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Selective Treatment Methods of the Refinery and Petrochemical Products by Solvent Extraction with Ionic Liquids

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Abstract

In the past few years, the number of studies regarding the application of ionic liquids (IL) as alternative solvents to extract value-added compounds from crude oil fractions has been growing. Ionic liquids can be considered as green solvents due to their very low vapor pressure and wide range of applications with unique physical and chemical properties. In petroleum and hydrocarbon industries, various solvents have been used for treating purposes. However, these solvents have their own limitations as environmental and economical issue. These limitations can be overcome by use of ionic liquids. This paper gives a survey on the latest most popular IL, from their applications to their feasible results in refinery and petrochemical streams. Especially the selective treatment of the Azerbaijan's crude oil fractions by IL was highlighted and achieved practicable and suitable results were indicated.

Key words: selective cleaning, ionic liquid, extractant, raffinate, desulphurization, dearomatisation

INTRODUCTION

The modern petroleum industry is confronting many challenges throughout the chain value, since the production and refining of crude oil to the manufacture of high-value petrochemical products. Conventional light and middle crude oil production reached a maximum and tends to decline. Also, some producing countries are dealing with heaviest and higher content of pollutants (sulphur, nitrogen and metals) crude oils. Such heavy and extra heavy crude oils (HCO) are more difficult to produce, transport, refine and convert to useful petrochemicals. Sometimes, conventional technologies may be applied but in the most cases, new technologies are needed in order to allow economical HCO production, transportation

through pipelines, avoiding pressure drops, pipeline clogging, and production stops due to asphaltting and paraffin aggregation and precipitation. Also, the higher content of heteroatoms in HCO makes them more difficult to refine because of mainly catalyst deactivation that decreases the efficiency of processes like desulphurization, denitrogenation and demetallization. Moreover, the crude oil composition largely varies from one oil field to another among deposits along the countries. Heavy and extra-heavy oil are characterized by an API gravity between $20 < \text{API} < 10$ and $\text{API} \leq 10$, respectively. The latter oils present a specific gravity near or above 1.0 g/cm^3 , *i. e.* they are as heavy or more than water, making crude oil dehydration, for example, very difficult to reach before refining [1].

In the petrochemical industry, aromatic hydrocarbons have an important contribution to the octane number, and therewith anti-knock resistance, of a carburant fuel. On the other hand, due to their high boiling point, the aromatics content has to be limited since it affects the boiling properties of a fuel. Nevertheless, aromatics are, in general, carcinogenic and their combustion products contribute to greenhouse gas emissions; and in diesel motors to soot formation. Especially, benzene as an extremely carcinogenic component has to be removed. Within recent years the demand for 'clean' fuels is increasing and most likely will increase even more towards fuels with almost zero content of particular aromatics, *e. g.* benzene and toluene. Another aspect of aromatics removal is their economic value; aromatic hydrocarbons are an important raw material for the production of polymers and therewith for plastics, for the production of dyes. In addition to mono aromatics, diesel typically contains poly aromatics such as naphthalene, anthracene and the like. Naphthalene and anthracene are important raw materials for the production of several different products. Furthermore, carburant fuels contain sulphur and nitrogen containing compounds, mostly of aromatic nature, that are responsible for sour gases and NO_x emissions. Hence, conventional processes for this type of separation are extraction or extractive distillation with polar, organic solvents (see Table 1) [2–5].

However, for feeds with low aromatic content (<20 %) those conventional processes are not suitable since their aromatic capacity is too low [6–9].

A modern refinery is a highly integrated industrial plant, the main task of which is to efficiently produce large yields of valuable products from a crude oil feed of variable composition. Product improvement is the treatment of petroleum products to ensure that they meet utility and performance specifications. It usually involves changes in molecular shape (reforming and isomerisation) or in molecular size (alkylation and polymerisation) and it can play a major role in product improvement [10, 11]. Additionally, numerous refinery processes are affected by the presence of sulphur and nitrogen containing aromatic hydrocarbons, especially sulphur aromatics since they act as catalyst poison. Regarding the above mentioned points, it is evident that aromatic hydrocarbons, sulphur, nitrogen, metal contents, *etc.* have to be separated from the main petroleum and petrochemical streams. However, this separation is challenging due to overlapping boiling points and azeotrope formation. Sulphur that is present in transportation fuels leads to sulphur oxide (SO_x) emissions into the atmosphere and causes many environmental problems. It also inhibits the performance of pollution control equipment on vehicles. Therefore, it is necessary to minimize the negative health and environmental effects from automobile exhaust with reducing the sulphur content in fuels at its lowest. Most of the countries are going to make mandatory to have the fuels as "S-free" (by definition <10 ppm) sooner or later. These efforts aim to limit SO₂ emission from the fuel engines and to protect equipment from corrosion. Moreover,

TABLE 1
Conventional processes and solvents

Process	Company	Solvent	Separation	Feedstock
Arosolvan	Lurgi	NMP (1-methyl-2-pyrrolidone (aq))	Extraction	Hydrogenated pyrolysis gasoline Hydrogenated coal gas Oil-gas benzene
Morphylane	ThyssenKrupp – Uhde Chlorine Engineers	NFM (N-formylmorpholine)	Extractive distillation	Hydrogenated pyrolysis gasoline Catalytic reformat
Morphylex (Aromex)	ThyssenKrupp – Uhde Chlorine Engineers	NFM (N-formylmorpholine)	Extraction + extractive distillation	Hydrogenated pyrolysis gasoline Catalytic reformat
Sulpholane	UOP/Shell	Sulpholane (Tetrahydrothiophene 1,1-dioxide)	Extraction (Extractive distillation)	Catalytic reformat
DMSO	IFP	DMSO (dimethylsulphoxide)	Extraction	Hydrogenated pyrolysis gasoline Catalytic reformat

lower sulphur content of fuels would allow the use of other catalysts for the reduction of NO_x emission, which is also an important issue. Thus, the increased reductions of statutory sulphur content in fossil fuels as gasoline or diesel have forced to intensify research into all the possible methods of desulphurisation [12].

Although, in the petroleum industry, low-sulphur fuels are often obtained from hydrocracking processes or hydrotreating processes among which hydrotreating processes have been highly effective for the reduction of sulphur levels [13].

Over the last decade, environmental regulations focus attention on reduction of emissions from the transport sector with the purpose of improving air quality and welfare [14]. For this purpose, refinery products quality (sulphur and nitrogen content) shall be decreased. According to the Directive of the European Union, gasoline and diesel fuels in Europe should not exceed 10 ppm of total sulphur content starting from 2010 [15]. US regulations established a maximum of 15 ppm for diesel starting from 2006 and 30 ppm for gasoline starting from 2005 [16]. To meet the needs for producing clean fuels, decreasing the sulphur content of crude oil becomes an urgent task. These requirements can be achieved with high temperature and pressure. Furthermore, these cause more complicated process and economical high cost.

On the other hand, ionic liquids (IL) show some interesting properties that would allow the separation of aromatic hydrocarbons from aliphatic hydrocarbons to substitute classic solvents with improving performance and less damage to the environment.

Therefore, in this work ionic liquids are examined and compared to conventional solvents and treating processes in order to investigate their extraction and separation capacity for petrochemical streams with low aromatics content and for refinery treating processes.

IONIC LIQUIDS PROPERTIES

Ionic liquids are salts with melting temperatures below $100\text{ }^\circ\text{C}$ – a result of their low-charge density and low symmetry ions [17–19]. Ionic liquids offer new opportunities for the development of extraction solvents. The IL known today are based on different large, organic cations combined with a great variety of organic and inorganic anions. Compared to molecular solvents, IL have the advantage of being liquid over a wide range of temperatures and of having a non-volatile nature [20–26]. The latter property has been the reason to call IL “green solvents” and to start their development as alternative, environmental-friendly solvents.

The properties of an IL are determined by the combination of cation and anion. Due to the large number of possible ion combinations, which gives the opportunity to *tailor* a specific solvent for a particular separation, IL are also called *designer solvents*. Since, in recent years IL gained more and more interest for different fields of application in process chemicals, Maase suggests the classification in performance chemicals and engineering fluids [27]. Figure 1 shows a selection of the most common IL cations and anions.

Ionic liquids have been mentioned for the first time in the open literature in 1914. Walden syn-

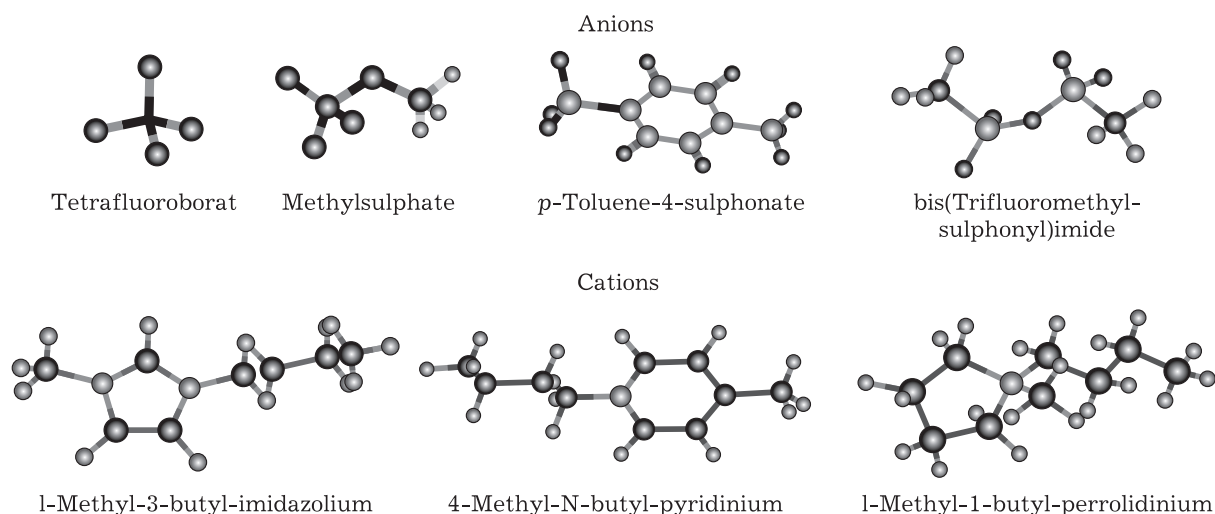


Fig. 1. Typical ionic liquid anions and cations.

thesised ethyl ammonium nitrate, a low melting point salt, which is liquid at 12 °C [28]. Ionic liquids, developed mainly by electrochemists in search of ideal electrolytes for batteries, have thus been used initially for those and related applications like semiconductors *etc.* [29]. When in 1992 the first water stable IL were reported, [30] the signal had been given for many other applications outside the field of electrochemistry. Since the 1990's scientists discovered IL, next to more widely electrochemical applications, applications were proposed for catalysis and/or reaction media, organic synthesis, separations, biotransformation, enzymatic catalysis and many more [31–36]. Also more and more applications on pilot plant and industrial scale are mentioned [27, 37]. The first IL based process on pilot scale, called Difasol, has been the dimerization of olefins with a biphasic, homogeneous catalyst developed by the Institute Française du Pétrole (IFP) [38]. Other applications on pilot plant or even industrial scale are acid scavenging (BASIL, BASF), [39] extractive distillation (BASF), [40] compatibilisers in pigment pastes (Degussa/Evonik), [41] cooling agent (BASF), [42] storage of gases (Air Products) [43] and more.

APPLICATIONS OF IONIC LIQUIDS

The potential of ionic liquids for new chemical technologies is beginning to be recognized as they have different application in many areas as solvent for synthesis, catalysis or extraction, as an enzyme-“friendly” co-solvent, in batteries, as lubricant additives, in polymerization, in synthesis of nanoparticles, in analytical chemistry, *etc.* A few applications to mention are following: purification of essential oils by extraction, separation of azeotropic mixtures, in hydrogen purification, in extraction of rare earth metals, in extraction of carboxylic acids, for removal of sulphur from refinery streams, in separation of isomers, for microfluidic separation using enzymatic reaction, in microextraction, for separation of fission products, in extraction and recovery of dyes, for extraction of ethanol *etc.* In addition to these applications of IL, it can be found that these noble solvents are very useful in many other fields with their recycle ability and without any impact on environment which is the most impressive factor in the present era of environmental concern [44].

The use of IL for the selective extraction of sulphur compounds from diesel fuel was described by Bössman *et al.* for the first time [45].

Keeping in mind that the most popular ionic liquids are undoubtedly the dialkylimidazolium salts, due to their easy synthesis and attractive physical properties, and based on the initial idea of the extraction of sulphur compounds by chemical interaction, these authors investigated the extraction with Lewis and Brønsted acidic IL employing mixtures of *n*-butyl-3-methylimidazolium chloride and *n*-ethyl-3-methylimidazolium chloride with AlCl_3 . Even though AlCl_3 based IL are effective for the removal of S-containing compounds [45], they often form dark precipitates and they are sensitive to water presence [46] generating HCl and making them unstable in air and of limited practical utility.

Ionic liquid extraction power for DBT has been proved to be not uniquely based on chemical interactions involving the acid proton, so different cation/anion combinations of neutral IL were tested [45], showing that desulphurisation is hardly affected by the chemical nature of the anion being the size of ions important for the extraction effect. A possible explanation for this behaviour may be that solubility of sulphur-containing compounds (DBT and derivatives) is dependent on steric factors in the IL.

The first step in the work is the selection of the IL. The main concern about an *a priori* choice of a solvent for an extraction purpose is about solubilities. It is needed to search for a solvent which dissolve preferentially the organic sulphur-containing compounds and the nitrogen-containing compounds with the minimal or non-appreciable solubility of the rest of the fuel constituents. Solubility tests were performed with thiophene, pyridine and several different hydrocarbons [47].

The objective of this paper was the researching of extraction processes for the removal of multiple aromatics, heteroatoms and different substances from several petrochemical streams by means of IL. In recent years, many IL have been developed for these purposes. Some different IL works are given below.

IONIC LIQUID ASSISTED EXTRACTION OF NITROGEN AND SULPHUR-CONTAINING AIR POLLUTANTS FROM MODEL OIL AND REGENERATION OF THE SPENT IONIC LIQUID

Removal of air pollutants, such as nitrogen and sulphur containing compounds from model oil (dodecane) was studied. Nitrogen compounds are harmful impurities in petroleum products. In liquid fuels, nitrogen compounds act as precursors for nitrogen oxides (NO_x), which are envi-

ronmental pollutants. Nitrogen compounds are known to be poisons for acidic and metallic refinery catalysts and, thus, they cause problems in the petroleum hydrotreatment. Nitrogen compounds have also been considered to be responsible for the colour and gum formation as well as for formation of deposits. Nitrogen compounds in petroleum products, when combusted, have carcinogenic and mutagenic properties [48].

Furthermore, the adsorption of nitrogen-compounds on catalysts is higher compared to that of sulphur compounds, even though their reactivity is lower. Thus, as the concentrations of the refractory sulphur compounds in the oil have been lowered *via* normal hydrodesulphurisation (HDS) process, the nitrogen compounds present in the oil could inhibit the HDS process through their competitive adsorption on the catalyst surface [49, 50]. The removal of such HDS catalyst inhibitors could promote the improvement of the HDS conditions and thus, contribute in reducing the difficulties of meeting the strict emission specifications in the transportation fuels.

Non-catalytic processes for the selective removal of N-compounds have been studied, whereby basic N-compounds, such as pyridine and quinoline, have been removed by using ion-exchange resins [50]. Additionally, liquid-liquid extraction of nitrogen and sulphur compounds by using volatile carboxylic acids [51] and IL as extracting solvents have been demonstrated [49, 52].

Liquid-liquid extraction has been extensively used in industrial in the separation and purification of aromatic hydrocarbon, because of severe operation conditions and straightforward processes [53]. The use of conventional polar organic compounds such as glycol or sulfolane has been extensively applied for commercial extraction of aromatic hydrocarbons from aromatic-aliphatic mixtures [54]. However, due to the high volatilities of these chemicals, there are usually losses of extractants by evaporation. These organic compounds are generally toxic and flammable [54]. Liquid-liquid extraction has some general draw-

backs when conventional polar organic compounds are used. It is of particular importance to develop novel extractants with high distribution coefficients, high selectivity and low solvent losses.

Ionic liquids are organic salts composed of organic cations and inorganic anions, and their melting points are under or at ambient temperatures. Ionic liquids are interesting due to their tuneable properties, making them suitable as reaction media and extraction solvents among other applications [55]. It should be noticed that IL have negligible vapour pressures and, thus, the regeneration of spent IL with minor solvent losses might be possible. Ionic liquids have high chemical and thermal stabilities and a wide liquidus range [49, 50, 54, 55].

The aim of this work was to investigate the liquid-liquid extraction of a model oil, dodecane, with an IL, 1-ethyl-3-methylimidazolium chloride ([C2 mim][Cl]). The model oil contained pyridine and indole as basic and neutral nitrogen compounds, respectively, whereas dibenzothiophene was used as sulphur compound (Fig. 2).

Liquid-liquid extraction by using 1-ethyl-3-methylimidazolium chloride [C2 mim][Cl] was found to be a very promising method for the removal of N- and S-compounds. This was evaluated by using model oil (dodecane) with indole as a neutral nitrogen compound and pyridine as a basic nitrogen compound. Dibenzothiophene (DBT) was used as a sulphur compound. An extraction capacity of up to 90 mass % was achieved for the model oil containing pyridine; while only 76 mass % of indoles in the oil was extracted. The extraction capacity of a model sulphur compound DBT was found to be up to 99 mass %. Regeneration of the spent IL was carried out with toluene back-extraction with a 1 : 1 toluene to IL mass ratio was at room temperature. It was observed that, for the spent IL containing DBT as a model compound more than 85 mass % could be removed from the oil. After the second regeneration cycle, 86 mass % of the DBT was recovered from the IL to toluene. In the case of indole as the nitrogen

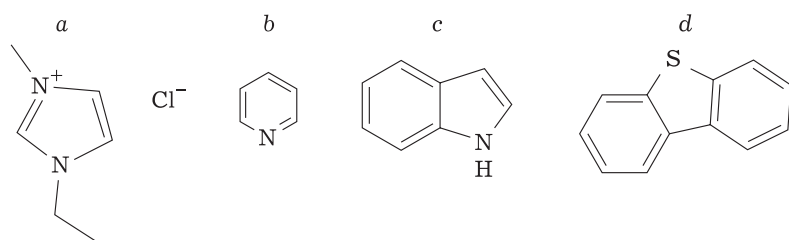


Fig. 2. Extraction of dodecane with (a) an ionic liquid [C2 mim][Cl]. Following compounds were used as model N- and S-containing compounds: (b) pyridine, (c) indole, (d) dibenzothiophene.

containing species, more than 99 mass %, of the original indole was transferred from the model oil to the IL. After the first-regeneration cycle of the spent ionic liquid, 54 mass % of the indole-in-IL was transferred to toluene. Thus, both extractions of nitrogen and sulphur model compounds were successfully carried out from model oil and the back-extraction of these compounds from the ionic IL to toluene demonstrated the proved the concept of the regeneration point of view [56].

LIQUID-LIQUID EXTRACTION OF AROMATICS AND SULPHUR COMPOUNDS FROM BASE OIL USING IONIC LIQUIDS

The viability of using IL as extractive solvents to remove naphthalene (aromatics) and dibenzothiophene (DBT; Sulphur) from base oil by liquid-liquid extraction was investigated. Production of high-class lubricating oil base stock (base oil) has received considerable attention in recent years because of more stringent environmental regulations and higher product specific cations to meet higher performance required by the end users. Group I class base oil is conventionally produced through solvent treatment, whereas production of higher base oil classes (Group II and III) requires hydroprocessing. Hydroprocessing includes hydrotreating (catalytic hydrogen treating) and hydrocracking processes, which have increasing importance in the petroleum refining industry in the desulphurization of light products (*e. g.*, fuels) and in base oil production [57–65]. The significant investment of the hydroprocessing coupled with the severe operating conditions, such as high temperature and pressure, high hydrogen demand, expensive catalyst and environmental impact, led to propose an alternative process involving mild operating conditions with low investment cost and environmental impact. Liquid-liquid extraction using non-conventional solvent, such as IL, is regarded as a potential option.

The experiments were designed using Response Surface Methodology (RSM) with 1-butyl-3-methylpyridinium dicyanamide [BMPY][DCA], 1-butyl-3-methylimidazolium dicyanamide [BMIM][DCA], 1-butyl-3-methylimidazolium thiocyanate [BMIM][SCN] and 1-butyl-3-methylimidazolium dimethyl phosphate [BMIM][DMP] IL. The sulphur compound and aromatics were analyzed using Total Sulphur analyzer and High-Performance Liquid Chromatography (HPLC) with high coefficient of determination *i. e.* R_2 values of 0.964 and 0.997, respectively. The effects of different

IL, temperatures, and IL to oil mass ratio (IL/Oil) were optimized. [BMPY][DCA] appeared as the most promising medium with 94.3 % of dibenzothiophene and 83.1 % of naphthalene removal after a single extraction step. The aromatics and sulphur removal efficiency of [BMPY][DCA] IL was 54.3, 78.3 and 82.9 %, 93.8 % at IL/Oil ratios of 0.4 and 1.8, respectively. An increase in temperature did not improve the extraction efficiency, but a slight decrease was noted. Results emphasized that extraction of aromatics and sulphur compounds from base oil can be achieved successfully using selected IL [66].

DEEP OXIDATIVE-EXTRACTIVE DESULPHURISATION OF FUELS USING BENZYL-BASED IONIC LIQUID

The dramatic environmental impact of sulphur oxides contained in engine exhaust emissions has been widely recognized in recent years. As result specifications regarding sulphur content in fuels are becoming more and more stringent [67]. Research on deep desulphurisation of gasoline is of great importance in both academic and industrial fields.

A traditional desulphurisation method is catalytic hydrodesulphurisation (HDS) using catalysts such as CoMo or NiMo [68], which requires both high temperature and high pressure. Also, HDS is only effective on aliphatic sulphur structures such as thiols, thioethers and disulfides, *etc.* Sulphur-containing aromatic compounds (including thiophene and its derivatives) are barely removed by this process. Due to this reason, alternative desulphurisation technologies have been developed, including adsorption [69], extraction [70], and selective oxidation [71]. Extractive desulphurisation is believed to be one of the best methods because the process operation is easy. However, using volatile organic compounds (VOC) as extractant leads to more environmental and safety concerns. Ionic liquids have been employed extensively in “green chemistry”. Ionic liquids have the characteristics of nonvolatility, nonflammability and high thermal stability. As a result, IL are considered as green solvents and are employed in processes of catalysis, chemical synthesis and separations. The use of IL as extractants to remove aromatic sulphur compounds in extractive desulphurisation has been reported in recent research studies [72–79]. In this work, four benzyl-based IL were synthesized and used for deep desulphurisation of model oil and real diesel fuel. The removal efficiencies of benzothiophene (BT) and dibenzothiophene (DBT) with [Bzmim][NTf2] and

[Bzmim][SCN] as extractants are higher than that with [Bzmp][NTf2] and [Bzmp][SCN] as extractants. The desulphurisation capability follows the Nernst's law. A reactive extraction mathematical model for desulphurisation was established. An oxidative-extractive two-step deep desulphurisation method was developed. DBT was first oxidized by H_2O_2 with CH_3COOH as catalyst and then the unoxidised DBT and uncrystallised dibenzothiophene sulphoxide (DBTO2) in model oil were extracted by [Bzmim][NTf2], and finally the removal efficiency was 98.4 % after one-stage extraction. Besides, the removal efficiency of 4,6-DMDBT was 96.4 % after oxidation and one-stage extraction processes. Moreover, the oxidative-extractive two-step deep desulphurisation method was also effective for desulphurisation of diesel fuel. The removal efficiency of sulphur reached up to 96 % after oxidation and three-stage cross-current extraction processes [80].

EXTRACTION OF NAPHTHENIC ACIDS FROM LIQUID HYDROCARBON USING IMIDAZOLIUM IONIC LIQUIDS

Naphthenic acids are a term generally used in petroleum industry to refer to a collection of carboxylic acids with empirical formula of $C_nH_{2n} + zO_2$ [81]. These compounds exist naturally in crude oil right from the reservoir. The crude oil with acid contents of more than 0.5 mg KOH/g is considered to be a high acid crude oil by the industry [82]. The total acid content in crude oil is determined according to ASTM 664 method and is expressed in mg of KOH required to neutralize 1 g of oil [83]. Currently, most of the oil producing countries is beginning to produce heavy crude oil with high contents of naphthenic acids. Therefore, a simple method for the effective removal of naphthenic acids is desirable. The problems associated with the presence of naphthenic acids in the crude oil can be avoided by a number of approaches, such as neutralisation, solvent extraction, adsorption, thermal decomposition, catalytic decarboxylation, and esterification. The most common and cost-effective method for isolation of naphthenic acids is the washing of diesel/kerosene fractions using an aqueous solution of alkali or alkaline earth metals, followed by acidification with mineral acids to recover the insoluble naphthenic acid [84]. Adsorption and solvent extraction had also been employed for acidity reduction in crude oils [85, 86]. Catalytic or non-catalytic esterification is another efficient method for the deacidification of crude oil. Decarboxylation is also successfully employed for processing of high-

acidity crude oils. Both thermal and catalytic decarboxylations are effective in removing naphthenic acid [87, 88]. All of the above methods suffer from various shortcomings. For instance, washing with alkali or alkaline earth metals will result in an incomplete removal of naphthenic acid because of its poor water solubility. In addition, the emulsion formed with higher distillate cuts is another drawback associated with caustic wash. The solvent extraction technique lacks environmental viability because of the generation of a significant amount of volatile organic solvent waste, while the adsorption technique is applicable only for low-temperature lighter distillate fractions. As for the decarboxylation process, it requires higher temperatures (>250 °C), which lead to corrosion problems. The presence of naphthenic acids in crude oil could cause severe corrosion to refineries processing units especially those operating at temperature above 230 °C [89]. Addition of corrosion inhibitor and utilisation of expensive corrosion resistant construction material for the processing unit are necessary. Lately, as the production of heavy crude oil continues to increase, these practises have become more unsuitable. In this paper, the capability of 1-*n*-butyl 3-methyl imidazolium IL with three different anions namely thiocyanate [SCN], octyl sulphate [OCS] and trifluoromethane sulphonate [OTF] are employed to extract naphthenic acids from a model liquid hydrocarbon and their efficiencies are investigated. Two types of carboxylic acids namely benzoic acid (aromatic type) and *n*-hexanoic acid (aliphatic type) are selected to represent the "model" naphthenic acids. In conclusion, the capability of three types of potential IL for extracting carboxylic acids from hydrocarbon phase has been evaluated through experimental and molecular simulation software. The 1-*n*-butyl-3-methyl imidazolium IL with anions namely octyl sulphate [OCS], trifluoromethane sulphonate [OTF] and thiocyanate [SCN] showed carboxylic acid removal up to 99 %. Based on computational molecular simulation, the capacity and selectivity of IL toward carboxylic acids were determined. The IL with [SCN] anion exhibits the highest capacity for benzoic acids and the highest selectivity for both benzoic and hexanoic acid [90].

DEEP DESULPHURISATION OF OIL REFINERY STREAMS BY EXTRACTION WITH IONIC LIQUIDS

This paper proposes the use of IL as extracting agent in liquid-liquid extraction as an alternative or supplemental technology for the desulphurisation of refinery streams. Early experiments on the

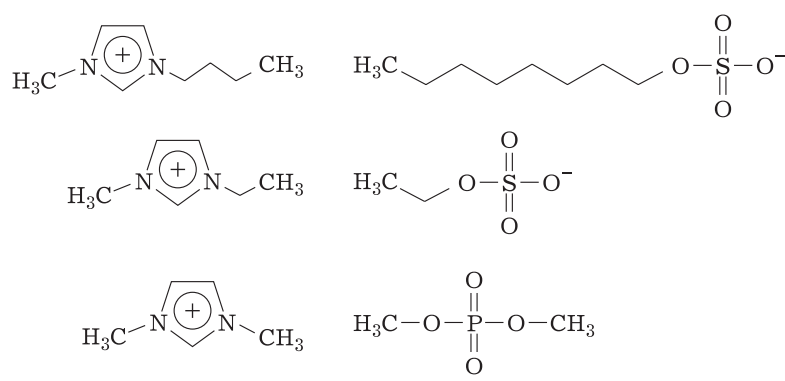


Fig. 3. Halogen-free ionic liquid suitable for extractive desulphurisation.

selective extraction of S-compounds from model diesel oil (mixture of *n*-dodecane with DBT derivatives) using chloroaluminate IL like [BMIM][AlCl₄] showed promising results [91, 92].

Nevertheless, the use of chlorometallate IL is not desired for technical large-scale applications due to their very limited hydrolysis stability and in some cases toxicity. Further screening experiments showed that tetrafluoroborate or hexafluoro phosphates IL are also suitable for the extraction of model sulphur compounds. Although IL of this type are significantly more hydrolysis stable, their use as a large scale extracting agent is not optimal because of the relatively high price of the starting material. Additionally the formation of hydrolysis products – especially HF – is observed at elevated temperatures and in the presence of water. To avoid these stability and

corrosion problems the present work concentrated on completely halogen-free IL for the extraction of S- and N-compounds. Very promising IL are 1-*n*-butyl-3-methylimidazolium octyl sulphate ([BMIM][OcSO₄]), 1-ethyl-3-methylimidazolium ethyl sulphate [EMIM][EtSO₄], and 1,3-dimethylimidazolium dimethyl phosphate ([MMIM][Me₂PO₄]) (Fig. 3). The available data suggest that the use of IL as an extracting agent for sulphur and nitrogen compounds from various refinery streams following the basic concept shown in Fig. 4 is feasible [93].

On the basis of the carried out studies, oxidation of sulphur compounds in the content of synthetic petroleum has been studied in petroleum- and petroleum-refined products, the model mixtures presenting different motor fuels in the presence of different catalysts – transition metal

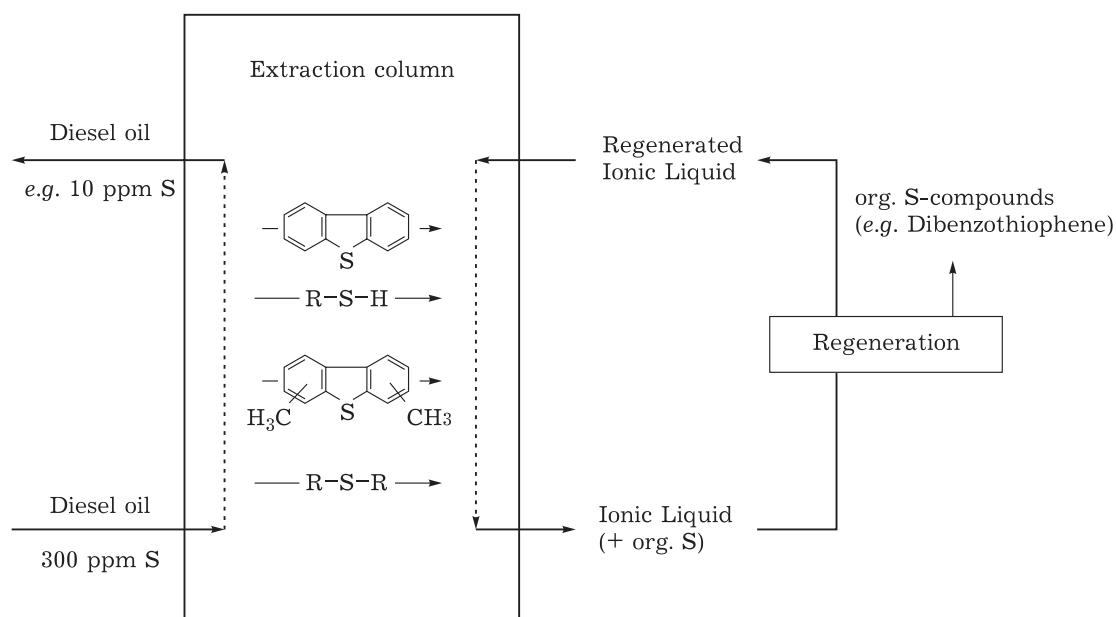


Fig. 4. Concept of deep desulphurisation of refinery streams by extraction with ionic liquids.

salts, mineral and organic acids, chiral IL and an efficient method has been suggested for removing of sulphoxides and sulphones [94].

SELECTIVE TREATMENT OF THE AZERBAIJAN'S CRUDE OIL FRACTIONS BY IONIC LIQUIDS

In this aspect, systematic researches have been carried out in the Y. H. Mammadaliyev Institute of Petrochemical Processes of the Azerbaijan National Academy of Sciences about treatment process of different types of Azerbaijan's crude oil fractions by extraction method with using the ionic liquid components as a selective solvent. Based on the results of experiments found that the using of the IL, which are synthesized on basis of formic and acetic acid, in the selective treatment process of diesel distillates, catalytic cracking gasoline, various oily distillates, transformer oil distillates, *etc.* was economically and ecologically efficiently [95–109].

It has been shown possible to achieve the complete treatment of aromatic hydrocarbon and 114–130 ppm sulphur containing European standards diesel fuel by using carboxylic acid and aniline or morpholine, acetic acid and N-methylpyrrolidone based synthesised IL as an extractant [95–97].

It is possible to reduce the total sulphur content to 30 ppm, the mercaptans to 7–8 ppm, and the aromatic hydrocarbons to 14 % of catalytic cracking and reforming gasoline by use of these IL as an extractant. The gasoline octane number is determined as 78–80 points by motor method [98–100].

The oil distillate (18 mm²/s at 100 °C) was obtained by using IL, which are synthesised on the basis of aniline and formic acid, from mixture of the Baku crude oil with low content of paraffin. The production condition of base oil (7.6 mm²/s, viscosity index: 78), which was taken from mentioned oil distillate with high output (94 %), has been determined [101, 103–105].

The results show that the application of IL which were used for oil distillates with viscosity 6.5 and 8.5 mm²/s at 100 °C, transformer oil distillates and selective treatment of Naftalan crude oil, was ecologically and economically feasible. The base oil was obtained with high purity (87.6 %), viscosity index is 8.5 mm²/s and the freezing temperature –2 °C by IL which were synthesised on basis of the morpholine and formic acid [102, 103, 108].

Ionic liquid synthesized based on formic or acetic acid and N-methylpyrrolidone were found to be perspective as a selective solvent in the process of cleaning oil-based distillates from the Ba-

lakhani and Neft Dashlari crude oil fields and meet TU 0253-021-46693103–2006; the acquisition conditions for hydraulic fluid named AMQ-10 were determined [106, 107]. It has been shown that the method of IL extraction is more economical and ecologically cost effective compared to the acidic contact method, which is 1.3 times lower.

A treatment method has been developed that provides higher degree of refining (88.5 mass %) characterized by more ecologically harmless and high-quality indicators than the current acid contact method of the transformer oil distillate using the Ion Liquid Extraction process. The regeneration condition of the ionic liquid extracting was determined and reusing with same effect was detected [100, 109, 110].

CONCLUSION

The focus of this research was to investigate main ionic liquids which are used as extractants in selective treatment processes of crude oil fractions and petrochemical products. The ionic liquids were found to be effective in the extraction of sulphur, nitrogen, naphthalene, dibenzothiophene and thiophene in model and real fuels at low temperature and pressure in comparison with traditional treating methods. Especially, the selective treatment of Azerbaijan's crude oil fractions by carboxylic acid and aniline or morpholine, acetic acid and N-methylpyrrolidone, formic and acetic acid based synthesized ionic liquids were found economically and ecological feasible. Comparison between the existing treatment methods and novel ionic liquids shows that ionic liquids will be green technology for treatment of the refinery and petrochemical streams in industrial level in the near future.

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