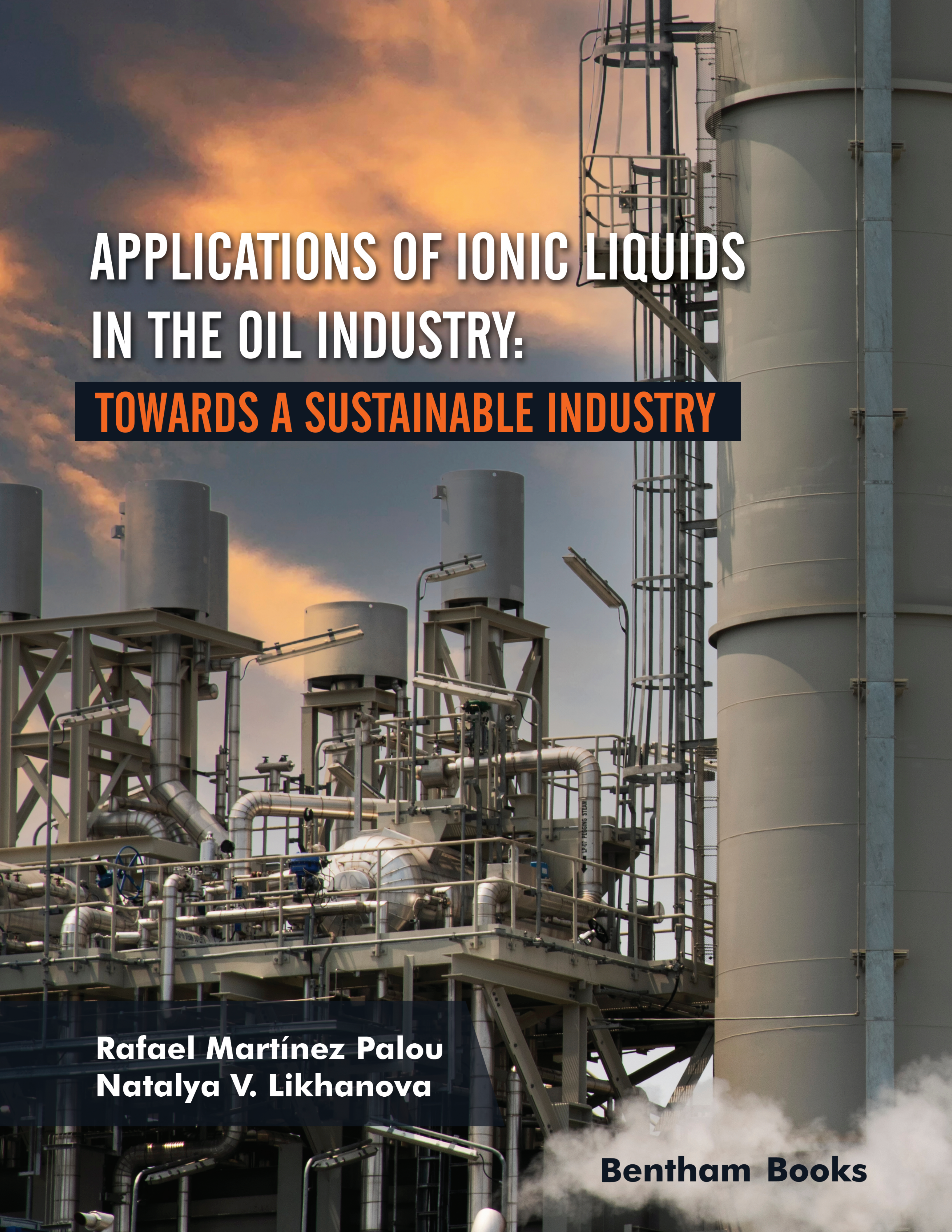

APPLICATIONS OF IONIC LIQUIDS IN THE OIL INDUSTRY:

TOWARDS A SUSTAINABLE INDUSTRY

Rafael Martínez Palou
Natalya V. Likhanova

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Applications of Ionic Liquids in the Oil Industry: Towards A Sustainable Industry

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Towards A Sustainable Industry

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FOREWORD

Ionic liquids represented a real revolution in Chemical Sciences in recent decades. They have attracted enormous research efforts due to their unique properties, with the potential to replace a range of small- and large-scale processes in which technological processes present severe problems of efficiency, high toxicity, and sustainability.

The Oil Industry has not been an exception, significant advances have been made in the last two decades in new alternatives to solve technical problems with the use of ionic liquids. In fact, the alkylation process for high-quality gasoline production is one of the remarkable industrial success stories that have demonstrated that ILs (Chapter 9 of this book) have the potential to solve safety, environmental and processing issues present in oil refineries.

The Mexican Petroleum Institute (IMP), which I had the opportunity to visit a few years ago, is a research center that has devoted relevant efforts to solving technological problems in the oil industry, being the leading institution in its country in the number of patents granted and their applications. Over the years, IMP has dedicated important resources to improve the technological processes of Petróleos Mexicanos with the use of ILs as the reader will learn through this book that can be a source of inspiration and consultation for students, academics, and researchers in the area.

With very best wishes for an enjoyable and fruitful reading.

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PREFACE

Ionic liquids (ILs) are ionic organic compounds, which unlike inorganic ionic compounds (salts), present, in general, very low melting points (below 100°C by and large) and in other cases, they are liquid at ambient temperature with negligible vapor pressure (non-volatile like common organic solvents), slight corrosive nature, low flammability and high chemical stability. These and other properties have positioned such compounds as “environmentally friendly” and drawn the researchers’ attention, exploring a number of applications in different chemistry fields like that of the oil industry.

In the present compendium, some of the works published by the Mexican Petroleum Institute (In Spanish: Instituto Mexicano del Petróleo, IMP) are reviewed. The IMP is a public institution that has been devoted to carry out research projects aimed at providing solutions to the Mexican Oil Industry since 1965, the year when it was founded, and the synthesis and field application of ILs for dealing with the technical challenges faced by such national industry represent some of the current works developed at this research center. General aspects and recent bibliography of different topics are reviewed; in addition, IMP contributions by means of scientific papers and granted patents on ILs synthesized and used to solve technological problems found in the Mexican oil reservoirs are discussed. In this context, the removal of solid, liquid, and gaseous pollutants and the breaking of emulsions that are formed naturally between crude oil and water, which increases the oil viscosity and makes the transport of heavy and extra heavy crude oil difficult, are drawbacks that can be attacked by employing chemical compounds to control water in mature fields. ILs can be used to inhibit corrosion (corrosion inhibitors, CIs), as inhibitors of the formation of methane hydrates in deepwater wells, and as catalysts to obtain alkylate gasoline by the reaction between isobutane and butene.

This book is addressed to passionate organic chemistry researchers interested in the wide universe of ILs and more specifically to experts in research works focused on the synthesis and use of chemical compounds to support and help the Oil Industry be safer and more sustainable.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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CHAPTER 1

Structure, Properties and Applications of Ionic Liquids

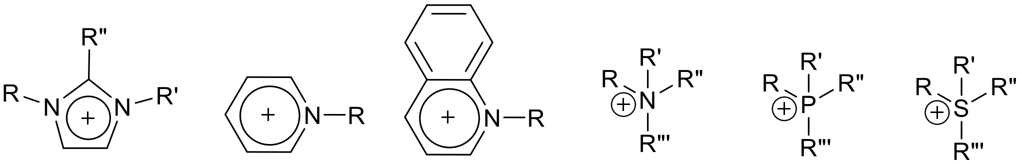
Abstract: ILs have attracted the attention of researchers in recent decades. The number of applications in which these unusual compounds show good performance has grown dramatically in the last century. This chapter presents an overview of ionic liquids, their structure, properties and general applications that have made them one of the families of chemicals to which most research efforts have been devoted.

Keywords: Applications, Catalysis, Dissolution, Electrochemistry, Energy storage, Extraction, Ionic liquids, Properties, Polymerization reactions, Solvent, Synthesis, Separations, Synthesis of nanomaterials.

INTRODUCTION

Over the last two decades, ILs have strongly drawn the attention of the scientific community due to their interesting physical properties [1, 2] and applications as solvents with exceptional properties in organic synthesis [3 - 6], catalysis [7 - 10], biocatalysis [11 - 13], liquid-liquid separations [14], extraction [15 - 19], dissolution, [20-23] synthesis of nanomaterials [24], polymerization reactions [25, 26], electrochemistry [27, 28], and energy storage [29].

ILs are ionic compounds in which at least the cation is of organic type and have the particularity of being liquid compounds at ambient temperature or close to it (< 100°C), which makes them different from other ionic compounds or molten salts that display very high melting points (> 800°C). Fig. (**1.1**) shows the general structure of the most common cations present in ILs.



1 2 3 4 5 6

Fig. (1.1). Some typical IL cations. R, R', R", R"' represent alkyl, benzylic or alkyl-functionalized chains.

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The cations can be of the heterocyclic type, derived from imidazole (**1**), pyridine (**2**) or quinoline (**3**) or aliphatic compounds such as quaternary compounds derived from amines (**4**), phosphorous (**5**) or sulfur (**6**) compounds. ILs have the special feature of displaying a heteroatom (nitrogen, phosphorous or sulfur) with a positive charge or electron deficiency, which in the case of aromatic derivatives, are delocalized through the ring.

In the case of anions, they can be inorganic or organic and their type affects significantly the physicochemical properties of the ILs [30].

Some of the most common ions found in ILs are as follows: Cl^-, Br^-, $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[AlCl_4]^-$, $[FeCl_4]^-$, $[AuCl_4]^-$, $[InCl_4]^-$, $[NO_3]^-$, $[NO_2]^-$, $[SO_4]^-$, $[SCN]^-$, $[AcO]^-$, $[N(OTf)_2]^-$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$, $[PhCOO]^-$, $[C(CN)_2]^-$, $[RSO_4]^-$ and $[OTs]^-$.

The possible combinations between cations with different chain types (R) and anions allow the generation of more than 2 million of ILs with diverse physical and chemical properties [31]; some of the characteristics that make ILs so attractive in different chemical areas are the following:

Negligible vapor pressure. For this reason, ILs are considered as environmentally friendly solvents and exceptional substituents of common organic solvents, which in most cases are volatile, toxic and handled in high volumes in industrial processes.

Not flammable. This property makes them safe to be handled.

Excellent catalyst properties. The catalytic properties of these compounds are exceptional and the number of examples featuring processes where ILs have worked as catalysts is increasing exponentially in the scientific literature.

High ionic conductivity. The structure of both the cation and anion considerably We agree with the proposed change the ionic conductivity of ILs, which in general is very high.

Wide electrochemical potential window. Thanks to this feature, numberless applications in electrochemical processes are possible.

Broad thermal stability interval. For the same organic cation, the thermal stability can vary within a more or less wide interval; for this reason, these ions can be employed in processes that take place at relatively high temperatures (between 200 and 400 °C).

Variable dissolving properties. Wide range variability of the properties to dissolve organic compounds or to be dissolved in common organic solvents. The structure of both the cation and anion affects considerably the solvent properties of ILs.

Easily recyclable. ILs can be purified and reused for various cycles for many applications without altering significantly their properties or activity. The regeneration process is generally carried out by washing with conventional organic solvents and subsequent vacuum drying.

Synthesis of ILs

In general, ILs are synthesized by means of nucleophilic substitution reactions through which an alkyl halide reacts with a heteroatom in a heterocyclic or aliphatic compound, where the free electron pair from such heteroatom is involved in the formation of a new heteroatom-carbon bond, thus generating electron deficiency in the heteroatom in question.

The classical synthesis methodology of ILs occurs through the alkylation of a heteroatom with short-chain alkyl halides; for this reason, in general, at the first synthesis stage, the ILs present a halide as anion. At the second stage, the anion can be exchanged or modified through either a metathesis or acid-base reaction.

The cation in the ILs can be symmetric or asymmetric. In the case of the symmetric ILs, the reaction includes a previous stage at which the heteroatom-hydrogen bond is broken through the treatment of the heterocycles with a strong base (sodium hydride, NaH, in most cases).

The synthesis requires heating conditions under reflux with or without the presence of a solvent. The reaction time will depend mainly on the reactivity of the alkyl halides, and according to them, the reaction time can be from 24 to 72 h.

Since ILs are not volatile (practically negligible vapor pressure), purification cannot be carried out by distillation and, in general, it is performed through washings employing organic solvents capable of eliminating soluble impurities without dissolving the IL.

The preparation methods of ILs by conventional heating require many reflux hours in organic solvents, however, in the last years, synthesis methodologies using microwaves, with which both alkylation and metathesis reactions are accelerated dramatically, have been described. The microwave synthesis methodology of ILs became very popular due to the high product yields in a few reaction minutes [32]. Likewise, ILs have been a very useful auxiliary tool for microwave organic synthesis [31, 33].

CHAPTER 2

Application of ILs in the Removal of Pollutants Present in Gasoline and Diesel

Abstract: This chapter presents an overview of ionic liquids application for the removal of some pollutants such as sulfur, nitrogen and others that are present in considerable concentrations in fuels such as gasoline and diesel and which must be removed because they cause major environmental problems, and which can be extracted by different liquid-liquid extraction procedures using ILs.

Keywords: Ionic liquids, Pollutants, Gasoline, Diesel, Liquid-liquid extraction, Sulfur, Nitrogen, Fluoride.

INTRODUCTION

Oil consists mainly of hydrocarbons that present high combustion efficiency; however, it is inevitably accompanied by other organic and inorganic compounds such as water, sulfur, nitrogen, oxygenated and halogenated organic compounds, resins, inorganic salts and carbon dioxide, among others. Most of these compounds can be highly pollutant to the environment and additionally, some of them diminish the combustible properties of hydrocarbons. Through the refining process of crude oil, it is possible to separate partially some contaminants and in turn, new pollutants such as those known as greenhouse effect gases, which are the main promoters of acid rain, are produced; for this reason, these compounds should be separated as exhaustively as possible from the oil derivatives generated during the refining process [1].

The sulfur content varies according to the origin of crude oil and since that many sulfur compounds vaporize within the same boiling interval of the primary product, these compounds are present too, polluting them (Table **2.1**) [2, 3].

At the industrial level, the removal of sulfur compounds is carried out by a hydrotreatment process called Hydrodesulfurization (HDS) [4, 5]. Around 40% of the total gasoline mixture comes from either atmospheric residues or vacuum distillates that produce FCC gasoline, which contributes to 85-95% of the sulfur content and olefins in the FCC effluents (Fig. **2.1**) [6 - 10].

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Table 2.1. Some of the pollutants present in the different oil fractions.

Fraction	Main Pollutants
Gasoline: Naphtha, Naphtha for Fluid Catalytic Cracking (FCC).	Mercaptans (R-S-H), Sulfides and Disulfides (R-S-S-R).
Jet Fuel: Heavy naphtha, middle distillate.	Benzothiophene and its alkyl derivatives.
Diesel: middle distillate, light cycle oil (LCO).	Alkyl benzothiophenes, dibenzothiophenes and its alkyl derivatives.

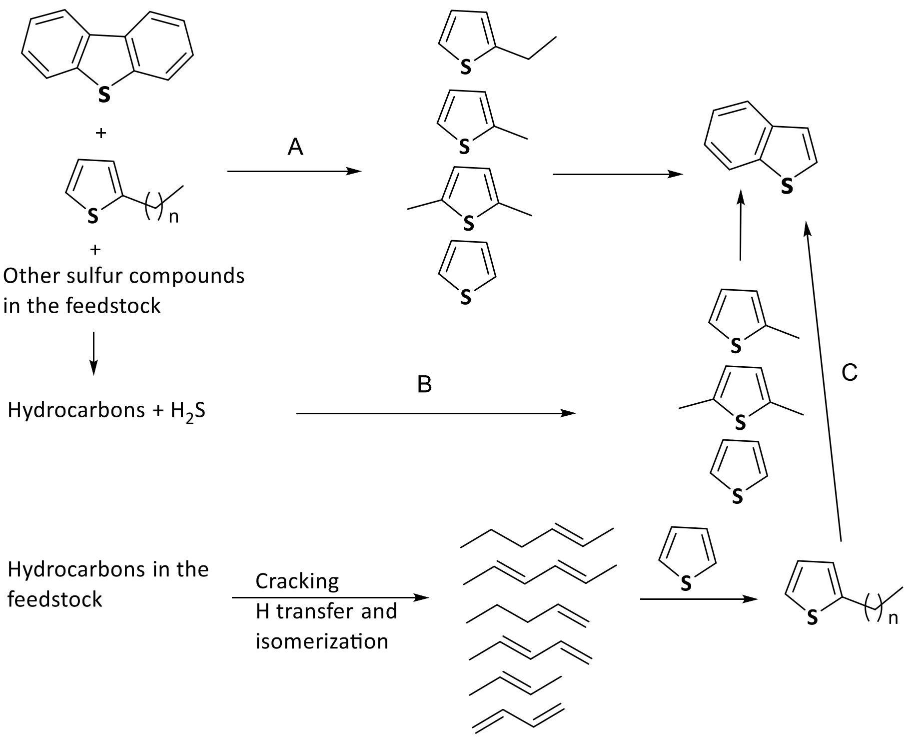

Fig. (2.1). Schematic representation of the formation and recombination of sulfur compounds through the FCC process: (A) transformation of heavy sulfur compounds in the feedstock, (B) reaction between H_2S (produced by the desulfurization of feedstock impurities) and olefins or diolefins resulting from the catalytic cracking of the feedstock, and (C) cyclization of alkylthiophenes formed during the process.

The FCC of gasoline promotes the direct combination and transformation of sulfur compounds present in the feedstock, producing many impurities [11].

Not all sulfur compounds can be eliminated through conventional techniques, and for this reason, they have to be submitted to more severe treatments. Thiophenic compounds, especially the 4,6-dialkyl-substituted compounds are difficult to be transformed into H_2S due to their chemical stability and steric hindrance of the interaction between the sulfur atom in their structure and the catalyst surface [12].

The oil refining industry must adapt itself to the environmental legislation and engine design changes, which in turn are adapted to environmental requisites. The necessity of protecting both automobile parts and industrial pieces of equipment from corrosion, the commercial opening among different countries, and release of the international oil prices are factors that have increased the demand for more and better fuels from the oil refining industry [13, 14].

To reach these goals, using the current HDS technology, higher temperatures, pressure, more efficient reactors, and more active catalysts are needed, which implies an important increase in the process cost [15].

Environmental Problems Due to the Presence of Sulfur Compounds in Fuels

The main source of atmospheric pollution is the use of fossil fuels as energy suppliers. Huge amounts of oil, gas and coal are, in the order of millions of tons, consumed every day, and the combustion residues are expelled into the atmosphere as solid particles, smoke and gases that trigger problems such as acid rain. Some studies have stated that automotive vehicles contribute to more than 90% of emissions, and for this reason, many environmental strategies are aimed at this sector.

The main pollutants associated with combustion are particles, SO_x, NO_x, CO_2, CO and hydrocarbons; in general, the industry is responsible for 55% of the sulfur dioxide (SO_2) emissions and the rest of the contribution is due fundamentally to transport [16].

Combustion gases from oil derived fuels play a major role in both acid rain, planet heating (global warming) and in the increase of the tropospheric ozone and carbon monoxide levels, which are highly toxic for human beings [17].

The main components of acid rain are formed from primary pollutants such as sulfur dioxide and nitrogen oxides through the reactions presented in Fig. (**2.2**).

The primary pollutants emitted by combustion (reaction (1), (2) and (3) suffer additional oxidation and the products can react easily with atmospheric humidity (4) and (5) and remain dissociated as part of the fog, snow, or rain, thus producing acid rain or fog.

CHAPTER 3

Application of Ionic Liquids in CO_2 Capture

Abstract: The oil industry is the industry that generates the most carbon dioxide (CO_2) worldwide, therefore the development of alternatives for the capture, use and transformation of CO_2 into products of greater added value is of great interest. This chapter presents an overview of ionic liquids application for CO_2 capture.

Keywords: Ionic liquids, CO_2, Environmental pollution, Absorption, Adsorption, Epoxides, Carbamates.

INTRODUCTION

The CO_2 emissions from the use of fossil fuels are a constant worry worldwide, for their concentration increase in the atmosphere is strictly related to the growing world energy demand and at the same time, it is one of the greenhouse effect gases with a higher impact on global warming and climatic change [1]. Although the development of new energy sources with low emissions of contaminants has to be a long-term goal in our societies, in the near future, the development of efficient technologies for the capture, storage and recycling of CO_2 is probably the only available strategy for controlling the CO_2 levels emitted into the atmosphere. On the other hand, oil refining is one of the industries that produce the highest CO_2 emissions and for this reason, the IMP is very interested in the research works on this topic.

The use of diverse technologies to capture, store and transform CO_2 could provide a mid-term solution to mitigate the environmental impact and allow the human society to keep on using fossil fuels as energy sources at least until renewable energy technologies become ready for their large-scale application [2].

From the Industrial Revolution, the atmospheric concentration of CO_2 has increased by approximately 35% of its original concentration, reaching a level above 400 ppm; for this reason, it has been considered one of the main climatic change factors and then, it is imperative that the atmospheric emissions be reduced, being one of the topics to which researchers have paid more attention in the current century.

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The oil industry is one of the main sectors contributing to the generation of CO_2 and its capture and separation from other gases such as hydrogen and methane are vital. Until now, the development of efficient, economical and environmentally friendly technologies for separating these gases continues being one of the most important challenges faced by this industry.

The CO_2 capture technologies are commonly classified according to the process point where they are applied. Any technological planning involving the application of any of these alternatives will involve an increase in the energy demand of the process, given the energy required for CO_2 separation. Fig. (**3.1**) shows the schematic representation of different alternatives: pre-combustion, post-combustion and oxy-combustion [3].

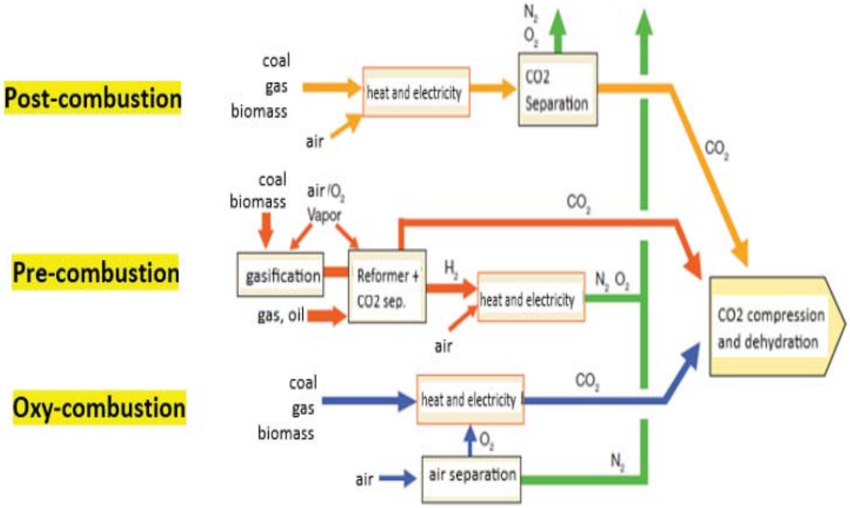

Fig. (3.1). Processes and CO_2 capture at different stages.

The post-combustion CO_2 capture technologies separate CO_2 from the gas current at the outlet of the conventional combustion process of fossil fuel. These technologies are located downstream in the process and keep on with the traditional installation of gas depuration equipment for a given pollutant, CO_2 in this case. Most industrial processes that require fossil fuels use air as a carburant; then, this technology can be applied directly without provoking alterations of the very process, which offers high flexibility and adaptation capacity to the installation operative conditions [4].

These systems start from a current with very low CO_2 concentration and a huge flow of combustion gases. Such characteristics in these systems require a large energy amount, which becomes evident in the high investment and operation costs of the currently developed technologies [5]. Fig. (**3.2**) shows the different available alternatives for the application of the post-combustion CO_2 capture technology [6].

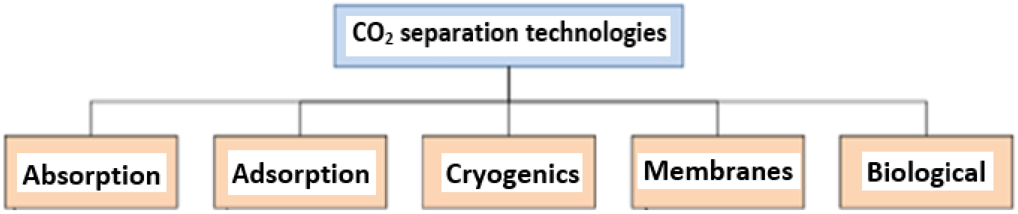

Fig. (3.2). Main CO_2 capture technologies.

In general, the methods to remove CO_2 from gaseous effluents have to comply with the following characteristics: high absorption capacity, fast kinetics, capability of being regenerated and stable through time within a wide operation range [7].

Despite all the efforts, there is not a scaled CO_2 capture procedure yet that could be economically viable, complying with all the previously described requisites; for this reason, many government programs with important investment have been promoted to attend this problem that continues to be a very active research topic.

CO_2 Capture with ILs

The CO_2 capture mechanisms depend on the chemical structure of the employed materials and their properties. In this context, ILs are among the most promising chemical products. These liquids can ease the CO_2 capture without losing solvent in the gas current. ILs have low toxicity and volatility and can be designed with the right properties for efficient CO_2 capture. The evident interest in using ILs for this purpose is confirmed by the increasing number of scientific reports in this area (Fig. **3.3**).

In the last years, multiple studies have been carried out to explore the perspectives of ILs to be applied in the separation of gases. In the case of ILs for capturing CO_2, the search has been focused on not-supported ILs [8 - 19], and on ILs supported on membranes (SILMs) [20 - 30].

CHAPTER 4

Application of ILs in the Breaking of Emulsions Found in the Oil Industry

Abstract: Emulsions are commonly found in oil and cause major operational problems, so emulsion breakage is a major issue in this industry. Among the alternatives for breaking emulsions is the use of de-emulsifying products and among them, some ILs with amphiphilic properties have gained an important place by demonstrating a very good efficiency as emulsion breakers in combination with other methods such as heating.

Keywords: Amphiphilic, Demulsifiers, Emulsions, Ionic liquids, Microwave, O/W, W/O.

INTRODUCTION

Emulsions are of great importance in the oil industry, for naturally, oil is found as an emulsion. Due to the presence of congenital water in oil wells, natural crude oil emulsifiers and temperature and pressure conditions, the formation of simple and complex emulsions is favored; the most common emulsion is the one where oil is the continuous phase with emulsified water drops within. The emulsion is the result of the coproduction of water in the oil reservoir.

An emulsion is a lyophobic colloid (a solution that cannot be formed by spontaneous dispersion) and has a dimension close to 1000 nm. When a system consisting of surfactant, water and oil is stirred, one of the liquid phases is dispersed as drops (with diameters from 1 to 100 µm), thus producing an emulsion [1]. The aim of employing surfactants is, on the one hand, to ease the extension of the interface during the emulsion formation process, and on the other hand, to stabilize the emulsion by retarding the coalescence of the dispersed phase drops.

Emulsions are stabilized by the presence of an emulsifying agent, which is normally an amphipathic species that forms a surface film on the interface between each colloidal drop and the dispersion medium, thus reducing the interfacial tension and preventing coagulation.

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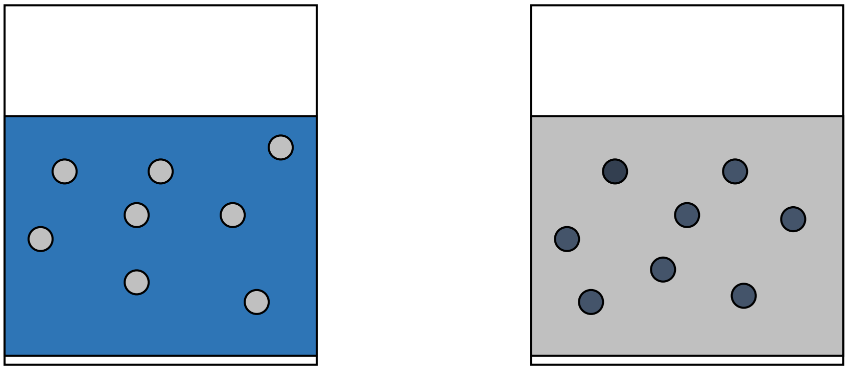
There are three essential requisites for an emulsion to be formed [2];

- Two immiscible liquids like water and oil.
- Enough stirring to disperse one of the liquids as droplets within the other liquid.
- An emulsifying agent for stabilizing the drops dispersed within the continuous phase.

In the oil industry and specialized literature, English nomenclature is used to define emulsions. The two immiscible liquids are referred to as water (W) and oil (O), either these are the very liquids or they represent the polar and nonpolar phases.

The most common emulsions are those with water drops dispersed within the oil phase and are referred to as water in oil (water / oil) emulsions and less common are those known as inverse emulsions, where oil is the dispersed phase and are referred to as oil in water (oil/water) emulsions (Fig. **4.1**).



W/O (Water in Oil) O/W (Oil in Water)

Fig. (4.1). Schematic representation of the two types of emulsions found in the oil industry.

W/O (Water in Oil) O/W (Oil in Water)

There are also complex emulsions, *e.g.* the dispersion of oil drops in water drops, which in turn are dispersed in a continuous oil phase (oil/water/oil; O/ W/O). The type of the formed emulsion depends on different factors.

Three main criteria are necessary for the formation of a crude oil emulsion: the contact of two immiscible liquids, a surfactant component working as an emulsifier agent and enough stirring for dispersing a liquid within the other as drops.

Some emulsions are separated in their water and oil phases once removed from the sea surface whereas the most stable emulsions can last for days and even years. Stability is a consequence of the small drop size and the presence of an interfacial film of emulsion drops that make stable dispersions [3].

On the other hand, colloidal species can be gathered in different ways and three processes are considered to reach stability:

1. Creaming: This phenomenon is the opposite to sedimentation and is the result of the formation of a kind of cream with different density between the two liquid phases, which creates a concentration gradient of drops, two or more drops are grouped, being in contact in just certain points and practically without a change on the total surface. Creaming is generally considered undesirable, as it makes storing and manipulation difficult, but it can be useful in special cases, mainly when an emulsion is to be concentrated. As it has been already stated, the migration process is referred to as creaming as long as the substance particles remain separated. This is what establishes the ideal difference between flocculation (where the particles are grouped) and emulsion breaking (where the particles get together).

2. Aggregation: It occurs when drops are very close for a long time without attraction forces acting on them. The species preserve their identity, but lose their kinetic independence. The segregation of droplets can lead to fusion and formation of bigger drops until the phase is separated.

3. Coalescence: Two or more drops get together to form a bigger unit with total surface reduction. The coalescence mechanism occurs through two stages: film drainage and film breaking.

These and other aspects related to the emulsion theory in the oil industry are discussed in Chapter 11 of the book ‘Ionic liquids as Surfactants. Applications as demulsifiers of petroleum emulsions by Rafael Martínez-Palou and Jorge Aburto, in the book: Ionic Liquids, Current State of the Art. Intech. 2015, p. 305-326 [4].

Different studies have demonstrated that the physicochemical action mechanism of dehydrating or demulsifying agents is associated with the optimal formulation of the system (SAD = 0, where SAD stands for Surfactant Affinity Difference) [5].

The optimal formulation is defined basically as an equilibrium state between the surfactant affinities to aqueous and oil phases. The effects exerted by the different formulation variables (salinity, ACN, EON, WOR and temperature, among

CHAPTER 5

Application of ILs in the Transport of Heavy and Extra-heavy Crude Oils

Abstract: In the oil industry, in general, and in Mexico, in particular, the use of heavy crudes in the refining process has increased considerably. The processing of these heavy crudes implies an important technological challenge, and their transportation can sometimes be complicated. Among the alternatives for transporting this type of crude is the formation of invert emulsions in which ILs can play an important role, which is discussed in this chapter.

Keywords: Ionic liquids, Heavy-oil, Extra heavy-oil, Asphaltenes, Resins, API, Viscosity, Demulsifiers, Surfactants.

INTRODUCTION

Currently, most crude oil extracted from wells in Mexico, and in many other countries, is heavy oil (density equal to or below 20 ° API). The complex composition of these crude oils makes them difficult and expensive to be produced and transported through pipelines due to their low mobility and flow capacity, which are the result of high viscosity and specific gravity [1].

Heavy oil has been defined as oil with API gravity below 20°, which means that its relative density is above 0.933. It is any type of crude oil that does not flow easily. Density is usually defined in terms of API degrees (American Petroleum Institute) and is related to the specific gravity, the denser the oil, the lower the API density. The API densities of the liquid hydrocarbon range from 4° for bitumen rich in pitch up to 70° for condensates [2].

In general, heavy oil has attracted less attention as an energy resource due to the difficulties and costs associated with its production. It has been stated that there are more than 6 trillion barrels [1 trillion m^3] of oil in place (OIP) attributed to the heaviest hydrocarbons, equivalent to triple of the combined conventional oil and gas reserves in the world, thus deserving more careful attention [3].

Natural heavy crude oils display a wide density and viscosity spectrum. The viscosity at reservoir temperature is in general the most important measurement

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for a hydrocarbon producer because it determines how easily oil will flow. Density is more important for oil refining, for it is a better indicator of the distillation derivatives. Unfortunately, there is not a clear correlation between both parameters. Intermediate or low-density crude oil with high paraffin content in a cold and shallow reservoir can have a higher viscosity than heavy crude oil, free of paraffin in a deep reservoir with high temperature. The production, transport and refining of heavy crude oil present special problems in comparison with light crude oil [4].

The physical properties that distinguish the heavy crude oils from the light ones include higher viscosity and density and the molecular weight comparison. Extra-heavy crude oil can even display viscosities above 10.000 centipoise (10 Pa·s) and 10° in the API index.

The oil density varies scarcely with temperature and for this reason, it has become the most used standard parameter in the oil industry to classify crude oils. Table **5.1** shows the classification of crude oils according to their densities.

Table 5.1. Classification of oils according to their API densities.

Crude Oil	Density (°API)
Extra-heavy	<10.0
Heavy	10.0 – 22.3
Intermediate	22.4 – 31.1
Light	31.2 – 39
Superlight	> 39.0

The reduction of the mobility rate is the main goal of the non-thermal recovery methods either by diminishing the oil viscosity or by increasing the viscosity of the displacing fluid.

The viscosity of fuels is correlated with the material average molecular weight, and it provokes frequently plugging problems both during oil extraction and transport. Examples of this are the Mexican crude oils “Maya” and “Ku-Maalob”, which present compact asphaltenic aggregations whose values range in the interval from 6000 to 50,000 cp whereas the density is found between 22 and 8° API. An additional disadvantage is that the reservoir is far from the refinery and for this reason, a treatment enabling the crude flow through the country pipeline system is needed. The proposed solutions for transporting heavy and extra-heavy crude oil have been focused on the reduction of pressure drops in the transport systems originated by the increase in the fluid viscosity and friction generated between the fluid and pipe.

The high gravity of the crudes is generally due to the presence of bulky and complex molecules with high aromaticity such as asphaltenes and resins [5].

Asphaltenes are polyaromatic and polycyclic molecules that have heteroatoms and metals and represent the non-volatile-polar fraction of oil that is insoluble in *n*-alkanes. Asphaltenes appear surrounded and stabilized by resins and it is known that they have an electric charge and form aggregates by supramolecular attraction among them and tend to precipitate due to pressure, temperature and oil composition changes, which generate the plugging of pipelines and evident increase in the oil's viscosity [6 - 9].

When isolated, asphaltenes are dark brown to black molecules; they form amorphous powder with specific gravity above the unit; their average molecular weight oscillates between 750 and 10000 g/mol and do not have a defined melting point, but decompose at temperatures between 300 and 400°C or even higher [10]. The IMP has made every effort in the research of the asphaltene structures [11], which has helped importantly to elucidate them and understand the electron distribution and aromaticity, which have been explained through the rule developed by Dr. Ruiz-Morales [12 - 16].

Chemically, the asphaltene structures consist of aromatic and aliphatic polycyclic systems with the presence of naphthenic acids, heterocycles, substituted phenols and carboxylic acids and contain metals such as nickel, vanadium and iron. The asphaltene structures are not well defined, but several possible structures have been proposed to explain the composition and properties of the asphaltene fraction. A hypothetical structure of the asphaltenes is shown in Fig. (**5.1**).

Resins are defined as the non-volatile-polar fraction of crude oil that is soluble in *n*-pentane, *n*-heptane~~,~~ and aromatic solvents such as toluene, but insoluble in methanol and propanol. Resins are also dark brown to black molecules and are semisolid compounds with specific gravity close to unity and their molecular weight ranges from 500 to 2000 g/mol, being highly adhesive materials. The resin content in crude oils is between 2 and 40 wt.%. The molecular species are the same as those in aromatic compounds, but in resins, they have both higher molecular weight and polarity, presence of heteroatoms and lower hydrogen-carbon rate than that of aromatic compounds. The resin fraction consists of carbon, hydrogen, oxygen, nitrogen, and naphthenic acids.

CHAPTER 6

Application of ionic liquids as Corrosion Inhibitors in the Oil Industry

Abstract: The oil industry presents corrosion problems from crude oil extraction and transportation to the refining process, making it a highly demanding industry in terms of corrosion inhibitors. This chapter reviews the concepts related to the topic of corrosion and reviews the advances in the use of ILs to mitigate corrosion in different corrosive environments typical of this industry.

Keywords: Ionic liquids, Corrosion inhibitors, Acid environment, Basic environment, Carbon steel, Copper, Bottle test, Pipelines, Electrochemical techniques, Corrosion mechanism.

INTRODUCTION

Since most pieces of equipment, pipelines, mechanical parts, etc. are made of iron alloys, specialized personnel working at different production and processing centers, where these elements are omnipresent, know that they are unavoidably susceptible to become rusty due to diverse operation and environmental conditions. Because of this constant threat, industrial and commercial performance is seriously affected, which is reflected in economic and material drawbacks. As an example of the seriousness of this situation, the Gross Domestic Product [1] of countries such as the United States of America and Great Britain has been hit with corrosion-related losses that represent 3 or 4% of it.

Unfortunately, the negative effects caused by corrosion are not only represented by those mentioned above, but also by human affections, for the integrity and sanitary conditions of employed personnel and industrial-center inhabitants are at stake. In this sense, one of the economic activities that depict the complex picture formed by all the non-positive outcomes resulting from rust is the extraction, transportation, and refining of oil [2].

Among the solutions that have been envisaged to diminish the occurrence of corrosion in industrial environments, the synthesis of chemical compounds known

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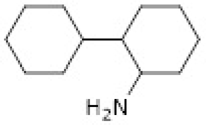
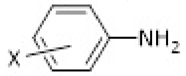
as corrosion inhibitors (CIs) is found and their application has proven to be highly effective for this purpose. Although different inorganic compounds such as metal salts, nanomaterials and lanthanides [3] display corrosion inhibition properties, organic compounds have turned out to be highly effective at the industrial level and especially in the oil industry. Some of the most common families of organic compounds studied as CIs are amides with long alkyl chains (fatty amides) [4, 5], some pyridinic compounds [6 - 8], 1,3-azoles [9 - 11], different types of polymers [12], drugs [13], and imidazolines [14 - 16], the latter being the most common inhibitors used to prevent equipment and carbon steel or copper pipes that are in contact with oil from being corroded.

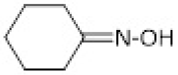
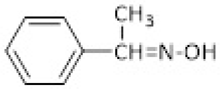
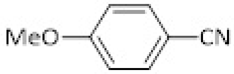
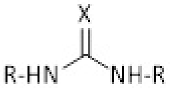
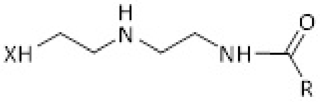
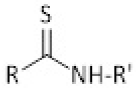
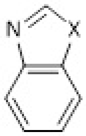
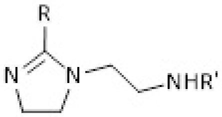
These compounds, when used in formulations in which they are added at concentrations between 50-500 ppm, can slow down considerably the corrosion process.

Table **6.1** shows characteristic structures of organic compounds that have been evaluated as CIs in the oil industry.

Table 6.1. Some families of chemical compounds employed as CIs in the Oil Industry.

Chemical Family	Chemical Structure	Applications	Refs.
Primary amines and diamines	Alkylamines (n =2-18) CH_3-$(CH_2)_n$-NH_2 Diamines (n = 2-8) H_2N-$(CH_2)_n$-NH_2	Mainly used as CIs of carbon steel and other metals in acidic media.	[17, 18]
	Cycloalkylamines 		[19]
	Aromatic amines (X = H, NO_2, CH_3, Cl, COOH) 		[20]
Secondary, tertiary and ethoxylated amines	Bencylamines  Ethoxylated amines CH_3-$(CH_2)_n$-NH-$(OCH_2CH_2)_n$	Used as CIs of carbon steel in acidic media.	[21, 22]

(Table 6.1) cont.....

Chemical Family	Chemical Structure	Applications	Refs.
Oximes	Alkylic  Arylic 	Used as CIs of carbon steel in acidic media.	[23]
Nitriles	Alkylic $R\text{-}C\equiv N$ Arylic 	Used as CIs of carbon steel and other alloys in acidic media.	[24]
Ureas and thioureas	 X= O, S, R = alkyl, aryl	Used as CIs of carbon steel and other alloys in acidic media.	[25]
Amides and thioamides	Amides  Thioamides  R, R' = alkyl	Mainly used as CIs of carbon steel in acidic media.	[26, 27]
Imidazoles	 R = akyl, aryl	As CIs of carbon steel and copper alloys in basic media.	[28]
Benzoazoles	 X = N-R, S, O	As CIs of carbon steel and copper alloys in basic media.	[29]
Imidazolines	 R = akyl, aryl; X = NH_2, NHR, OH	CIs of carbon steel in CO_2 and other acid environments.	[30]

CHAPTER 7

Ionic Liquids as Inhibitors of Hydrate Formation in Deepwater Wells

Abstract: The extraction of crude oil in deep waters represents a major technological challenge. One of the most common problems in these oil and gas extraction conditions is the formation of gas hydrates that can cause plugging and hinder the transportation of crude oil. For this reason, great efforts have been made in the development of hydrate inhibitors, among which ILs have shown to be a very promising alternative. In this chapter, the development and evaluation of ILs as hydrate inhibitors are discussed.

Keywords: Anti-agglomerant, Clusters, Deepwater, Imidazolium, Ionic liquids, Hydrate inhibitors, Long alkyl chain, Low temperature, Low toxicity, Methane, Oil, Pyridinium.

INTRODUCTION

Gas hydrates are chemical compounds formed and stabilized when a small molecule (such as methane, ethane, H_2S, CO_2, and others) is trapped inside a solid structure formed by water molecules that could agglomerate to form ice-like structures [1]. The formation of this type of hydrate is very common in deepwater oil wells, where low temperatures and pressures favor the formation of this type of cluster that generates many problems in the transport of hydrocarbons in these areas, since they plug the pipelines generating operational and safety consequences and production stoppages.

Structure of Methane Hydrates

By their structure, gas hydrates can be classified into three types [2]:

SI structure: It is a cubic structure of 12 Å, made up of 46 water molecules in which two types of "cages" stand out: pentagonal dodecahedral (512) and tetradecahedral (51262). They are most frequently found in nature and store only small gas molecules. (CH_4, C_2H_6, CO_2 y H_2S).

SII structure: It is also a cubic structure of 17.3 Å, with 136 water molecules and is made up of two types of cages: one of type 512 and one hexadecahedral

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(51264). The most common molecules it can store are nitrogen, propane, and isobutane. This structure is typically found in natural gas production.

Structure H: Less common than the previous ones, it consists of three types of cages: a 512 type, an irregular dodecahedron (435663) and an irregular icosahedron (51268). Fig. (**7.1**) shows the structure of the hydrates described above.

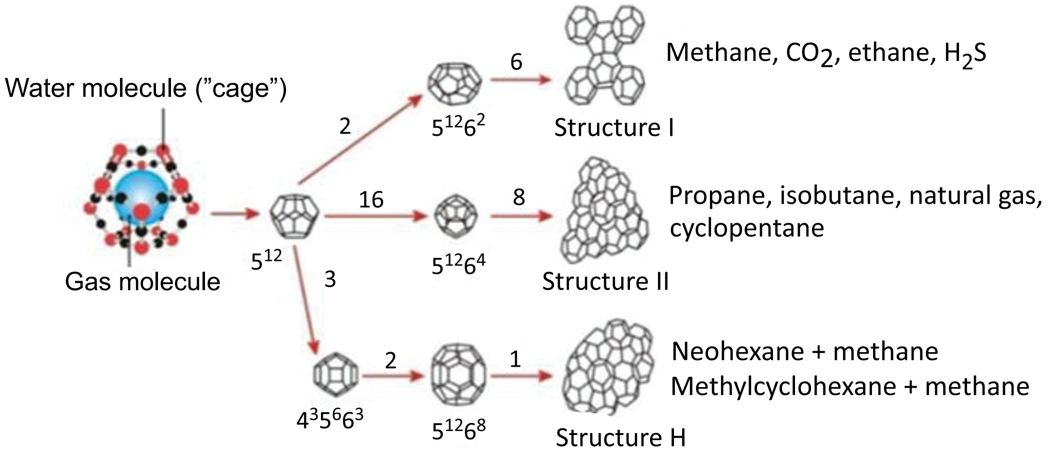

Fig. (7.1). Types of gas hydrates and their composition and structure. [Available *via* license: Creative Commons Attribution 4.0 International (https://creativecommons.org/licenses/by/4.0/)].

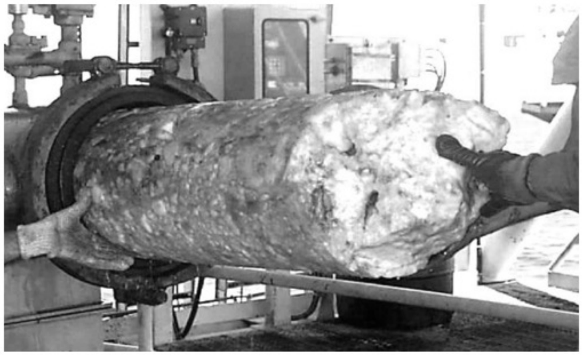

Fig. (7.2). Pipeline plugged by gas hydrates. [Available *via* license: Creative Commons Attribution 4.0 International (https://creativecommons.org/licenses/by/4.0/)].

The three types of hydrates have a structure similar to ice and when proliferating in production pipelines, they cause their plugging, significantly limiting and preventing the flow of hydrocarbons, which generates production stoppages. These blockages are favored when low temperatures (below 5 °C), high pressures, and the presence of high-velocity gases in the presence of water occur together. In the production and transport of natural gas in deep waters, this occurs at the seabed level, where these conditions are favored (Fig. **7.2**).

Different methods have been studied and applied to prevent hydrocarbon clathrate hydrate plugs, including maintaining a suitable temperature in pipelines by insulation, electrical heating, pressure reduction or water removal, but these methods are often very expensive [3].

Thermodynamic Equilibrium of Hydrate Formation

Hydrate formation is a crystallization process that takes place in two main stages: nucleation and hydrate crystal growth. Nucleation is a microscopic phenomenon and at this stage, the system reaches a metastable state in which the crystals (nuclei) agglomerate until they reach a critical size, whereupon the crystal growth stage begins [4].

A typical Pressure-Temperature thermodynamic diagram of hydrate-forming systems consists of: the hydrate envelope (HLV phase equilibrium curve), the hydrate stability region (left) and hydrate-free region (right), and the degree of system subcooling (ΔTsub). The ΔTsub is defined as the difference between the equilibrium temperature (Teq), and a temperature (Ti) in the hydrate stability region reached by the system and at which crystal growth occurs, at a given pressure (ΔTsub= Teq - Ti) (Fig. **7.3**) [5].

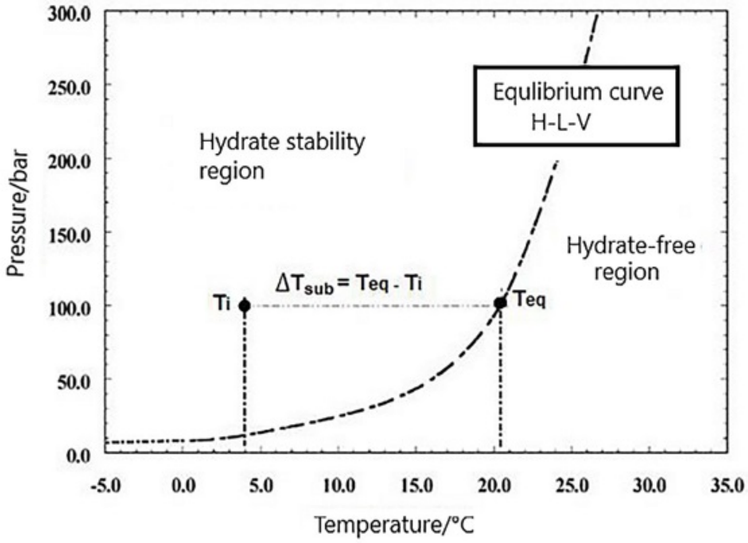

Fig. (7.3). Pressure *versus* temperature diagram typical of gas hydrate formation.

CHAPTER 8

ILs Applied to Enhance Oil Recovery Processes

Abstract: The application of chemical products, particularly polymeric products, is undoubtedly one of the most helpful and effective alternatives for EOR processes and changes in oil mobility. Appropriate chemical products provide more favorable interfacial conditions to the flow of petroleum, reducing the interfacial tensions between water and oil, and therefore, increasing the miscibility of these two compounds, and allowing the oil to flow in the porous medium. In this context, ionic compounds and particularly ILs are proving to be important auxiliaries in the performance of chemicals used for this application, particularly in extreme conditions of temperature and salinity.

Keywords: Ammonium, Anionic, Cationic, Tertiary recovery, Enhanced Oil Recovery, High salinity, Interfacial tension, Ionic liquids, Miscibility, Permeability, Switterionic, Vinylpyrrolidone, Wettability alteration.

INTRODUCTION

In the hydrocarbon market, at the international level, Mexico has diminished its participation due to the decrease in the production of fossil fuels at the national level in such a way that in 2013, the production reached 2.52 mbpd; in 2015, 2.26 mbpd; in 2017, 1.94 mbpd; in 2018, 1.83 mbpd; and in July, 1.69 mbpd. From 2014, because of the fall in the price of hydrocarbons, the inversion in the exploration at global level diminished 60% and PEMEX reduced its investment to 37%. Although the exploration and production activities are regulated, it is important that projects ensuring the sustainability of the Mexican energy industry be developed. In this sense, the production projects in conventional reservoirs of mature fields are a good option to keep the Mexican oil industry in the black. From the last century (1950s) up to date, Mexico had several secondary recovery [1 - 3] projects, mainly those featuring the injection of water into the fields: San Andrés in 1961; Tamaulipas-Constitutions in 1968; El Golpe, La Venta, Antonio J. Bermúdez, Sitio Grande, Cuichapa, Rodador and Magallanes in the years 1970-1978; Ogarrio in 1983; Abkatún-Pol-Chuc in 1991, *etc*. Also, the injection of nitrogen into the reservoir Cantarell and thermal recovery through vapor at the Samaria field has been carried out as part of several projects. As for the tertiary oil recovery, Mexico practically avoided the injection of chemical compounds

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(surfactants and polymers), while in other countries, this practice is very common and only restricted by the relationship between the oil price and cost of the injected chemical.

About 2.0 × 1012 barrels (0.3 × 1012 m^3) of conventional oil and 5.0 × 1012 barrels (0.8 × 1012 m^3) of heavy oil will remain in reservoirs around the world once the conventional recovery methods become exhausted. It should be kept in mind that the tertiary oil recovery methods can reach recovery factors above 60% whereas surfactant and polymer flooding belongs to well-known enhanced recovery methods that imply low risk and application under wide reservoir conditions. The aim of injecting polymers is to improve the sweeping efficiency in the reservoir and diminish the mobility contrast between water and oil when oil has a higher viscosity than that of the injected water. To date, there are more than 150 references worldwide and 30 years of experience in polymer flooding, however, the method employing surfactants is even more popular among the residual oil recovery processes, for it can be used at low surfactant concentrations, thus provoking important diminution of the interfacial tension (IFT) between oil and water [4]. Frequently, different chemical injection ways, including those featuring binary mixtures such as alkali/surfactant (AS), surfactant/polymer (SP), alkali/polymer (AP) or alkali/surfactant/polymer (ASP) have been used in tertiary recovery processes. The residual oil saturation and recovery process can be described indirectly by means of the capillary number (Nc), which is defined by the equation (1).

$$Nc = \frac{\mu \nu}{\sigma \cos \theta}, \qquad \textbf{(1)}$$

where μ is the viscosity of the displacing fluid, ν is the Darcy displacement velocity, cos θ is the contact angle and σ is the IFT between the displacing (water) and displaced (oil) fluids. Higher Nc means higher oil recovery; then, after the secondary oil recovery process by water injection, Nc ranges from 10−7 to 10−6 whereas with tertiary recovery processes, Nc can reach up to 10−2, thus reducing the oil residual saturation to the minimum. The increase in the viscosity of the displacing fluid (μ) using polymer solutions augments the number of capillaries less than 100 times while the application of surfactants to reduce the IFT (σ) can increase Nc 1000 times [5 - 6].

Currently, there are four types of surfactants: anionic, non-ionic, cationic and zwitterionic (Fig. **8.1**). ILs represent a particular case of the cationic or zwitterionic surfactants, for they are liquid salts (at ambient temperature) with organic cation.

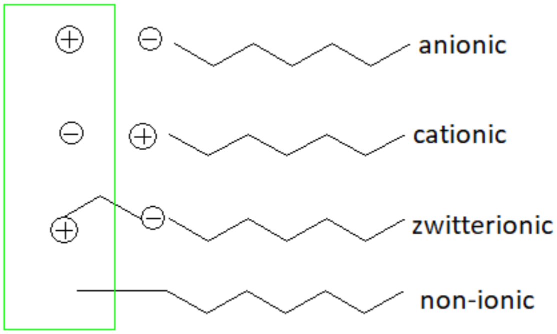

Fig. (8.1). General structure of surfactants.

Cationic surfactants are capable of desorbing oil irreversibly from the rock surface through the formation of ion pairs between the surfactant and carboxylic groups of crude oil naphthenic acids; for this reason, cationic surfactants are better agents of the wettability change than the non-ionic or anionic surfactants. There is a comparative study featuring an anionic surfactant derived from alkyl benzene sulfonic acid and the cationic surfactant cetyltrimethylammonium bromide (CTAB), where the authors showed that although the effect exerted by the cationic surfactant diminishing the IFT was more efficient than that displayed by the anionic one, it could recover up to 55% of crude oil while CTAB recovered as much as 70% [7].

The potential of the mixed system of cationic surfactants 1-dodecyl-3-methylimidazolium chloride and sodium dodecyl sulfate was evaluated through the analysis of IFT reduction, emulsion stability, wettability alteration and additional oil recovery tests by rock core injection, identifying a synergistic effect, which can be attributed to the formation of pseudo-bidirectional systems by electrostatic attraction (Fig. **8.2**). In addition, the mixed systems exhibited emulsion stability and excellent tolerance to salt and temperature with the IFT reduction, accomplishing additional oil recovery up to 17% in the presence of 50 000 mg / L of NaCl and temperature equal to 85 °C [8].

Most papers devoted to ILs for EOR processes have been focused on studies considering the IFT reduction or rock wettability change, however, until now, all the works related to EOR processes have been carried out at laboratory level [9]. In general, in comparison with non-ionic and anionic surfactants, ILs are more efficient changing the IFT under high salinity conditions [10, 11]. By increasing the length of the side chain of the cationic part, the effect on the diminution of the IFT becomes more evident, producing the lowest values for 1-alkyl-

CHAPTER 9

Applications of ILs as Catalysts in the Reaction to Obtain Alkylate Gasoline

Abstract: Alkylate gasoline is one of the most valuable products produced in the crude oil refining process. This product is one of the main contributors to the gasoline pool because it has a high-octane rating and a low content of contaminants such as sulfur, nitrogen, and aromatic compounds. This chapter reviews the advances in the use of ILs as catalysts for the isobutene/butene reaction with the objective of developing a less hazardous and more sustainable process to obtain alkylate gasoline.

Keywords: Alkylate, Brønsted acids, Butene, High-octane, Ionic liquids, Isobutane, Lewis acids, Lewis/ Brønsted ILs, Low sulfur, Pool, Selectivity, Supported-ILs, Trimethylpentane.

INTRODUCTION

Today, the production of high-quality, environmental-friendly gasoline remains a major challenge. Current and future global specifications require the reduction of aromatics, sulfur and oxygenates in gasoline as a final product. For this reason, gasoline as an end product is obtained by blending hydrocarbons obtained in a series of processes (gasoline pool), including the alkylation reaction. Nowadays, the produced alkylate represents approximately 10% of global gasoline production.

In the oil field, the alkylation reaction between olefins and isobutane is of great interest because it allows the synthesis of 8-carbon synthetic hydrocarbons, mainly trimethylpentanes (TMPs, Fig. **9.1**) and other branched kerosenes, which give rise to gasoline of excellent quality and octane rating, high calorific value, low Reid pressure and low pollutant content, which is known as alkylation gasoline and is a major contributor to the gasoline pool.

This reaction results in a fuel that burns efficiently, increasing the engine life and creating lower emissions. By increasing the octane rating of fuels, the addition of lead to the alkylate is not necessary, thus avoiding the use of an environmentally harmful substance without affecting the engine efficiency [1].

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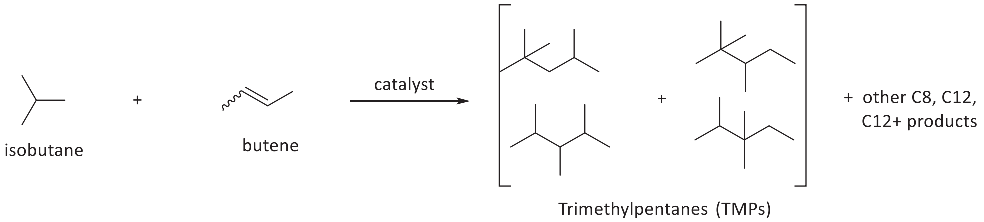

Fig. (9.1). Reaction to obtain alkylate gasoline.

In this context, Phillips alkylation technology is the most widely used in Mexico and internationally, employing HF as a catalyst. HF, besides being a very toxic product, is highly corrosive and must be used with a minimal purity of 99.5% and is used in conjunction with aluminum trichloride, which acts as a water absorbent and favors the catalyst performance [2].

Although in the alkylation process there are controls to retain the fluorinated compounds and HF produced in the process, latent risks cannot be totally averted due to HF leaks in industrial facilities, where clouds with lethal HF doses can form; so, their handling must be extremely careful, and also alkylation gasoline can be contaminated by HF and fluorinated organic compounds that are also highly toxic [3].

In order to contribute to the solution of this drawback, the IMP developed a technology to remove fluorinated compounds from alkylation gasoline, which was discussed in Chapter 2 of this book [4].

The alkylation process with H_2SO_4 is also widely used worldwide as it is a potentially less hazardous technology, although the process is less efficient than with HF, requiring a large amount of catalyst and the octane yield in the alkylate is lower. It also involves a high consumption of water that must be treated to remove the remaining hydrocarbons. The sulfuric acid alkylation technology has certain advantages over H_2SO_4: it is less volatile and toxic, the required isobutane/butene ratio is lower than that of HF, and distillation and isobutane recovery costs are relatively lower [5 - 7].

Because of all the limitations described for the catalysts used commercially in this technology, researchers in the area have devoted great efforts to the development of new, more efficient and environmentally friendly catalysts with the aim of making the process of obtaining alkylation gasoline a more efficient and sustainable technology [8].

In this sense, the alkylation reaction has been extensively studied with solid catalysts such as zeolites [9 - 11], heteropolyacids [12, 13], and Nafion-based nanocomposites [14 - 16]. These types of catalysts have also proved to be very efficient carrying out this reaction, reducing significantly toxicity risks and operating costs by forming a process with a solid heterogeneous catalyst that is neither toxic nor corrosive; however, these technologies have not been extended so far because the catalysts deactivate quickly and present difficulties for regeneration and reuse and tend to form oligomers and unsaturated hydrocarbons [17]. Currently, China has installed a commercial plant with this technology (ALkyclean^{TM}), using the zeolite-based catalyst Alkystar^{TM} by Albemarle [18].

ILs as Catalysts to Obtain Alkylate Gasoline

Currently, ILs are the most explored alternative as catalysts for the isobutane/butene alkylation reaction and in our opinion, the most promising candidates to replace the acids used commercially in the alkylation process. Fig. (**9.2**) shows the different types of ILs with acidic properties that have been studied and those that will be discussed in the following sections.

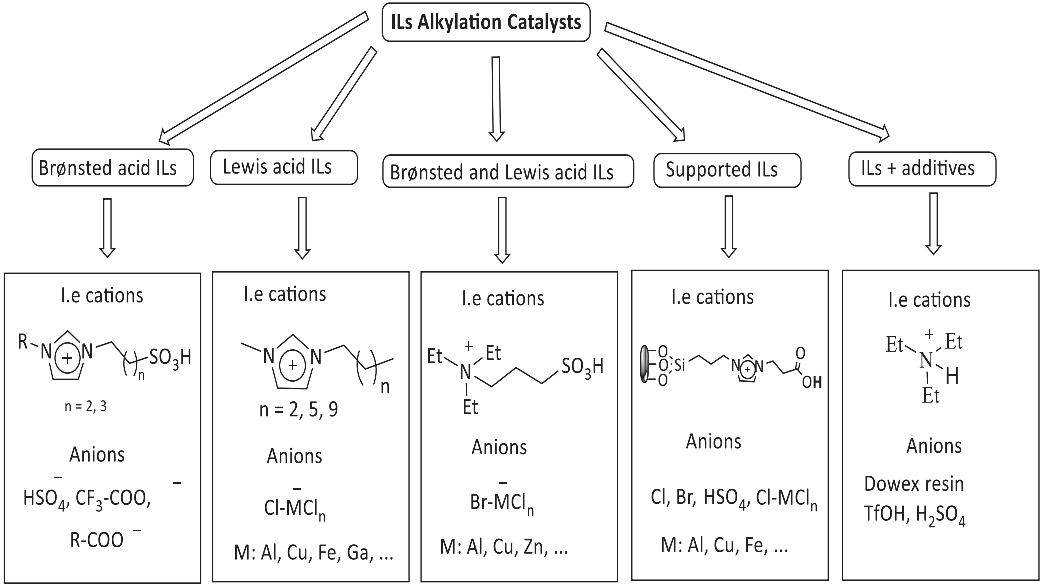

Fig. (9.2). Acidic ILs studied as alkylation reaction catalysts.

This topic has been studied by different authors in recent years [19 - 22], including the review published by IMP researchers titled New Insights into the Progress on the Isobutane/Butene Alkylation Reaction and Related Processes for High-Quality Fuel Production. A Critical Review. Energy Fuels 2020, 34 (12), 15525–15556 [23] by Díaz Velázquez, H.; Likhanova, N.; Aljammal, N.;

CHAPTER 10

Other Applications of ILs in the Petroleum Industry

Abstract: In this chapter, we will discuss some other applications that are of great importance in the oil industry and in which ILs have played an important role; however, the IMP has not yet ventured into these topics, at least not with the use of ILs. The topics discussed in this chapter are the separation of light hydrocarbons, separation and extraction of aromatic and aliphatic hydrocarbons, extraction of bitumen from oil sand, and application of ILs in shale stabilization processes.

Keywords: Aliphatic hydrocarbons, Aromatic hydrocarbons, Bitumen extraction, Extraction, Ionic liquids, Separation.

INTRODUCTION

The separation of light hydrocarbons is a subject of great importance in the oil industry. This process refers to the room-temperature separation of gaseous or liquid hydrocarbons, saturated and unsaturated, including olefins, dienes, and alkynes. The separation of these products is of interest to add value to these pure hydrocarbons or to transform them into other added-value compounds; for example, the synthesis of polyethylene and propylene requires the use of high purity monomers. Also, the separation of mixtures of hydrocarbons is important both because of their use as end products or for the preparation of feedstocks employed in clean energy processes [1].

One of the alternatives for light hydrocarbon separation is by means of cryogenic energy [2]. Extractive distillation [3, 4] and separation with the aid of porous materials [5] and metal-organic frameworks (MOFs) have also been studied [6].

Separation of Light Hydrocarbons Employing ILs

A novel option that has been intensively studied for the separation of light hydrocarbons in recent years is the use of ILs as effective solvents, as they represent environmentally friendly technology [7].

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Some results of the successful application of ILs for the selective separation of different light hydrocarbons are described below in chronological order. In 2008, Ortiz *et al*. studied the selective adsorption of propylene from its mixtures with propane by chemical complexation with silver ions in IL solutions of 1-butyl-3-methylimidazolium tetrafluoroborate (silver salt concentration = 0.25 M in form of $AgBF_4$) as functions of temperature and pressure. In all cases, gas solubilities increased with pressure and decreased with the system temperature.

The process with silver in the presence of IL proved much more effective for the selective adsorption of propylene in the presence of propane due to the fact that the silver cation becomes chemically more active forming silver-olefin complexes. The complete regeneration of the reaction medium containing the IL can be carried out at room temperature, 800 rpm of stirring rate and at 20-mbar vacuum for 3 h.

However, despite the silver-containing ILs provide tailorable selectivity to olefins, in our consideration, these results would be difficult to produce on a large scale due to the high cost of the $AgBF_4$ reagent involved in the process [8].

In 2010, researchers at the German University of Erlangen-Nuremberg carried out the screening of a family of ILs with imidazolium cation and one ammonium-type IL in order to find the most suitable prototype for propene/propane separation using the extractive distillation method (Fig. **10.1**). This study showed that the IL structure significantly influences the selective propene adsorption. In general, all the tested ILs preferred the selective propene separation in the presence of propane and it was observed that the gas solubility increased with the growing length of the alkyl chain linked to the imidazolium ring and in the same sense, the ability of the IL to separate the gases decreased. The best performing prototype was the IL containing the $[B(CN)_4]$ anion, which is highlighted in red in Fig. (**10.1**) [9].

In 2011, Hu *et al*. published a review featuring a critical discussion of the current state of knowledge of the key factors influencing the solubility of gases in ILs, including sample purity, experimental methodology, "molecular" characteristics of ILs, temperature and pressure. In this review, it was concluded that the presence of ion conformational equilibria and the formation of ionic and non-polar domains in the ILs influence significantly the solubility of gases in ILs with physical adsorption. The work is mainly focused on gases such as CO_2, SO_2, N_2, O_2 and CH_3 and on the separation of their mixtures.

The increased flexibility of the anion structures, and the substituents on the head and tail of the cation contribute to increase the free volume and decrease the cavity formation energy. The joint use of these findings is of great importance when we note the fact that the use of ILs will depend on whether their viscosity and chemical stability are suitable for a given application [10].

Cation	Anion
R = Me, R_1 = Bu	Tf_2N
R = Me, R_1 = Pr	Tf_2N
R = Me, R_1 = Et	Tf_2N
R = Me, R_1 = Me	Tf_2N
R = Bu, R_1 = Bu	Tf_2N
R = Pr, R_1 = Bu	Tf_2N
R = Et, R_1 = Bu	Tf_2N
R = Et, R_1 = Pr	Tf_2N
R = Me(aryl), R_1 = Me	Tf_2N
R = Me, R_1 = Bu	DCA
R = Me, R_1 = Et	DCA
R = Oc, R_1 = Me	Tf_2N
R = Oc, R_1 = Me	$C(CN)_3$
R = C_6CN, R_1 = Oc	Tf_2N
R = C_6CN, R_1 = Me	Tf_2N
R = Me, R_1 = Et	$C(CN)_3$
R = C_6CN, R_1 = Me	$C(CN)_3$
R = Et, R_1 = Me	$B(CN)_4$

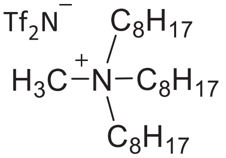

Fig. (10.1). ILs evaluated in the propene/propane separation using the extractive distillation method (Mokrushin *et al*., 2010).

In 2013, Xing *et al*. [11] studied the solubility of ethylene and ethane in three ILs at 303.15 K: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf_2]), 1-butyronitrile bis((trifluoromethyl)sulfonyl)imide ([CPMIM][NTf_2]), and dual-functionalized [$(CP)_2$IM][NTf_2] (Fig. **10.2**). It was found that the symmetric IL showed the highest separation selectivity to ethylene/ethane on [$(CP)_2$IM][NTf_2]. Theoretical calculations employing

FINAL CONCLUSIONS AND FUTURE PROSPECTS

Many studies on the application of ILs in the Oil Industry have been described in this book. Due to the unique properties of ILs, this class of materials has been considered as a very attractive alternative to be used in many fields and the obtained research results are very attractive in most of the applications.

On the other hand, the possibility of synthesizing a large number of ILs with physicochemical properties such as acid-base, viscosity, and solubility that can be modulated makes this family very interesting to attend different problematics and processes.

In spite of the fact that the effectiveness of ILs has been proven in the laboratory through various types of experiments with excellent results, there still exists a gap in demonstrating the application of ILs on high scale. From those described in this book, the use of ILs to produce alkylation gasoline is the only application that has been demonstrated on a large scale with commercial technologies available at high level such as Ionylation and Isoalky. Even in these cases, the technologies are still limited in their application by catalyst chemical stability problems (high moisture sensitivity) that characterize ILs with Lewis acidic properties.

One of the advantages of ILs is their practically zero vapor pressure, which apparently makes them environmentally friendly solvents and ideal substituents of volatile organic solvents in the development of sustainable processes; however, this issue must be faced rigorously, since many ILs have high toxicity and low biodegradability problems.

Another problem that plagues most ILs is their high cost. Currently, there are already suppliers of ILs in large volumes and this limitation will be solved as more efficient and sustainable ILs are developed.

Notwithstanding, in our opinion, the limitations that currently exist regarding the industrial-scale applications of ILs may be resolved as research progresses and is carried out through a more comprehensive approach. Many research works are under progress to reduce the production cost of ILs and develop processes based on ILs synthesized from natural and biodegradable raw materials; likewise, truly efficient, economical, and sustainable regeneration processes are being conceived. More refined screening methods will have to be developed for the selection of an IL for a specific application. With all these considerations, we hope that in the near future, more and more large-scale uses of ILs in the chemical and oil industries will be part of the aforementioned success stories.

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Rafael Martínez Palou

Dr. Rafael Martínez Palou studied Chemistry at Havana University and completed his MSc. (1998) and PhD. (2001) in Chemical from the National School of Biological Sciences of the National Polytechnic Institute in Mexico City. He did a postdoctoral stay at the Mexican Institute of Petroleum (IMP), where he was subsequently hired as a Scientific Researcher. In 2016, he carried out a research stay at the Imperial College of London sponsored by the Newton funds from the U.K. In 2019, he presented the research project "Technology for the transport of heavy crude oil through the formation of crude oil emulsions in water" and was the winner of the call to participate in the Acceleration Program of the Mexican Energy Council (COMENER) in the Entrepreneurship & Commercialization Center at the University of Texas Rio Grande Valley in 2020. He worked as researcher at Mexican Petroleum Institute since 2002, where he has been a Research Project Leader in the development and application of organic chemical products for the oil industry and in the valorization of biomass products. He is currently serving in the Research Department for the Development of Catalysts and Chemical Products and is the leader of research projects and professor at the institute's own graduate school. He belongs to the National System of Researchers, level III (2019-2023).

Natalya Likhanova

Dr. Natalya Likhanova is a Mexican researcher who has been working at the Mexican Petroleum Institute for the past 19 years. She pursued doctoral studies in Chemical Pharmaceutical Sciences and her Ph.D. degree was awarded in 2001 by the Higher Attestation Commission of Ukraine for the thesis work entitled “Synthesis and study of physical, chemical and biological properties of 1-R-4-hydroxy-2-oxoquinoline-3- carboxylic acid alkylamides,” which was developed at the National Academy of Pharmacy of Ukraine. Her areas of expertise include: organic synthesis, ionic liquids, and oil recovery by chemical processes. She has been the leader of 9 research projects for oil production. She has more than 70 publications in JSR journals with more than 2300 citations as an Impact Evidence of her work. Dr. Likhanova became the proud recipient of a certificate of recognition bestowed upon her by the prestigious Applied Surface Science journal for the most cited article in 2006-2010. As for her academic and research contributions, she is currently a member of the National System of Researchers of Mexico., and was distinguished by the Board of Directors of the Mexican Academy of Sciences with a Research Award in the area of Engineering and Technology in 2015; in addition, in 2018, she received an award from the Mexican Petroleum Institute for the training of human resources. At present, Dr. Likhanova is a regular member of the Mexican Academy of Sciences and has been invited and participated as an international evaluator of research projects.