amines causes them to be emitted into the atmosphere upon heating and possibility of forming toxins such as nitrosamines due to their unstable nature. Amines also take part in reactions which produce waste products which are corrosive to process equipment. This is especially true for MEA. During the regeneration/recycling process, there's a high requirement for energy in order to break the chemical bonds formed between CO₂ and amine. This causes the amines to be degraded and affects their CO₂ capture efficiency. This makes them unrecyclable and need to be replaced frequently [20] [21] [22]. Figure 3 shows a flowchart for Flue Gas sweetening and CO₂ capture Processes [23].

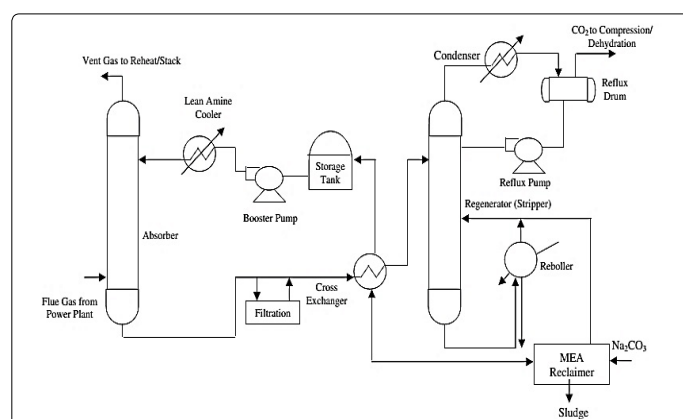


Figure 3. Flowchart for Flue Gas sweetening and CO₂ capture Processes [23]

In recent times ILs have been considered for the capture of CO₂ due to their wide range of physical and chemical properties. They can be modified by their cationic and anionic moieties to serve as efficient CO₂ capture medium by absorption through physical solubility and ionic interactions [23].

Kumar et al [12]. discussed some of these methods elaborating their advantages and disadvantages [3] [24]. ILs received attention for their potential as a CO₂ and possibly H₂S absorber in the past few years for their ability to dissolve these gasses at higher mole fractions [3] [25]. They also possess physical and chemical properties which allow them to be tailored for a specific application environment [3] [26] (negligible vapor pressure, high thermal stability and the varieties of possible combinations between the anions and cations to compose a tailor made IL are some of them). An important requirement of the material used to separate CO₂ from other component of flue gas is the selectivity property in removing the CO₂ without affecting other components in the gas mixture. Some of the ILs have such properties and thus they are becoming attractive alternative for such uses [27].

The study of CO₂ capturing using ILs was first conducted by - Blanchardet. Al [28] which proved higher affinity to CO₂ compared to amines. Following their study, many researchers showed interest in studying these compounds for gas processing in persuasion for a greener technology. Studies have been conducted on the solubility of CO₂ in ILs and also to understand the phase behavior of IL-CO₂ combination. Other studies focused on theoretical aspects such as the interaction between CO₂ and the anions present in the ILs. The general findings are that solubility of CO₂ is highly dependent on the nature of the anionic component in the ILs rather than the cationic nature of the molecule [26] [27].

Klahn and Seduraman [29] studied 10 different pure and CO₂-saturated ionic liquids through molecular dynamics simulator based on empirical force field on liquid-phase charges. The partial molar volume of CO₂ in ionic liquids (ILs) varies from 30 to 40 cm³/mol. The study shows that the absorption of CO₂ does not affect the overall organization of ions in the ILs, neither solubility of CO₂ in ILs is influenced by the direct CO₂-ion interactions. Instead, a strong correlation between the ratio of unoccupied space in pure ILs and their ability to absorb CO₂ is found. Rather the preformed unoccupied space between the ions is dispersed and expanded throughout the ILs accommodate CO₂ [29]. This phenomenon is explained in Figure 4.

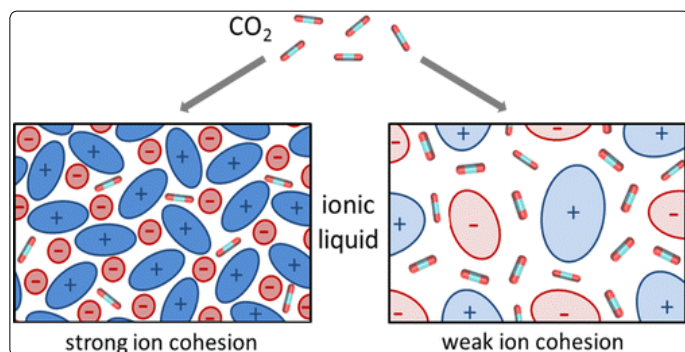


Figure 4. CO₂ Solubility in Ionic liquids [29]

Kumar and Cho [12] have summarized a list of ILs used for both CO₂ and H₂S capturing process (Table 3). Experimental results on CO₂ solubility in ILs with the experimental conditions and the type of IL used are also available in the public domain [3].

Table 3: List of ILs used by previous investigators for H₂S and CO₂ Capturing [12]

Name of I	Abbreviation	H ₂ S	CO ₂ and H ₂ S
1-Butyl-3-methylimidazolium hexafluorophosphate	[BMIM][PF ₆]	✓	✓
1-Butyl-3-methylimidazolium chloride	[BMIM][Cl]	✓	✓
1-Butyl-3-methylimidazolium tetrafluorophosphate	[BMIM][BF ₄]	✓	✓
1-Butyl-3-methylimidazolium hexafluorophosphate	[BMIM][PF ₆]	✓	✓
1-Butyl-3-methylimidazolium triflate	[BMIM][TfO]	✓	✓
1-Butyl-3-methylimidazolium bis (trifluoromethyl)sulfonylimide	[BMIM][Tf ₂ N]	✓	✓
1-Butyl-3-methylimidazolium hexafluorophosphate	[BMIM][PF ₆]	✓	✓
1-Butyl-3-methylimidazolium tetrafluorophosphate	[BMIM][BF ₄]	✓	✓
1-Butyl-3-methylimidazolium bis (trifluoromethyl)sulfonylimide	[BMIM][Tf ₂ N]	✓	✓
1-Hexyl-3-methylimidazolium hexafluorophosphate	[HMIM][PF ₆]	✓	✓
1-Hexyl-3-methylimidazolium tetrafluorophosphate	[HMIM][BF ₄]	✓	✓
1-Hexyl-3-methylimidazolium bis (trifluoromethyl)sulfonylimide	[HMIM][Tf ₂ N]	✓	✓
1-Ethyl-3-methylimidazolium hexafluorophosphate	[EMIM][PF ₆]	✓	✓
1-Ethyl-3-methylimidazolium bis (trifluoromethyl)sulfonylimide	[EMIM][Tf ₂ N]	✓	✓
1-(2-Hydroxyethyl)-methylimidazolium hexafluorophosphate	[HOEMIM][PF ₆]	✓	✓
1-(2-Hydroxyethyl)-methylimidazolium triflate	[HOEMIM][OTf]	✓	✓
1-(2-Hydroxyethyl)-methylimidazolium tetrafluorophosphate	[HOEMIM][BF ₄]	✓	✓
1-(2-Hydroxyethyl)-methylimidazolium bis (trifluoromethyl)sulfonylimide	[HOEMIM][Tf ₂ N]	✓	✓
1-(2-Hydroxyethyl)-3-methylimidazolium tetrafluorophosphate	[HEMIM][BF ₄]	✓	✓
1-Ethyl-3-methylimidazolium methylsulfate	[EMIM][EtSO ₄]	✓	✓
1-Butyl-3-methylimidazolium hexafluorophosphate	[BMIM][PF ₆]	✓	✓
1-Ethyl-3-methylimidazolium methylsulfate	[BMIM][MeSO ₄]	✓	✓

Several studies have shown the possible and efficient use of ILs as a mean for CO₂ capturing. However, their high cost is a disadvantage which led to the suggestion of pairing them with an amine. This led to IL-amine blends which have the advantages of both ILs and amine in achieving higher efficiency and reducing cost. Other advances in improving the efficiency of ILs for CO₂ capturing are to emulsify the insoluble amines in a continuous phase of ILs. This provided a more cost effective solution [3] [30].

Ionic liquids as a substitute of surfactant for EOR

In an effort to meet the growing energy demand, tertiary recovery or enhanced oil recovery methods are employed after primary and secondary recovery of oil. Conventional oil recovery such as primary recovery produces only about 5–10% of the total oil in the reservoir. Secondary recovery up to 40% or more by means of water and/or gas flood are recorded in many oil fields. Chemical EOR methods involve the use of chemical additives in flood water to improve its potential to release trapped oil and push out from the reservoir rocks. Some of the common chemical flooding methods are

surfactant flooding, polymer flooding, alkaline flooding, micellar flooding and Alkali-Surfactant-Polymer flooding (ASP). A properly selected surfactant solution has the ability to lower the interfacial tension between water and oil from 10–30 dynes/cm to the order of 10^{-3} dynes/cm, thus breaking up the oil into micro-droplets so that they can be extracted from the pores by hydrodynamic force of the chase water. They also help in altering the wet ability of the reservoir rocks which may be a favorable attribute in recovering additional oil. In some cases co-surfactants (such as octanol) are used to augment the surfactant flood process. In polymer flooding, polymers are added to injection water which enhances viscosity of flood water thus ensuring the mobility ratio between the displacing fluids and the displaced fluid below unity which in turn improves volumetric sweep efficiency. In alkaline flooding, high pH alkaline water is injected into the reservoir which reacts with the acidic components of the crude oil and form surfactants in-situ. Due to the large quantities of surfactants required to displace meaningful amounts of extra oil, the use of surfactants becomes uneconomical in most situations. A solution to this drawback of surfactant usage is the development of Alkaline-Surfactant-Polymer (ASP) flooding. This type of flooding involves the injection of a chemical formulation made up of an alkali with some amount of surfactants into the reservoir. This reacts with the crude oil to form micro-emulsion at the flood front, which is later swept from the pores of the reservoir rock by high viscous polymeric fluid.

In this section we will discuss the latest development on new solvents and surfactant-IL combinations as an alternative to conventional surfactant flooding process. The chemical structure of the conventional surfactants are made up of a polar hydrophilic part and often a long-chain, non-polar hydrophobic part while in a surfactant-IL system, the surface activity maybe associated to the anion, the cation or both bi-amphiphilic or catanionic surfactants³¹. Some advantages of ILs over traditional surfactants, which make them good candidates to replace surfactants are that they are mostly liquid and non-volatile, they can be specially designed for specific tasks or reservoir conditions and they have a relatively high viscosity which prevents them from phase-fingering phenomenon due to unfavorable mobility ratio. They also do not require co-surfactants since they have strong cohesive forces which enable them to form stable micelles without the need of additional chemicals [32].

Lago et al. [32] investigated tri-hexyl-(tetradecyl)-phosphonium-chloride $[P_{66614}] [Cl]$ ionic liquid for its ability to act as a surfactant in reducing interfacial tension (IFT) between crude oil and water at room temperature. The objective of the study was to evaluate the possibility of ionic liquids to be used for miscible EOR. The surface activity of $[P_{66614}] [Cl]$ was studied through measurements carried out to determine the IFT, density, and viscosity of an equilibrium phase formed by various mixtures of the IL $[P_{66614}] [Cl]$, water and dodecane. They also studied the effect of salinity on the surface activity of the IL by replacing the water with a brine solution (4% (w/w) NaCl). This is done since some reservoirs contain high

salinity brine formation. For the binary system of water and $[P_{66614}] [Cl]$, the interfacial tension was reduced to 1.8 mN/m. When $[P_{66614}] [Cl]$ was added to a binary system of water and dodecane to form a tri-phasic system, the interfacial tension measure changed from 52.2 mN/m to about 1.4 mN/m. Even though the interfacial tension obtained was not close to the values obtained in conventional surfactants, the results encouraged further investigations with other ILs and combination of ILs. With regards to the replacement of water with brine, it was observed that the ionic liquid in the mixture shielded any effects of the salt. They also observed an increase in the viscosity of the water phase when ionic liquids were added. This may be a very useful property since it could prevent the flood water from seeping through high permeability regions or fractures and thus delay high water cut production. This may also help to decrease the water-oil mobility ratio within the reservoir which may lead to more efficient oil recovery. Subsequently Lago et al [33]. Also investigated the influence of temperature, on the phase behavior, viscosity and interfacial tension of a mixture of water, $[P_{66614}] [Cl]$ and Dodecane (at atmospheric temperature and at 75°C). The binary mixtures of $[P_{66614}] [Cl]$ and dodecane were found to be completely miscible at 75°C, while the same binary system at 25°C was seen to be partially miscible. A triphasic system was created between water, dodecane and $[P_{66614}] [Cl]$ and it was observed that there was little influence of temperature on the equilibrium compositions³³. Hezave et al [34]. conducted a study to observe how the IL 1-dodecyl-3-methylimidazolium chloride $[C_{12}mim] [Cl]$ could reduce interfacial tension (IFT) between water and crude oil. It was observed that there was a decrease in interfacial tension up from 39.98 mN/m to 6.87 mN/m at 5000 ppm concentration of $[C_{12}mim] [Cl]$. Surprisingly when the IFT was measured again between formation brine and crude oil there was a significant decrease in IFT with only 100 ppm of $[C_{12}mim] [Cl]$. This reduction in IFT with low concentrations of IL in salt water compared to higher concentrations when IL in distilled water is attributed to the absence of any ion either positive or negative in the distilled water. Thus the IL molecules were incapable of arranging themselves freely at the oil-water interface because the high charge density of ILs lead to molecular repulsion. However, in saline water the presence of negative charges neutralize the positive surface charges of the cationic part of IL. This resulted in an easier accumulation of IL molecules at the oil-brine interface, and further reduction in IFT [34]. The effect of NaCl concentrations on IFT of IL-crude oil system was also investigated at different concentrations of the IL $[C_{12}mim] [Cl]$. It was observed that at NaCl concentrations up to 100,000 ppm (far higher than reservoir formation brine), the IL significantly reduces the IFT to values lower than conventional surfactants.

The effects of temperature on the interfacial tension between $[C_{12}mim] [Cl]$ and crude oil was also considered for the study. The temperature was varied from 293.15 K to 333.15 K. It was noted that the minimum temperature corresponding to a minimum interfacial tension is the phase invasion temperature (PIT). At temperatures below the PIT, there is a

reduction in IFT, however at temperatures above the PIT, further increase in temperature resulted in an increase in the IFT. This can be explained as being the result of the surfactant or $[C_{12}mim][Cl]$ adsorption onto the interface and diffusing into the oil phase, resulting in emulsion inversion as the ionic liquid content is accumulated to some extent [34] [35] [36].

Hezave et al [34]. Further looked into different families of ionic liquids and their functionality in harsh reservoir conditions such as high salinity and high temperature, at which most surfactants lose their functionality. Success in this direction would boost chemical EOR applications in the reservoirs where presently no solution is available.

Interfacial tension (IFT) measurements were conducted between crude oil and four different types of IL solutions namely $[C_{12}mim][Cl]$, $[C_8mim][Cl]$, $[C_{12}Py][Cl]$ and $[C_8Py][Cl]$ using the pendant drop and spinning drop techniques to measure the effects of NaCl concentrations, temperature and absence/presence of ions. Their results showed that all the four ILs were more effective in the presence of salinity in reducing IFT as compared to conventional surfactants. The functionality of the ILs are seen to diminish as the temperature increased, and this was attributed to the presence of nitrogen atoms in the imidazolium and pyridinium based ILs. It was concluded that the ILs exhibited good properties in reducing IFT in harsh reservoir salinity conditions. However, before implementing these ILs to a field scale, further studies should be conducted to design an IL solvent which can also withstand high reservoir temperatures and also their adsorption on reservoir rocks should be studied. One of the main drawback of surfactants is their high adsorption on the reservoir rocks which leads to a change in rock wettability towards more water wet conditions thus favoring release of oil and improved recovery. However this property has negative impact on the economics of EOR. Therefore these new ILs as a substitute of surfactant flooding should be designed to optimize the adsorption on the reservoir rocks at the same time keeping in mind the economics of the project.

Further studies on the over, the effects of $[BMIM][ClO_4]$ on the interfacial tension of oil– water and oil recovery are tested. Results shows that $[BMIM][ClO_4]$ can improve the mobility of heavy oil by reducing the IFT of oil–water and increase the recovery factor by 79.94% [37].

Shaktivel et al [38]. performed similar experiments using ionic liquids with imidazolium cation and various anions to study how these ionic liquids could lower the interfacial tension in crude oil-water systems and the synergic effect of ionic liquids and NaCl in lowering the IFT of crude oil-water systems. The Wilhelmy plate method was used to study the surface tension and interfacial tension of aqueous solutions of the ionic liquids and crude oil systems, with and without salinity effect while considering the concentration of the ILs and also the effect of temperature on the system. The ionic liquids synthesized and used in this experiment are 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium tetra-fluoroborate, 1-butyl-3-methylimidazolium dihydrogen phosphate,

1-butyl-3-methylimidazolium hydrogen sulfate, 1-butyl-3-methyl-imidazolium hexa-fluorophosphate, 1-hexyl-3-methylimidazolium bromide, 1-hexyl-3-methyl-imidazolium hydrogen sulfate and 1-octyl-3-methylimidazolium chloride.

The interfacial tension of the crude oil-water systems is greatly dependent on the adsorption of IL molecules at the interface between crude oil and water. In this study, it was observed that the concentration of ILs also affects the interfacial tension between crude oil and water [39]. The IFT measurements at 288.15 K between crude oil and water, with concentration change from 0 to 50 ppm, was observed to decrease from 36.24 to 25.86 mN/m for IL $[C_4mim][Cl]$ and for $[C_8mim][Cl]$ it was reduced from 36.24 to 23.26 mN/m. It can be inferred from the rest of the experiments that, the longer the alkyl chain length, the more effective the IL is at reducing the IFT at lower concentrations. The IFT of crude oil-water systems were also measured in the presence of ionic liquids in presence of NaCl. The synergetic effect of NaCl and ionic liquids was observed as the IFT was reduced from 21.37 to 9.26 mN/m, where as only IL at a concentration of 1000 ppm the IFT was reduced from 21.20 to 19.58 mN/m [39] [40].

Aside from focusing on the reduction of IFT some researchers also observed the changes in rock wettability and relative permeabilities. Dahbag et al [41]. conducted studies on different IL solutions to observe how they change the wettability of a reservoir rock. Initially, they screened different ILs based on their solubility in different brine compositions, thermal stability and IFT reduction in high salinity and high-temperature conditions. After selecting the most suitable ionic liquid, they went on to conduct several core flooding experiments at reservoir conditions using Berea sandstone cores to investigate the ability of the ILs to adsorb on rock surfaces and change their wettability. After the initial screening of nine ionic liquids, tetra-alkyl-ammonium sulfate was found to be the most potent ionic liquid. IFT measurements of tetra-alkyl-ammonium sulfate with crude oil at different IL concentrations and high solution salinity showed a reduction in IFT even with increasing levels of salinity. Temperature and pressure had little effect on these measurements. The tendency for adsorption on rock surfaces at reservoir conditions was observed and even in high salinity ionic solution. After core flooding experiments, wettability changes were confirmed by performing contact angle measurements. Wettability changed from slightly oil wet to mediumwater-wet condition as the IL concentration was increased [41].

In most research works, the imidazolium family of ILs with chloride counter-ions are given maximum attention. In some studies counter-ions and /or pyridinium, ammonium and phosphonium cations are used. In a study by Rodriguez-Palmeiro et al [31]. A surfactant-IL comprising of 1-dodecyl-3-methylimidazolium cation and acetate anion $[C_{12}mim][OAc]$ was synthesized and used for a series of dynamic interfacial tension studies in varying temperature, water salinity and some alkaline additives. The results obtained with the new surfactant ionic liquid were compared with the results found from the literature of similar ionic liquid but with different

counter-ions which were halides (chloride, bromide, and iodide). The effects of aggregation of $[C_{12}mim][OAc]$ was investigated and it was seen to exhibit a lower critical micelle concentration and a better tendency for micellization over adsorption at the interface and lower spontaneity for micellization [31].

Promising results were also obtained from dynamic interfacial tensions of aqueous solutions of $[C_{12}mim][OAc]$ with crude oil various compositions. From the results, there was a lowering of the interfacial tension and higher stability in presence of salts (up to 4%wt NaCl). In presence of alkalis, the interfacial tension was further reduced. In most literature where surfactant ionic liquids were used, interfacial tension values were reduced to as low as 1mN/m. Results obtained from Rodriguez-Palmeiro et al. [31], show a lower interfacial tension of at least one order in magnitude, with larger effects being observed when strong alkalis like NaOH are used.

Heavy Oil dissolution and Viscosity reduction

One of the challenges of the upstream petroleum industry is the recovery of heavy and extra heavy crude oil, which is estimated to be more than double the volumes of conventional light to medium crude oils discovered throughout the globe. The heavy fraction (wax, asphaltenes and resinous compounds) present with the crude oil are responsible for the higher viscosity and density of the crude oil which poses challenges not only in production but also in surface processing and refining [42]. Because easily extractable lighter oil reserve is steadily decreasing, the industry is becoming rapidly dependent on economic extraction of the heavy and extra-heavy oil that was previously considered uneconomical.

For the purpose of heavy oils recovery, thermal methods (steam injection and in-situ combustion) are the most successful methods, while non-thermal methods such as miscible gas injection and solvent injection found limited success in real field scenario. The problems of transporting heavy and viscous crude oils through long distance pipelines and assuring its flow is another great challenge that sometimes make the project un-economic. Since the resistance to flow is originated from the oil microstructure, partial upgrading through the modification of the microstructure by heating and solvent dilution have been the most widely applied methods in pipeline transportation of heavy oils. Dilution of heavy and extra heavy oil is achieved through the addition of less viscous crude oils, condensate, gasoline, kerosene or naphtha [43] of which light hydrocarbons and condensates (C_5+) are the most widely used diluents [44]. However the high price of the diluents, difficulties in separation and recycling, availability of light oils close to heavy oil fields, and the environmental and climate specific issues put serious restraints on heavy oil dilution process. There is also the issue of compatibility between the crude and the solvents which may result in solids precipitation and plugging. This necessitates increasing solvent polarity [45] or use of aromatic solvents to prevent asphaltene precipitation and the resulting flowline blockage [44], thus increasing operational cost as well as the environmental concerns. These constraints along

with data from early works encouraged studies on ionic liquids as a replacement/aid for solvent dilution which is the topic of discussion of the flowing section.

One of the initial works on heavy oil upgradation was tried with 1-butyl-3-methylimidazolium chloride [BMIM][$AlCl_4$] ionic liquid reported by Fan et al. [46]. More than 60% of oil viscosity could be reduced by treating with [BMIM][$AlCl_4$] in presence of transition metal salts (Fe & Ni). The process was seen to be more efficient viscosity reducer when certain amount of sulfur was present in the oils and the water content in the oil was less than 10%. Further progress on the similar class of ILs, the modified versions of 1-butyl-3-methylimidazolium tetrachloroferrate [BMIM][$FeCl_4$], were prepared by Shaban et al [47]. and studied through physicochemical methods and catalytic activity measurements, with special emphasis on the reaction temperature and the water content in the heavy crude oils. It was found that [BMIM][$FeCl_4$] family of ILs have the best effect on the heavy crude oil upgradation between 70–90°C temperature and water content less than 8% [47].

Saaidet al [37]. further investigated on a different class of BMIM ILs. They synthesized 1-butyl-3-methylimidazolium perchlorate, [BMIM][ClO_4], and studied their effect on viscosity, density, SARA (saturates, aromatics, resins and asphaltenes) contents, elemental compositions and molecular weight. The results indicated that the presence of [BMIM][ClO_4] significantly changes the composition of the heavy oil which resulted in reduction of viscosity and density of the crude and improved flow ability.

Sakthivel et al [38]. Investigated a set of eight different ionic liquids along with five solvents, namely heptane, toluene, decane, ethyl acetate, and hexane to assess the possible dissolution effect on heavy crude oils. The ionic liquids used in this study were: diethylammonium phosphate $[Et_2NH_2]^+[H_2PO_4]^-$, diethylammonium sulphate $[Et_2NH_2]^+[HSO_4]^-$, triethylammonium acetate $[Et_3NH]^+[CH_3COO]^-$, triethylammonium tetrafluoroborate $[Et_3NH]^+[BF_4]^-$, triethylammonium sulphate $[Et_3NH]^+[HSO_4]^-$, tripropylammonium sulphate $[Pr_3NH]^+[HSO_4]^-$ and tributylammonium sulphate $[Bu_3NH]^+[HSO_4]^-$. Usually the treatment of heavier hydrocarbons such as asphaltene is done by aromatic solvents such as benzene, xylene, and toluene. Even though these aromatic solvents are efficient asphaltene dissolvers, they are however volatile and hazardous to human. In these experiments about 10% of ionic liquids were dissolved in organic solvents and their dissolution effect on the heavy crude oil studied. It was observed the $[Et_2NH_2]^+[H_2PO_4]^-$ exhibited good performance in the dissolution of heavy oil in the presence of toluene. $[Et_3NH]^+[CH_3COO]^-$ performed better in heptane, decane, and hexane, and most interestingly in ethyl acetate solvent the $[Et_2NH_2]^+[H_2PO_4]^-$ IL exhibited much improved results. The efficiency of the dissolution of heavy oil by solvents was in the following order; toluene > heptane > decane > ethyl acetate > hexane. This work shows that with minimal addition of ionic liquids to heavy crude oil the dissolution effect is markedly enhanced. Further research on

the similar path were conducted using only ionic liquids without any solvents to identify the effect of only ionic liquids on the dissolution of heavy crude oil and asphaltenes in heavy crude oils [2] [38] [48] however the results are not so promising.

In continuation to the previously mentioned studies, Sakthivelet al [38] [49]. conducted further research on the use of ionic liquids to dissolve and reduce the viscosity of tankbottomsludge (TBS) with ILshaving imidazolium cation [BMIM]⁺ and various anions such [Cl]⁻, [Br]⁻, [BF₄]⁻, [H₂PO₄]⁻, [HSO₄]⁻ and [PF₆]⁻. UV-visible spectrophotometric techniques were used to observe absorbance intensity with respect to a particular ionic liquid for a concentration range from 10 to 70 ppm. IL content of 10 ppm was found to be adequate for nearly complete dissolution. They also carried out dissolution studies of the tankbottom sludge in the presence of ionic liquids in different solvents such as toluene, heptane, decane, hexane and ethyl acetate and found that [BMIM]⁺[PF₆]⁻ gave better dissolution performance in toluene and hexane, while in heptane [HMIM]⁺[Br]⁻ performed better. [BMIM]⁺[H₂PO₄]⁻ performed better in the presence of decane and [BMIM]⁺[H₂PO₄]⁻ and [BMIM]⁺[Br]⁻ gave better dissolution of TBS in the presence of ethyl acetate irrespective of the weight ratio of TBS:ILs [49]. Another explanation for the effective dissolution of tankbottom sludge containing ionic liquids could be due to the fact that there is an interaction between the ionic liquids and the asphaltenes which eventually breaks the asphaltene macro-structure. This is because there is an interaction between the cationic part of the ionic liquid and the heteroatomic functional groups of asphaltenes (which is the major constituents of the TBS) such as Sulphur, Oxygen, and Nitrogen. The heteroatoms of the asphaltenes contain at least one lone pair of electrons which are available for the ionic interaction. At higher concentrations of the ionic liquids, the asphaltene molecules are effectively surrounded by ILs and solvated by the interaction forces. Arresting of the heteroatom activity in the asphaltene/resin moiety leaves the asphaltene/resins moiety with only hydrocarbons which dissolve easily in the organic solvent [50]. Further studies on the interactions between asphaltenes and ionic liquids can lead to the development of an environmentally friendly inhibitor to mitigate flow assurance issues in the oilfield.

Synergistic effect of ionic liquids along with brine has also been studied. It is observed that, solubility of heavy crude oil in the presence of ionic liquids and the solvents increases about 60 % when water content is minimum. Reduction of interfacial tension is more effective in presence of salt in the mixture. The above findings reveal that it may be possible to minimize the amount of organic solvents that may be required to upgrade heavy oil and tank bottom sludge and may also help in surface and subsurface flow-assurance issues by employing suitable IL-Solvent combinations.

Ionic Liquids for Asphaltene Inhibition

As discussed above the precipitation and deposition of heavy organics in crude oil like wax and asphaltenes poses great challenge during crude oil production, transportation

and storage, of which the concern for asphaltene deposition is significantly higher. Agglomeration and deposition of asphaltenes can be caused due to change in pressure, temperature, pH and composition of crude oil [51]. These depositions can occur in the near wellbore reservoir, sub-surface production tubing, surface flowlines and oil processing facilities, which often leads to a decline in production of oil and/or complete shut-in of the well, resulting in loss of production and additional operating cost for remediation and cleaning operations [52]. Waxes are long chain paraffin components of crude oil and rather easy to handle, mostly by heat management, which is not the case for asphaltene. Asphaltenes are extremely complex molecules, defined as "the heaviest components of crude oil which are insoluble in lower alkanes (n-pentane or n-heptane) but soluble in aromatic solvents such as benzene, toluene, and xylene. The chemical structure of asphaltenes is uncertain due to their complex and uncertain nature [53] [54] [55]. When asphaltenes precipitate and deposit in the reservoir, they may cause permeability and porosity reduction and also wettability alterations from water-wet to oil-wet [56], an unwanted phenomenon which results in lowering oil relative permeability flow efficiency. It is observed that reservoirs which undergo enhanced oil recovery (EOR) processes like hydrocarbon gas or miscible CO₂ injection are faced with severe asphaltene problems regardless of crude oil density and viscosity. Therefore prior to implementing any enhanced oil recovery project, it is recommended that a careful study of the probability of asphaltene precipitation and deposition be carried out in order to consider the preventive measures or mitigation strategies [54] [57] [58].

In the likelihood of asphaltene precipitation, chemical treatment techniques such as asphaltene inhibitors are employed to prevent the aggregation of asphaltene molecules and to enhance their stability in the crude oil. In most cases however, the solvent treatments are carried out to dissolve already precipitated asphaltene in the wellbore and surface flow lines. Some conventional asphaltene dissolvers are toluene, xylene, and benzene, however, these chemicals are flammable, carcinogenic, dangerous to handle and harmful to the environment [59].

The next generation asphaltene inhibitors are based on their surfactant characteristics and the most prominent among them is the dodecylbenzenesulphonic acid (DBSA). These surfactants must have the ability to stabilize the suspended asphaltene colloids and also dissolve asphaltenes in the molecular level through acid-base interactions [40] [50] [60] [61] [62]. Recently, ILs have attracted attention in the area of asphaltene inhibition due to their effectiveness in dissolution of heavy crude oil, and also the ability to disperse asphaltenes in crude oils [63] [64] [65].

One of the early investigations performed by Hu and Guo [63] was on the effect of ionic liquids and amphiphiles on the inhibition of asphaltenes precipitated from CO₂ injected oil reservoirs, where miscibility between oil and CO₂ occurred. Ionic liquids with different types of cationic groups and anions

were investigated, with emphasis on the effect of the cation tail lengths, head groups, cation and anion combination and the concentration of the ionic liquids. The studies were performed on oil with CO₂ in miscible condition (above minimum miscible pressure) and the asphaltene precipitation was measured quantitatively. The study revealed that the ionic liquids with cation being p-alkylpyridinium and with a chloride anion [C_npy] [Cl] showed effective inhibition with decreasing alkyl chain length, in the following order: [C₁₂py] [Cl] < [C₈py] [Cl] < [C₄py] [Cl]. The shortest chain cation performed better than longer chain length cations. While comparing ionic liquids of different cations but the same anion, [C₄iq] [Cl] was observed to be more effective than [C₄py] [Cl] in inhibiting CO₂ instigated asphaltene precipitation [63].

Direct coal liquefaction (DCL) is a source of various industrial chemicals and liquid fuels. Asphaltenes, which constitute about 25 wt. % of the DCL product, is a rich source for aromatic chemical precursors, which needs to be extracted from the DCL product prior to shipment. Bai et al [64]. developed a series of Protic ionic liquids (PIL) using N-methylimidazole, 3-methylpyridine and triethylamine cations combined with formate, acetate, propionate and benzoate anions to extract asphaltenes from DCL product at room temperature showing higher yields compared to conventional solvents. The extracted asphaltenes have lower H/C ratios, higher degree of aromaticities, lower sulfur contents, no ash contents and nearly no quinoline insolubles. Increasing alkyl chain length of anions enhanced extraction yields whereas extraction yields of asphaltenes varied with different cations of PILs in accordance with the order of N-methylimidazolium[MIM]⁺ < triethylammonium[TEA]⁺ < 3-methylpyridinium [MPy]⁺. Hydrogen bonding, π-cation interactions, and charge-transfer between complexes are attributed as the responsible functions for asphaltene dissolution [64]. Junaki et al [65]. prepared IRAN91, an IL prepared from mixing of AlCl₃ with [Et₃N] HCl for upgradation of heavy oil and asphaltene stabilization purposes. The compound is seen to reduce the asphaltene content, viscosity, and average molecular weight of the heavy oil significantly. Viscosity is reduced from 1800 to 644 cP, Average molecular weight came down from 2840 to 384 and the asphaltene precipitation is reduced from 15 to 7%. The important phenomena observed in this process is the formation of a complex between the IL and the organic sulfur in heavy oil, which weakened the C-S bonds resulting in the drop of average molecular weight and higher stability of asphaltene in the oil [65].

Adeniji et al [66]. carried out a series of experiments to study the properties of the imidazolium IL cation with various anions targeting asphaltene dispersion. The ILs synthesized and used in these studies were 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium nitrate and 1-methyl-1H-imidazol-3-ium-2-carboxy-benzoate. Through computational simulations [66] they inferred that the interactions between the ionic liquids and the asphaltenes occurred through the

π-π interaction between cation and asphaltenes via hydrogen bonding, similar to the observations made by Bai et al. [64]. Based on the interaction energies, the order of reactivity between the asphaltenes and ionic liquids were deduced. The interaction energies of 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium nitrate and 1-methyl-1H-imidazol-3-ium-2-carboxybenzoate were -55.4×10⁴, -44.1×10⁴ and -54.8×10⁴ kcal/mol, respectively. From the interaction energies, it was inferred that 1-butyl-3-methylimidazolium chloride presented the smallest interaction energies and was a better candidate in the dispersion of asphaltenes.

From the above results and several other similar studies (which could not be discussed for space constraints) it can be inferred that ionic liquids have good potential in keeping the asphaltene in solution and contain the oilfield flow assurance problem in an effective and environment friendly manner.

Summary and Conclusion

This review article discussed the available literature information about the applications of ionic liquids in the petroleum industry. More effort has been given to the upstream applications of ILs as there are several reviews available on the downstream applications of ILs, which is not the case for upstream application of ILs.

Many ILs are proven to be promising in CO₂ capture and imidazolium-based ILs are found to be most promising in reducing IFT even at high temperature and high salinity environments which make them suitable for high temperature EOR applications. This paved ways for further researches in order to develop ionic liquids with improved properties which could replace surfactants currently used for chemical enhanced oil recoveries, particularly in high temperature and high salinity reservoirs which are not suitable for surfactant application. It is also seen that ILs can find potential applications in heavy oil recovery, upgradation for pipeline flow and controlling sludge precipitation in storage tanks. Asphaltene inhibition and better flow assurance particularly in miscible gas EOR project is another potential area where ILs can be used with case specific studies.

At present the major drawback of applying ionic liquid in large quantity is their cost. As much as they are green solvents, which makes them potential substitute for volatile organic solvents, they are quite expensive, which so far has restricted their use in the oil and gas industry. Even though some literature suggests the method of recycling and reuse, rapid applications of ionic liquids in the petroleum industry will not be anytime soon, due to their cost. However, if cost effective means are found to synthesize them on a large scale, they could be widely used to replace many potentially harmful and volatile organic solvents and chemicals currently used in the oil industry.

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