



**SATBAYEV
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**KAZAKH NATIONAL RESEARCH AND TECHNICAL UNIVERSITY
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**INSTITUTE OF CHEMICAL AND BIOLOGICAL TECHNOLOGIES
DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING**

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**«ION-LIQUID EXTRACTIVE SYSTEMS FOR IMPROVING THE
PERFORMANCE OF DIESEL FUELS»**

DIPLOMA WORK

5B072100– «CHEMICAL TECHNOLOGY OF ORGANIC SUBSTANCES»

ALMATY 2020



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DIPLOMA WORK

«ION-LIQUID EXTRACTIVE SYSTEMS FOR IMPROVING THE
PERFORMANCE OF DIESEL FUELS»

5B072100– «Chemical technology of organic substances»

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РЕФЕРАТ

Есеп берудің мазмұнында: 30 бет, 9 сурет, 4 кесте, 30 пайдалынған әдебиет.

Түйінді сөздер: Денитрогенизация, иондық сұйықтықтар, экстракция, дизель отыны.

Жобаның мақсаты: Дизель отынын тиімді денитрогенизациялау үшін иондық сұйықтықтарға негізделіп жасалған жаңа экстракциялық жүйелерді жасау.

Қолданылған әдістер мен аппаратуралар: Дизель отынын денитризациялау процесінде технологиялық, графикалық және жылу есептеулер жүргізілді. Модельдік отынды синтездеу үшін Сокслет экстракторы қолданылды. Бұл процесте Fisons EA 1108 Costech жану жүйесінің бағдарламалық микропроцессорлық контроллері қолданылады. Реагенттердің қайнау температурасын бақылау үшін термоэлектрлік түрлендіргіш Gallenkamp Model аппараты таңдалды.

Жобаның нәтижелері: Дизель отынын құрамында азот бар қосылыстардан сапалы тазартуды жүзеге асыратын, құрамында металл бар ионды-сұйық экстрактивтік жүйелер құрылды.

Практикалық қолданылуы: Қазақстандағы МӨЗ-де дизель отынының пайдалану қасиеттерін жақсарту.

РЕФЕРАТ

Отчет содержит: 30 стр., 9 рис., 4 табл., 30 использованных источников.

Ключевые слова: Денитрогенизация, ионные жидкости, экстракция, дизельное топливо.

Цель дипломной работы: Разработка новых экстрактивных систем на основе ионных жидкостей для эффективной денитрогенизации дизельного топлива.

Использованные методы и аппаратура: В процессе денитрогенизации дизельного топлива проводились технологические, графические и тепловые расчеты. Для синтеза модельного топлива использовался экстрактор Сокслета. В процессе используется программный микропроцессорный контроллер фирмы Fisons EA 1108 Costech Combustion System. Для контроля температуры кипения реагентов выбирается термоэлектрический преобразователь Gallenkamp Model apparatus.

Результаты дипломной работы: Были созданы эффективные металлосодержащие ионно-жидкостные экстрактивные системы, осуществляющие качественное очищение дизельного топлива от азотсодержащих соединений.

Практическое использование: Повышение эксплуатационных свойств дизельного топлива на НПЗ в Казахстане.

ABSTRACT

The report contains: 30 pages, 9 Fig., 4 table, 30 references used.

Key words: Denitrigenation, ionic liquids, extraction, diesel fuel.

Purpose: Development of new extractive systems based on ionic liquids for efficient denitrogenation of diesel fuel.

Methods and equipment: In the process of denitrogenation of diesel fuel, technological, graphic and thermal calculations were carried out. For the synthesis of model fuel, a Soxhlet extractor was used. The process uses a Fisons EA 1108 Costech Combustion System software microprocessor controller. To control the boiling point of the reagents, a Gallenkamp Model apparatus thermoelectric converter is selected.

Results: Effective metal-containing ion-liquid extractive systems have been created that carry out high-quality purification of diesel fuel from nitrogen-containing compounds.

Practical use: Improving the operational properties of diesel fuel at a refinery in Kazakhstan.

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INTRODUCTION

Ionic liquids represent the combination of scientific and practical specific actions to increase the quality of the environment. The merging of these concepts into one whole becomes a great achievement of our time in the process of intensification of industrial processes and high technologies.

In 1998 the twelve principles of "Green Chemistry" were formulated by P. Anastas and D. Warner. This information intended as a recommendation to use them in practice:

- preventing wastes is less demanding rather than to recycle it;
- maximum conversion of the initial materials to the target products should be ensured;
- usage of reagents for synthesis techniques with least impact for flora and fauna;
- when creating new reagents it is crucial to combine the extending of work efficiency with the reduction of toxicity;
- minimize the usage of solvents and auxiliary reagents by inserting recycle;
- should seek for dealing with the energy-saving technologies, in conditions as close to normal;
- under specific economic and technical conditions, initial reagents (raw materials) used in the reaction must be renewable;
- avoid usage of pointless intermediate processes without necessity;
- strive to use selective catalysis;
- chemicals than have been used as reagent should not be biodegradable and should not create environmental problems;
- control over hazardous substances in the environment should be improved;
- minimize the rate of pollution that poses a danger to the environment.

"Green chemistry" focuses on:

- new synthesis methods, including catalytic processes;
- renewable energy, source of raw materials;
- replacement of solvents.

In Kazakhstan, experts in the field of "Green Chemistry" focus on the solution of scientific and applied problems in special academic and educational institutions, including a rapidly developing field - the chemistry of ionic liquids (IL). Chemistry of IL is one of the most substantial in solving the problems of "Green chemistry" [1].

The main constituent of the entire mass of IL is imidazolium salts.

By definition, ionic liquids are composed of ions. Historically, they had an arrangement of definitions: ionic melts, molten salts, ionic liquids, liquid electrolytes, liquid salts, ionic glasses. All of the above, the term "ionic liquid" for this period is considered as the most common.

Ionic liquid satisfies conventional criteria and has a melting point range of up to 100 ° C.

Interest in ionic liquids dates back to the second half of the last century. The development of IL occurs simultaneously with the outstanding discoveries of the same century in biological resources on land and sea, electrochemistry, chemistry, oil and gas processing, nuclear energy, materials science, solar energy, etc areas [2].

This work consists of methods of creating effective monocationic ion-liquid systems capable of extracting nitrogen compounds (quinoline) and sulfur (thiophene) from diesel fuels.

The purpose of this work is the engineering of new extractive systems based on ionic liquids for the effective denitrogenation of diesel fuels; a way to achieve the goal is to use metal-containing ionic liquids for the extraction of nitrogen compounds from diesel oils.

The goal might be archived by solving the following problem: the synthesis of monocationic metal-containing ionic liquids and the study of their extractive ability concerning nitrogen compounds contained in diesel fuels, the identification of metal-containing ionic liquids having the maximum affinity for nitrogen compounds.

The scientific novelty of the work is the creation of extractive systems based on metal-containing ionic liquids capable of extracting nitrogen compounds from diesel fuels: the method of extractive denitrogenation that we are developing is hydrotreating, the process of removing heteroatoms from petroleum products as a result of hydrogenation of sulfur and nitrogen compounds.

1 Literature review

1.1 General review of ionic compounds

Ionic liquids are composed of organic salts, the melting point of which is usually taken as 100 ° C. As early as 1914, ethylammonium nitrate, a salt with a melting point of 12 ° C, was first synthesized. Increased demand for these compounds arose only at the end of the last century. The reason for the demand was the critical state of the ecosystem associated with anthropogenic impact. These actions became the foundation of “green” chemistry.

The ionic liquid consists of organic or inorganic anions and organic cations, the total number of combinations is within 10^6 .

The term "ionic liquids" implies a substance that is in a liquid state of matter at a temperature below 100 ° C and consisting of organic cations [3].

Examples of IL can be 1,3-dialkylimidazolium, N-alkylpyridinium, tetraalkylammonium, tetraalkylphosphonium, trialkylsulfonium with various anions: Cl⁻, [BF₄]⁻, [PF₆]⁻, [SbF₆]⁻, CF₃SO₃⁻, [(CF₃SO₂)₂N]⁻, ROSO₃⁻, RSO₃⁻, ArSO₃⁻, CF₃CO₂⁻, CH₃CO₂⁻, NO₃⁻, [Al₂C₁₇]⁻.

The nature of the anion represents a significant effect on the properties of IL — viscosity, melting point, electrochemical stability, and thermal stability. The polarity, hydrophilicity or hydrophobicity of ionic liquids can be optimized by selecting the appropriate pair of cation and anion. Each new anion, cation provides additional opportunities for varying the properties of IL [4].

High demand and attention to IL explained by the discovery of their following remarkable properties:

- 1) a wide interval of the liquid state (more than 300 ° C) and low melting points ($T_m < 100$ ° C);
- 2) high electrical conductivity;
- 3) satisfactory dissolving ability with respect to various chemical compounds and polymers of various origins;
- 4) catalytic activity, which leads to an increase in the selectivity of organic reactions and the yield of the target product;
- 5) non-volatility and reusability;
- 6) incombustibility, non-explosiveness, non-toxicity and the consequent absence of harmful effects on the environment;
- 7) boundless possibilities to direct synthesis of ionic liquids with desired properties.

Qualities 3 and 4 make especially attractive ionic solvents for the synthesis of polymers. Ionic liquids act as unique chemicals in chemical research, catalysis, organic synthesis, as well as in other fields, including biochemical processes. Currently the amount of ionic liquids described in the literature is enormous (about 300). Potentially, the variety of ionic liquids is almost unlimited, unless limited only by the availability of suitable organic molecules (cationic particles) and inorganic, organic and metal complex anions [5].

According to various estimates, the number of possible combinations of cations and anions in such ionic liquids can reach 1018.

The methods of preparing IL are quite simple and can easily be scaled. The most commonly used three main synthesis methods are:

- exchange reaction between a silver salt containing necessary anion B⁻, and halogen radical with the necessary cation A⁺: $Ag^+ + B^- + A^+ Hal^- \rightarrow A^+ B^- + AgHal$
- quaternization reaction of an N-alkyl halogen derivative with metal halides: $=N^+ - AlkHal^- + MHal_n \rightarrow N^+ - AlkMHa1_{-n+1}$
- ion exchange reactions on ion exchange resins or clays.

Another practically important direction in the synthesis of ionic liquids is their preparation directly in the reactor. In this case, the corresponding N-alkyl halide and metal halide are mixed in the reactor, and an ionic liquid is formed immediately before starting the chemical process or catalytic reaction. Most often, ionic liquids are prepared based on a mixture of aluminum chloride with organic chlorides. When two solids are mixed, an exothermic reaction occurs, and eutectic mixtures with melting point up to -90 ° C are formed. As a rule, this is a clear, colorless, or tan liquid (the color is due to the presence of impurities and local overheating of the reaction mass during the preparation of the ionic liquid) [6].

Ionic liquids, due to the variety and characteristics of their properties, have been very attractive for catalysis and organic synthesis. Regarding the “environmental friendliness” of ionic liquids, such issues should be reevaluated in subsequent studies, although, in general, the fact that they are recyclable, non-combustible and have low saturated vapor pressure, even without taking into account those gains in productivity and selectivity, examples of which were given in the review, makes them a full member of green chemistry. Obviously, due to their high cost, ionic liquids are unlikely to find wide application in large-tonnage processes, unless additional advantages of heterogeneous systems will be found. At the same time, small-tonnage chemistry, primarily metal complex catalysis, may turn out to be a beneficial area for their use, as well as electrochemistry in general and electrocatalysis in particular [7].

The ionic liquid can be obtained from amines, phosphates, and sulfonates.

Quantization is the first step in the synthesis of IL, where the NR₃ amine undergoes an alkylation reaction, R'X alkyl (sulfates, halides) are used, therefore an ionic liquid [R'R₃N] + X⁻ is created. Quaternization process involves quite simple steps: the solvent (ethyl acetate, toluene, etc.) mixed with an amine and an alkyl halide, heated in the presence of inert gas. The reaction time and the process condition are determined by the reactivity of the alkylating agent. Also, the reaction condition depends on the nature of halides, for example, chlorides are weaker than bromides and even more so than iodides.

After anion X, which has obtained by the quaternization reaction, the ionic liquid probably will be replaced by another anion A, through a metathesis reaction with Lewis, Bronsted acids. It is possible to replace the anion with an ion exchange resin. The halogen-containing ILs are ion-exchanged [8].

Most ILs arise from cations, which in turn do not contain acidic protons. IL synthesis can be divided into two stages: anion exchange to obtain the desired product and the formation of the desired cation.

Due attention was paid to the formation of IL-based on 1,3-dialkylimidazolium cations.

The techniques mentioned here were proposed by Wilks and others to create 1-alkyl-3-methylimidazolium salts ([RMeIm]⁺), which apply to other cations [9].

Imidazole salts have lower melting points in comparison to 1-alkylpyridinium.

The quaternization reaction of imidazolium compounds is considered to be a universal and most feasible way to obtain ionic liquid on a laboratory, industrial scale. We point out some features in more detail.

As indicated above, the formation of cations by protonation of the bases with free acid possible to achieve by quaternization of amine, phosphine, with the help of halogen alkyl to a greater extent.

The protonation reaction is used to form salts. An example of the formation of salts using a quaternization reaction is ethylammonium nitrate, which includes the addition of 3M nitric acid to a cooled aqueous solution of ethylamine. Excess in a small amount of amine is useful and can be removed together with water by heating to 60 °C in a vacuum.

The alkylation process has the following privileges:

- the maximum range of low-cost halide alkyls;
- reactions behaves calmly at moderate, normal temperatures.

It is necessary to mention that primary halide salts are mainly used as intermediates.

Currently, there are a number of reaction methods, but the simple experimental setup, which consists of a round-bottom flask, a reflux condenser, prevails. If possible, the reaction should be carried out in the presence of nitrogen or another inert gas. Crucial condition is to exclude moisture and oxygen during the quaternization reaction. It is necessary to exclude oxygen, especially in order to obtain a colorless halide salt [12].

An alternative possible way: to mix alkyl halide and 1-methylimidazole in special ampoules, degassed using freeze-thaw cycles, and seal under vacuum, heated in the oven for the required period of time.

The preparation of salts with short alkyl substituents is considered more complicated, for example, 1-methyl-3-ethylimidazolium chloride [MeEtIm] Cl, since chloroethane has a boiling point of 12 °C. The above reactions are carried out in an autoclave. Before use, chloroethane is cooled to a temperature below its boiling point. The autoclave has a positive role for large-scale preparation of quaternary salts.

The reaction is allowed to be carried out without solvent - all the liquid reagents are mutually mixed. The reaction products had not been mixed with the initial materials. Considering an excess of ethyl acetate, the most commonly used solvents might be alkyl halide, 1,1,1-trichloroethane, toluene [13].

In practice, 1-methylimidazole is well known and the most used starting material. 1-methylimidazole can be purchased at an affordable price and leads to most

cation, which takes many scientists' interest. There is a limited range of other commercially available N-substituted imidazoles, but most of them do not economically viable. This situation solvable since synthesis 1-alkylimidazoles can be carried out without much difficulty.

The literature contains little information on determining the purity of imidazolium halide salts by methods otherwise than standard spectroscopic measurements and microanalysis because these halide salts infrequently implement as solvents and serve as the source of the desired cation. The only impurities containing in larger quantities are unreacted feedstock and residual solvents.

The displacement of halide alkyls is not difficult, as well as solvents from the reaction, especially in the case of relatively volatile halide alkyls with short chains. But even the predominance of a small amount of unreacted 1-methylimidazole can lead to trouble in the next stages of the reaction. A significant elevated boiling point of about 198 ° C indicates that difficulties are expected to be removed from ionic liquids. Holbray explained the colorimetric determination of 1-methylimidazole based on the appearance of a blue complex ion of the type $[\text{Cu}(\text{MeIm})_4]^{2+}$. This complex is sensitive to 1-methylimidazole in the 0-3 mol% range of concentrations. These data do not contribute to solving the problem but make it possible to test the sample before use so that the reaction process proceeds under control.

The introduction of ionic liquids in various processes leads to an increase in efficiency by increasing selectivity, yield and reducing time, as well as improving the efficiency of the process due to the possibility of recirculation of ionic liquids without loss of quality. Ionic liquids are successfully used as a medium and catalyst in the Friedel Crafts etherification, alkylation and acylation reactions, condensation, carbonylation, synthesis of several organic compounds, and other reactions.

There are reports of the possibility of using ionic liquids to optimize existing technologies and processes associated with the oil industry. Currently, the use of ionic liquids for the purification of raw materials from aromatic compounds, sulfur and fluorine is not widely used in industry, however, ionic liquids have great potential and shortly can be used for preliminary purification of raw materials from nitrogen-containing compounds and deep desulfurization. Some ionic liquids serve as adsorbates to trap gases such as CO_2 and H_2S .

Low volatility, high electrochemical, thermal stability and conductivity open up wide possibilities for the use of ionic liquids in the energy field. Thus, based on ionic liquids, electrolytes for batteries, supercapacitors, converters, sensitized dyes of solar cells and thermoelectrochemical cells can be created. The possibility of using ionic liquids for the synthesis of highly effective catalysts for the oxidation of water has been reported. The use of ionic liquids as a reaction medium very often complicates the further analysis of reaction mixtures by mass spectrometric methods due to the low concentration of dissolved substances and the predominance of intense signals of ionic liquids (in the mode of both positive and negative ions). In laboratory No. 30 (IOKh RAS), an approach was developed that allows monitoring of chemical reactions and analysis of substances dissolved in an ionic liquid using mass spectrometry with electrospray ionization (E51-M5). Instead of preliminary chromatography and

extraction, and analytical quadrupole was used to separate the target particles in the ionic liquid [17].

Significant successes were achieved using ionic liquids for processing biomass, in particular cellulose, to monosaccharides to produce valuable furan derivatives, which are promising basic compounds for producing biofuels. Most preferred are chloride, acetate, formate and alkylphosphonate anions in combination with various cations; they contribute to the dissolution of cellulose due to the ability to form hydrogen bonds with the hydroxyl groups of carbohydrates.

Thus, the unique physicochemical properties of ionic liquids, such as low melting point ($<100\text{ }^{\circ}\text{C}$), high polarity, low vapor pressure, high chemical and thermal stability, and the ability to dissolve compounds of various nature, allow us to create new technologies, and also significantly improve existing ones. The properties of ionic liquids can be changed under the necessary conditions, modifying their components (cations and anions). This makes it possible to use ionic liquids in various fields of chemistry and technology, including biology and biotechnology. Currently, the areas of "bio" application of ionic liquids include:

- the production of ionic liquids from natural and biological materials (carbohydrates, amino acids), which are currently being studied in detail as economical and environmentally friendly environments for industrial use;
- processing of natural raw materials using ionic liquids as solvents or catalysts;
- enzymatic reactions in ionic liquids;
- obtaining bio-compounds and drugs based on ionic liquids [18].

1.2 Ionic liquids in catalysis

In recent years, both the volumes of pharmaceutical, chemical, paint and varnish, as well as other types of industries, and the variety of products they produce, have greatly increased. These processes often require the use of large quantities of volatile organic solvents, which cause great damage to the environment, and the disposal of which requires high costs, sometimes even with equal costs necessary for their production. In this regard, the fact that many countries prioritize those seeking new processes using alternative solvents that comply with the principles of "green chemistry" is reasonable.

These solvents include ionic liquids (IL), which have unique properties, which include: almost zero saturated vapor pressure, non-flammability, thermal stability, and many others. Ionic liquids are widely used in catalytic chemistry. At first they were used as media for carrying out catalytic processes, and in recent decades, as catalytic agents. A unique feature of these compounds is the possibility of obtaining ionic liquids that would meet the assigned chemical problem by varying combinations of cation-anion pairs. Also important is the fact that multiple uses of ionic liquids are possible, which opens up new paths for the implementation of closed technological cycles.

Ionic liquids are formed by inorganic or organic anions and organic cations, their diversity is so great that some estimates have approximately 106 possible

combinations. Examples of some anions and cations, as a rule, included in many well-known ionic liquids.

Halogen-containing ionic liquids can most easily undergo different ion-exchange processes. So, acidic ionic liquids can usually be obtained by mixing the ionic liquid $[R'R_3N] + X^-$ with a Lewis acid in the absence of a solvent.

Usually, ionic liquids are used as solvents in a number of different organic reactions catalyzed by metal compounds and directly. In this case, the ionic liquid can fulfill, in addition to the role of a solvent, the role of a catalyst if its anion includes a metal, for example, aluminum tetrachloride $AlCl_4$.

The limitations mentioned above on the practical use of ionic liquids contributed to the formation of a new trend in the 2000s - the creation of heterogeneous catalysts through adsorption, covalent immobilization of ionic liquids on porous carriers with the further introduction of the active component directly in the IL — a transition metal complex or salts, further capable of being recovered to metal. R. Fermann and his assistants became pioneers in this area; they introduced concepts such as SILP and SILC, which stands for “phase with deposited ionic liquid” and “catalyst with deposited ionic liquid”, respectively. The difference between these approaches are that in one case, physical adsorption of an ionic liquid is used, and in the other case, ionic liquids covalently bind to the surface through the functional groups of the latter.

It should be noted that in most cases, these catalytic materials can approach molecular catalysts with these properties, the active sites in which are strictly homogeneous. This phenomenon to a large extent creates the maximum selectivity of heterogeneous catalytic processes using active materials based on supported ionic liquids [19].

1.3 Physical and chemical properties of ionic liquids

Ionic liquids are molten organic salts that are in a liquid state and consist of bulk organic or inorganic anions and organic cations. The cations are asymmetric and are larger than anions. The cations are tetraalkylphosphonium (XI), N, N'-dialkylpyrazolium, alkylammonium (I), N-alkylpyrimidinium (VIII), alkylphosphonium (II), N, N'-dialkylimidazolium (IV), tetraalkylammonium (X), and alkylpyridinium ions), N-alkylpyridazinium (VII), and N-alkylpyrazinium (IX).

The anion role in IL can take place PF_6^- , BF_4^- , $AlCl_4^-$, Cl^- , Br^- , I^- , SCN^- , NO_3^- , $C(CN)_3^-$, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $RCOO^-$ etc.

The most important properties of IL are described by their ionic structure. In the literature, a large number of articles are devoted to attempts to establish a relationship between the ionic structure of IL and its physicochemical properties. In the work of Tokud et al, the ionic nature of an ionic liquid is the molar conductivity ratio $\Lambda_{imp} / \Lambda_{NMR}$, where Λ_{NMR} is the conductivity estimated using ion self-diffusion coefficients and the Nernst-Einstein relation and, where Λ_{imp} is the molar conductivity measured by the electrochemical impedance method. This expression $\Lambda_{imp} / \Lambda_{NMR}$ allows us to calculate the value of the effective ionic concentration C_{eff} and the degree of cationic anionic aggregation in the IL. The effective ionic concentration shows the

electrostatic forces of the ionic liquid makes it possible to estimate the saturated vapor pressure, and also to predict other physical properties of the ionic liquid [20].

The nature of the anion and cation shows the effect on the properties of the ionic liquid. By the method of selecting the constituent parts, it is possible to obtain the necessary chemical-physical properties from a ton of liquid. It is known: IL anion to a greater extent predicts its properties, that is, the chemical stability of the salt with respect to water, air. The presence of any anion can impart basic, acidic or neutral properties to an ionic liquid. If the organic cation is large, then this is the reason that ionic liquids do not crystallize at room temperature.

Melting point . The difference between molten salts and ionic liquids are that ILs contain large asymmetric organic cations that contain relatively low melting points. The most common factors where the dependence of the melting temperature of the ionic liquid is observed:

- the size of the anion - the melting temperature decreases with increasing size of the anion;
- conformational flexibility;
- the lower the melting temperature, the higher it is;
- packing coefficient of the molecule (density);
- its decrease lowers the melting point.

Thermal stability. IL, when heated, does not show a measurable vapor pressure and do not decompose. Most ionic liquids are thermally stable; according to the definition of differential thermal analysis and thermogravimetric analysis, they undergo decomposition in the temperature range 350–400 ° C. For different ionic liquids with identical cations, the thermal stability practically does not change, but a decrease is observed as the hydrophilicity of the anion increases. In this series, the relative stability decreases in the following order: Tf₂N⁻ → PF₆⁻ → BF₄⁻ → Hal⁻.

Density. Most ILs have a high density, which is explained by their ordered structure. The density value is affected by the molar mass of the anion.

Viscosity. In many cases, the viscosity of an ionic liquid is much higher than the density of water, and in its values is comparable to the viscosity of oils, decreases with increasing temperature. An increase in the viscosity of the ionic liquid is characterized by the replacement of the anion, possibly the cation in the composition of the compound, with an increase in the strength of the van der Waals interactions. The viscosity of an ionic liquid is affected by the symmetry of its constituent ions. For example, asymmetric ionic liquids have higher viscosity indices than symmetric ones, although the densities for ionic liquids were almost equal.

The crystalline properties of ionic liquids. Many ionic liquids are in a glassy state, therefore, it is difficult to crystallize them, many others can crystallize into one, as well as into several polymorphic modifications. To obtain the crystals used in the analysis, high-precision temperature control is required, achieved using zone crystallization or scanning calorimetry.

Hydrophobicity. The hydrophobicity of an ionic liquid in large cases is determined by the anion. If the ionic liquid contains hydrophilic anions, then the ionic liquid is subject to mixing with water in different ratios, you can notice the dependence

of the physical properties of the ionic liquid on the amount of water contained in the ionic liquid. Anions: PF₆⁻, Tf₂N⁻ provide hydrophobic ionic liquid, which is not mixed with water, and the removal of water from them to a small extent affects their properties. Plasticizing properties. Ionic liquids are a kind of plasticizers for polymers that improve their properties: the glass transition temperature decreases, thermal stability increases. Imidazolium-based ionic liquid plasticizes polymethylmethacrylate (PMMA) well. If compared with traditional plasticizers, then noticeably low volatility, high thermal stability, glass transition temperature decreases to 0 °C, therefore, the life of the material increases.

Electrochemical properties. There are properties that attract the use of IL in electrochemistry. These properties include a wide electrochemical window, ionic conductivity, electrochemical stability. The conductivity values of IL vary in the range from 1 to 10 mS/cm. Not so long ago, ILs were characterized based on the 1-ethyl-3-methylimidazolium cation and the anions of thiocyanate and dicyanamide, having a conductivity of about 20 mS/cm. The authors concluded: the conductivity of the ionic liquid depends on the type of cation, size, but does not depend on the parameters of the anion. With an increase in cation size, the conductivity value decreases due to a decrease in cation mobility; no correlations are observed with anions [21].

1.4 Imidazolium salts as ionic liquids

The imidazole family includes natural, synthetic compounds that have physiological activity. Imidazole is characterized by a weak physiological effect. Imidazole is less toxic. But the degree of physiological action and its orientation are largely determined by the nature of the substituent.

The chemistry of compounds containing imidazole residues is combined under the name imidazole chemistry. Imidazole first synthesized Debu (1858). Of the products of the reaction of glyoxal with ammonia, he gave birth to a compound of a new species and referred to it as glyoxaline.

Imidazole or 1,3 - diazole, glyoxaline are colorless crystals with a monoclinic lattice, which has good solubility in water, ethanol, benzene, but poorly in hydrocarbons. Molecules are characterized by a flat configuration and are associated due to hydrogen bonds. For imidazole, prototropic tautomerism is preferred, whereby positions 4 and 5 are equivalent.

Imidazole is characterized by aromaticity. For complete information on the basic properties and reactivity of imidazole, it is important to study the main resonant structures and their participation in the general structure. The relatively high acidity of the imidazole nucleus can be explained by the presence in the resonating system of a lone pair of electrons that belongs to the nitrogen atom of the group — NH. Consequently, to the formation of a certain positive charge on nitrogen, which, obviously, promotes protonation.

If a salt formation is observed, the anion is stabilized by resonance. Resonance is involved in a decrease in the electron density at another nitrogen atom, as well as a decrease in its basicity. But if salt is formed, then due to resonance one can observe

stabilization of the cation, an increase in basicity. We can say that the positive charge is not fixed on one of the nitrogen atoms, since the isomeric 1,4 - and 1,5 - dimethylimidazoles with methyl iodide form the same cation [22].

Alkyl groups, lead as electron-donating groups while contributing to an increase in the electron density of the nitrogen atom, which has basic properties and thereby increase the basicity.

The N - 1 atom causes acidity. At the N - 1 atom, N - aryl -, N - alkyl -, N - acyl derivatives are also easily formed. Atom N - 3 is the main center through which protonation and complexation proceeds. The presence of N 2 type atoms promotes electrophilic substitution at positions four and five, nucleophilic substitution at position two.

Carboxylation of imidazole is characteristic in positions four and five, metallization of N - alkyl - and N - aryl derivatives - in position two. Imidazole is resistant to many oxidizing agents and reducing agents: they are not oxidized by HNO₃, H₂CrO₄, KMnO₄, but the process of cleavage under the influence of peroxides occurs.

Alkylation reactions. Alkylation is the process of introducing an alkyl group into the molecule of an organic compound, as well as obtaining alkyl derivatives of chemical elements. Distinguish between C-, O-, N-, S - alkylation, depends on the atom of attachment of the alkyl group. Alkylating agents are often alkenes, alkyl halides, alcohols. The catalysts can be mineral (sulfuric acid H₂SO₄, hydrogen fluoride HF) and aprotic (AlCl₃, BF₃) acids. The mechanism is in-depth studied by the example of C -, O - alkylation.

It is known that tertiary alkyl halides undergo ionization most easily, in secondary it is more difficult, and primary hardly undergo ionization. The probability of the formation of the corresponding carbocations also decreases in this order.

Alkylation of imidazoles. The overall picture, if we do not focus on the mechanism of the direct introduction of substituents into the imidazole ring, then the reaction can be represented as a replacement of the hydrogen atom of the NH - group with a specific radical R (Figure 1):

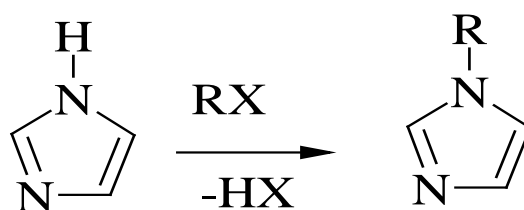


Figure 1 - Alkylation of imidazole

But N - substitution in the imidazole core is a complex mechanism. It must be remembered that when imidazole enters the alkylation reaction, it directly depends on the conditions, and sometimes in parallel, in the form of a base (SE₂ and SE₂ | -

mechanisms), anion (SE2 cB - mechanism), as well as in the form of a conjugated acid (SE2 cA - mechanism) (Figure 2).

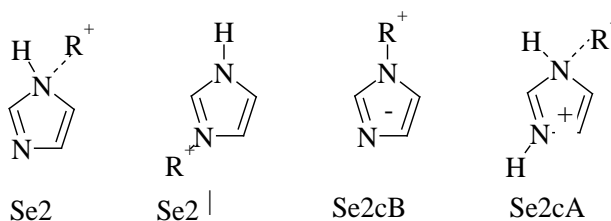


Figure 2 – N - substitution in the imidazole core

The classical method for producing N - alkyimidazoles is the reaction between alkyl iodide in a sealed tube and a heterocycle at values of 100 - 150 ° C. In this situation, the reaction proceeds mainly through the nitrogen atom - 3 (SE2^l - mechanism) (Figure 3):

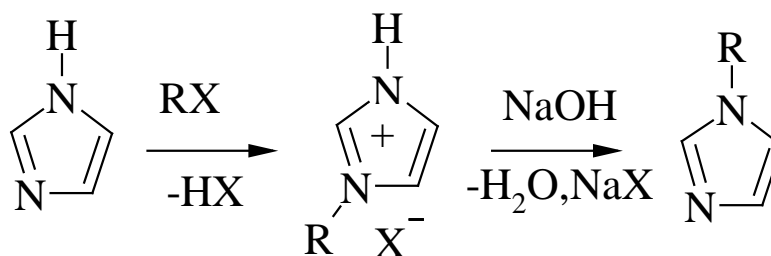


Figure 3 - The basic method of producing N – alkyimidazoles

When imidazole is alkylated in a neutral medium, the yield of N - substituted can reach 50%. Better values give the alkylation of imidazoles when using basic agents. If the nucleophilicity of nitrogen atoms in the imidazole anion is increased, then this will allow alkylation at a milder temperature [23].

1.5 Potential use of ionic liquids in the oil industry

The modern oil industry is facing many challenges throughout the chain, as the production and refining of crude oil to produce high-value petrochemical products is becoming difficult. Normal light and medium crude oil production peaked and tends to decline. In addition, some manufacturing countries are involved in the heaviest and highest content of pollutants (sulfur, nitrogen and metals), which are produced in countries such as Canada, China, Mexico, Venezuela and the United States. Such heavy and very heavy crude oils (HCOs) are more difficult to produce, transport, process and process into useful petroleum products.

Sometimes traditional technologies can be applied, but in most cases, new technologies are needed to ensure economical production of HCO, transport through pipelines, avoiding pressure drops, blocking pipelines and stopping production due to asphaltene and paraffin aggregation and decomposition. In addition, the higher content of heteroatoms in HCO makes them more difficult to refine due to mainly catalyst deactivation, which reduces the efficiency of processes such as desulfurization, denitrogenation and demetallization.

Moreover, the composition of crude oil varies significantly from one oil field to another among fields along the country. Heavy and super heavy oils are characterized by API densities of $20 < \text{API} < 10$ and $\text{API} \leq 10$, respectively. The latter oils have a specific gravity of about 1.0 g / cm^3 , i.e. they are heavier or larger than water, which makes dehydration of crude oil, for example, very difficult to get to refining. Therefore, the modern oil industry is faced with several problems of oil production and refining.

In recent years, ionic liquids (ILs) have attracted attention because of their properties and the versatility of potential applications in the oil industry. IL can be used to increase the fluidity of viscous and bituminous HCOs, which could increase oil production and transport, inhibit the aggregation of asphaltene and paraffins and reduce the deactivation of the refining catalyst by removing heteroatoms and coke from the fuel and the catalyst surface.

Due to the technological, environmental, and economic implications, this work tests current knowledge and potential uses of ionic liquids in the oil industry.

According to Speight (1999), crude oil is a mixture of gaseous, liquid, and solid hydrocarbons that are found in porous rock deposits called reservoirs that contain varying amounts of nitrogen, oxygen, and sulfur compounds, as well as traces of metals. Such a complex mixture can be divided into four component fractions: saturated (H), aromatic compounds (A), resins (C) and asphaltene (A).

Heavy and super heavy crude oils are mainly characterized by API gravity from $20 < \text{API} < 10$ and $\text{API} \leq 10$, respectively; and high viscosity ($> 10\text{-}10^4 \text{ Pa} \times \text{s}$). Such sections of crude oil are regional found in countries such as Canada, China, Mexico, Venezuela and the United States [24].

The use of transport fuel worldwide is developing at a very high speed. However, SO_x emissions from fuel combustion lead to environmental problems. Therefore, environmental laws were issued to limit the sulfur content and aromatic content of fuel.

There are two desulfurization methods: hydrodesulfurization (HDS) and non-HDS. In the past few years, most of the sulfur has been removed from the fuel through the HDS in refineries. However, sulfur and nitrogen-containing compounds remaining in the fuel, such as gas oil and diesel after HDS are mainly aromatic, compounds such as dibenzothiophene (DBT), carbazole and their alkyl derivatives. Consequently, conventional HDS require a higher temperature at a higher hydrogen pressure, which leads to higher operating costs and investments to obtain lower sulfur contents, reduce the deactivation of the HDS catalyst and comply with environmental standards. Room temperature ionic liquids have been used in a wide range of applications as green solvents for their low volatility and excellent thermal stability. With regard to crude oil

for the refining industry, the use of IL for desulfurization and dearomatization of diesel and gasoline fuels, as well as the reduction of naphthenic acids in oil, was reported.

In general, desulfurization, denitrogenation, and dearomatization were replaced by simple extraction or extraction in combination with catalytic oxidation in IL. Therefore, the removal of sulfur by simple extraction using IL shows low efficiency. Containing ILs can remove between 16-37% sulfur in gasoline.

Another approach using [BF₄]-containing ILs found that sulfur and nitrogen removal increased slightly with increasing heteroatom content in gasoline.

In addition, an important removal of sulfur and aromatic compounds in gasoline occurs first by increasing the IL / fuel ratio, and then several extraction cycles with IL. The removal of aromatic substances, mainly benzene, is an attractive subject of study, since the benzene content cannot exceed 0.62% in gasoline since 2011 in the United States. The extraction efficiency of nitrogen-containing compounds increases with a longer chain length of alkyl groups in the IL, and this was explained by an increase in volume. The extraction of the main quinolone can be facilitated by its coordination with the Zn center in the IL, but the extraction of indole is controlled by the interaction between the IL anion and the n-atom of the secondary amino group.

Conventional refining processes, like HDS, are typical catalytic in which the use of supported metals in the form of Al, Co, Mo, V, Ti is common.

Chemical oxidation in combination with IL extraction can increase dramatically compared to the simple extraction and removal of sulfur and nitrogen from automobile fuel without the formation of polluting gases.

ILs were successfully analyzed for the production, transportation and refining of crude oil under laboratory conditions. However, their potential local application remains to be proven. Many problems must be solved before IL can be applied at present in the oil industry. The economic, technological, environmental feasibility of large-scale production and use of ionic liquids must be approved before any oil company accepts their daily use.

The influence of the presence of IL in crude oil during production, transportation and refining should be confirmed in order to identify operational issues. Therefore, a lot of work is needed on the experimental factory and field scale to identify and eliminate possible operational problems, aspects of the infrastructure and processing of IL.

It is believed that IL have already opened a crucial window for safer, more environmentally friendly and individual solutions for the oil industry [25].

1.7 Removal of nitrogen compounds from diesel fuels

In recent years, the removal of nitrogen compounds from diesel oils has become an increasingly important topic for researchers, since N compounds will increase NO_x emissions during ion combustion and pollute the environment.

Hydrogenation technology is widely used to remove N-compounds from diesel in the oil industry. However, the technology cannot effectively remove certain

heterocyclic species due to the steric hindrance encountered by these compounds on the catalyst surface.

In addition, N-compounds, especially for basic N-compounds, can affect the activity of the hydrogenation catalyst and reduce the desulfurization efficiency; therefore, the traditional hydrogenation technology must be supplemented with other methods to reduce the content of nitrogen compounds in the feed [28].

Several recent studies have shown that ionic liquids with unique solvent properties have tremendous potential in removing N-compounds from fuel oils.

Imidazolium IL with the anion (EtSO₄)⁻ZnCl₂ achieved a very high extraction efficiency of N-almost 100% to neutral nitriles, but with moderate efficiency to basic nitriles. IL [Bmim] Cl showed a 48-58% extraction effect from direct diesel fuel, while in combination with ZnCl₂ its de-neutrification improved, with the removal effect of carbazole and pyridine they reached 93.8% and 97.8%, respectively. IL [S2] N (CN) can remove 96.8% carbazole and 63.5% pyridine from model oil. Brønsted acid IL, such as [Bmim] H₂PO₄, showed the best quinoline extraction rates, and the denitration rate reached more than 99% [29].

Since the physicochemical characteristics of the basic and neutral N compounds are very different, their simultaneous removal is necessary.

In this study, quinoline was chosen as representative of neutral and basic N-compounds to study the denitrification efficiency of several ILs based on imidazolium and the influence of operating conditions on the denitrification process was discussed [30].

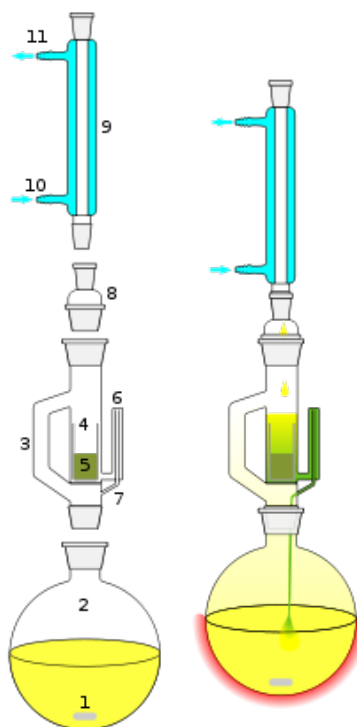
2 Experimental part

2.1 Materials and methods

Reagents: pyridine (> 99.5%, Alfa Aesar, USA); quinoline, indole (> 98%), iron (III) chloride hexahydrate (> 99%), zinc chloride, H₂O₂ (aqueous solution, 30 wt.%) and n-octane (Beijing Chemical Plant, China), hydrochloric acid (36, 6 wt.%), Ethyl alcohol (Chemreaktiv), 1-methylimidazole (Aldrich), ethyl acetate, acetonitrile (comp. Reagent). N-methylimidazole was further purified by distillation, the other chemicals were obtained without further purification.

A model fuel was prepared by dissolving an N-containing compound (pyridine, quinoline and indole) in n-octane.

Equipment: flat-bottomed, round-bottomed flask, funnel, dividing flask, water condenser, allonge, pump, Schlenk's vessel.



1 - Stirrer bar/anti-bumping granules; 2 - Still pot (extraction pot); 3 - Distillation path; 4 - Soxhlet Thimble; 5 - Extraction solid (residue solid); 6 - Syphon arm inlet; 7 - Syphon arm outlet; 8 - Reduction adapter; 9 - Condenser; 10 - Cooling water inlet; 11 - Cooling water outlet

Figure 4 – Soxhlet extractor

The extractor used a round bottom flask equipped with a reflux condenser containing the extracting solvent. In the center is a reservoir in which a sleeve is placed filled with a solid sample from which extraction will be carried out. The solvent is brought to a boiling point after it evaporates, it passes along the side outlet, falling into a reflux condenser, and condensation occurs and drains into the sleeve. While the sleeve is filled with solvent, the extraction of the substance into this solvent is observed.

When the liquid level in the sleeve reaches the upper level of the siphon, the sleeve is emptied, that is, the solution of the substance is drained into the original flask and the cycle repeats. As a result, the extractor makes it possible to perform multiple extractions due to the secondary use of a small amount of solvent. The extracted substance accumulates in the main flask. Efficiency increases because the sleeve is located above the flask and is heated by boiling solvent vapors.

All reactions were carried out under usual conditions, solvents were dried using established procedures and distilled immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh_2Cl , epichlorohydrin and 1-methylimidazole are purchased from Fluka and were used as received.

FTIR spectra were recorded from the KBr pellet on a Perkin-Elmer 1600 Fourier transform spectrophotometer and thermo gravimetric analysis of the catalysts was carried out on a Shimadzu DSC 60 A thermal analyzer up to $600\text{ }^\circ\text{C}$ at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

Elemental analysis was carried out on a Fisons EA 1108 Costech Combustion System CHNS-O instrument. Melting points were recorded by Gallenkamp Model apparatus with open capillaries. GC analyses were performed on a Shimadzu 2010 Plus Gas Chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) ($30\text{m} \times 0.32\text{mm} \times 0.25\mu\text{m}$).

2.2 Synthesis of ionic liquids and ruthenium catalysts based on ionic liquids

As a starting material we have chosen the ionic liquid - 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride, $[\text{C}_7\text{H}_{11}\text{N}_2\text{OCl}]\text{Cl}$. This ionic liquid was interesting for us, on the one hand, with the possibility of further functionalization, by replacing OH group with PPh_2 group (for coordination to a metal atom), on the other hand, due to the presence of C-Cl bond, required for further supporting of metal complex to nitrogen atom in NH_2 group of the copolymer substrate.

Thus, first we synthesized the compound 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride, $[\text{C}_7\text{H}_{15}\text{N}_2\text{OCl}]\text{Cl}$, 1 by the reaction of 1-methylimidazole and epichlorohydrin in ethanol at room temperature (Figure 5):

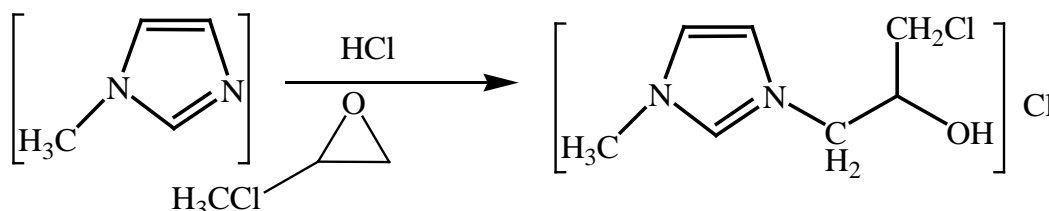


Figure 5 - The reaction of 1-methylimidazole with epichlorohydrin

This new compound was characterized by elemental analysis and IR spectroscopies. The IR spectrum shows a broad absorption band at 3357 cm^{-1} for the O-H stretching which is broadened and shifted toward lower frequency.

2.3 Synthesis of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride [C₇H₁₁N₂OCl]Cl, 1

To a stirred solution of 1-methylimidazole (20.733 g, 250 mmol) in ethanol (40 mL) at room temperature was carefully added concentrated hydrochloric acid (20.95 mL, 255 mmol). After addition of acid, the reaction mixture was cooled to room temperature and epichlorohydrin (24.057 g, 260 mmol) was added drop wise with stirring while maintaining the temperature at 25 °C. The reaction vessel was then sealed and stirred at room temperature for 24 – 48 h. The solvent was removed under reduced pressure with heating at 70 °C, followed by heating under high vacuum, to yield a liquid that became more viscous upon extensive drying, which was recrystallized from ethylacetate at 0 °C. The precipitated product was filtered and dried in vacuum yielding 1 as a off-white solid.

Yield 52.52 g, 98.1 %, m.p. = 94-95 °C.

IR, (KBr): ν 3357 (O-H), 3170, 3089 (aromatic C-H), 2985, 2856 (aliphatic C-H), 1575 (C=N), 1176 (C-N) cm⁻¹ (Figure 7);

Elemental Analysis: C₇H₁₁N₂OCl (175,0633 g/mol), calculated: C: 39.27, H: 7.06, N: 13.08; found: C: 39.18, H: 6.99, N: 13.00 (Figure 8).

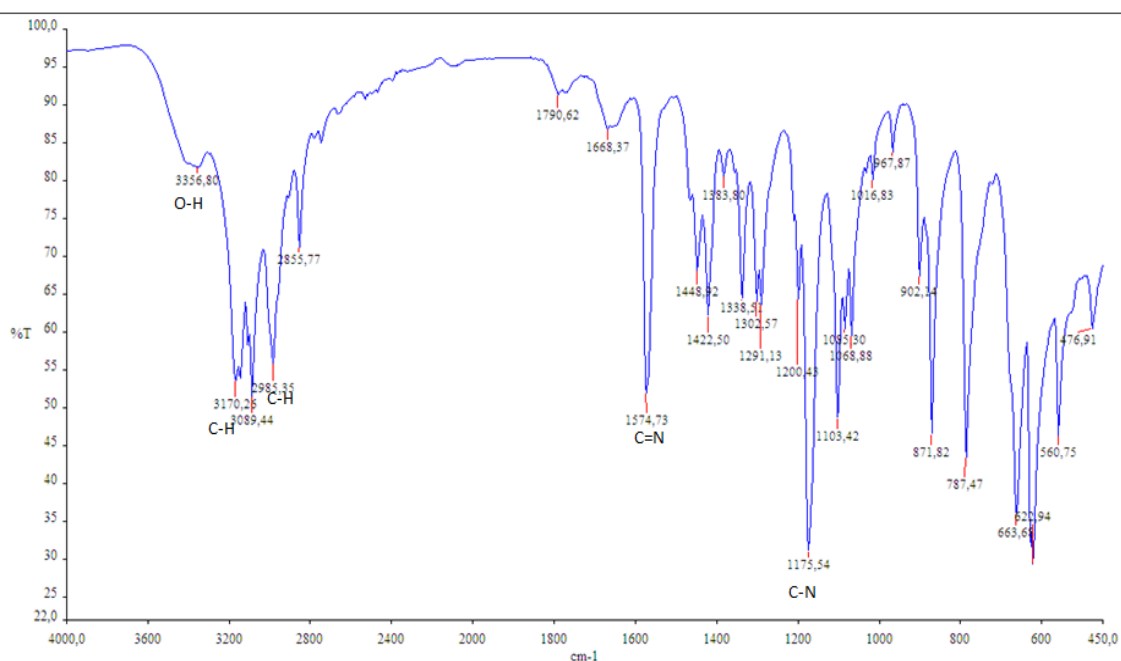


Figure 7 – IR spectroscopy of C₇H₁₁N₂OCl

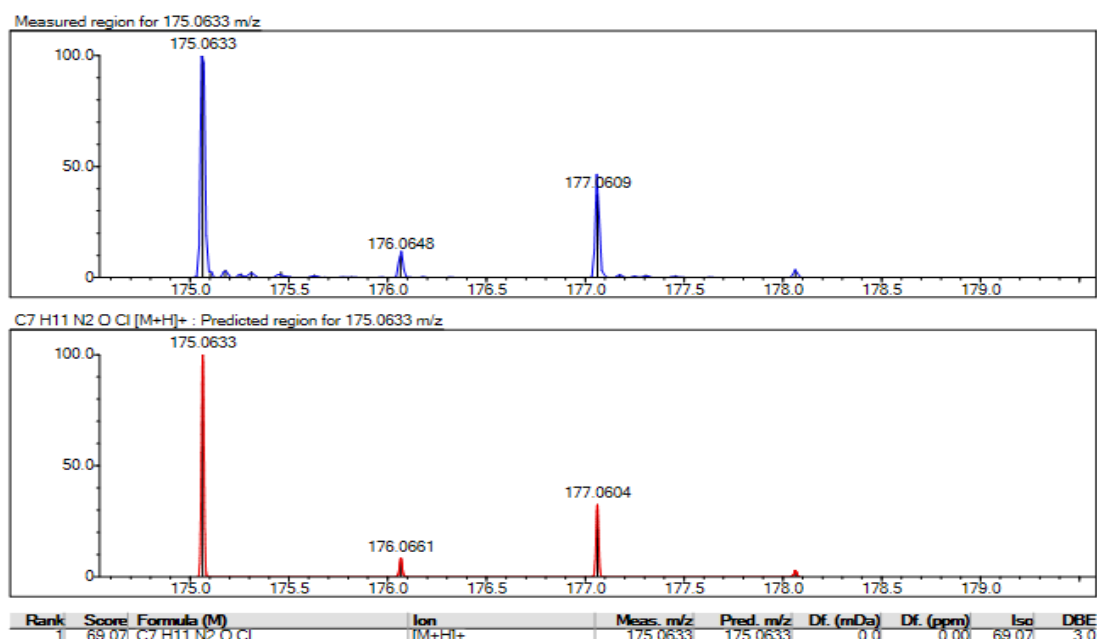


Figure 8 – Elemental Analysis of C₇H₁₁N₂OCl

2.4 Synthesis of phenyl based phosphinite ligands

Synthesis of 1-(3-chloro-2-(diphenylphosphanyl)oxypropyl)-3-methylimidazolium chloride [(Ph₂PO)-C₇H₁₄N₂Cl]Cl, 2.

A dry and degassed CH₂Cl₂ (20 mL) solution of 1-chloro-3-(3-methylimidazolidin-1-yl) propan-2-ol chloride under argon atmosphere (0.100 g, 0.467 mmol) was cooled to -78 °C in an acetone and dry ice bath. To the cooled solution was added drop wise a hexane solution of *n*-BuLi (0.293 ml, 0.467 mmol). After the addition, the mixture was stirred at -78 °C for 1 h and for another 30 additional minutes at room temperature. The reaction solution was cooled to -78 °C again and a solution of chlorodiphenylphosphine (0.105 g, 0.467 mmol) in CH₂Cl₂ (10 mL) was added drop wise to the reaction medium. Stirring was maintained for a further 1 h at -78 °C. Then the cooling bath was removed and the mixture was stirred for another 1 h at room temperature. Precipitated lithium chloride was removed by filtration under argon and then the volatiles were evaporated in vacuum to leave a viscous oily phosphinite ligand, 2.

Yield 0.180 g, 96.8 %.

IR: ν 3053 (aromatic C-H), 1434 (P-Ph), 1060 (O-P) cm⁻¹ (Figure 9);

Elemental Analysis: C₁₉H₂₄N₂OCl₂P (398.29 g/mol), calculated: C: 57.30, H: 6.07, N: 7.03; found: C: 57.18, H: 6.00, N: 6.96 %.

*Synthesis of [Ru((Ph₂PO)-C₇H₁₄N₂Cl)(η 6-*p*-cymene)Cl₂]Cl, 3.*

[Ru(η 6-*p*-cymene)(μ -Cl)Cl]₂ (0.077 g, 0.13 mmol) and [(Ph₂PO)-C₇H₁₄N₂Cl]Cl, 2 (0.100 g, 0.25 mmol) were dissolved in 25 mL of dry CH₂Cl₂ under argon atmosphere and stirred for 30 minutes at room temperature. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding 6 as a clear red solid.

Yield 0.162 g, 91.6 %, m.p. = 110-112°C.

IR, (KBr): ν 3053 (aromatic C-H), 1435 (P-Ph), 1047 (O-P), 532 (Ru-P) cm^{-1} (Figure 9);

Elemental Analysis: $\text{C}_{29}\text{H}_{38}\text{N}_2\text{OCl}_4\text{PRu}$ (704.49 g/mol), calculated: C: 49.44, H: 5.44, N: 3.98; found: C: 49.34, H: 5.32, N: 3.89.

2.5 Denitrogenation process

In this work, a 50 ml Schlenk's vessel was used. In this vessel, 1 g of ionic liquid was mixed with 5 g of model fuel.

Model fuel contains 5,000 ppm quinoline and indole, 20,000 ppm n-octane, as an internal standard in n-heptane.

The resulting mixture was stirred for 20 minutes. After stirring, left for 10 minutes at room temperature. In this case, 2 layers were formed (upper and lower).

After the extraction was complete, the top layer of heptane was analyzed by gas chromatography.

3 Results and discussion

3.1 Denitrogenation using IL

Denitrogenation of a model fuel containing 5,000 ppm quinoline and 20,000 ppm N-octane as an internal standard in N-heptane was carried out at room temperature using ionic liquids and ruthenium catalysts based on ionic liquids ([C₇H₁₁N₂OCl]₂Cl, 1; [(Ph₂PO)-C₇H₁₄N₂Cl]₂Cl, 2; [Ru(η 6-p-cymene)(μ -Cl)₂Cl]₂, 3).

The Nernst distribution coefficient K_N , defined as the mass ratio of the nitrogen content in IL to the nitrogen content in model fuel [mg (N) g (IL) / mg (N) g (oil)], was measured for each extraction. As indicated in table 1, all IL showed K_N values in the range of 2.4-6.5, which is equivalent to the recovery of quinoline 33-54%.

3.2 Synthesis of ionic liquids and ruthenium catalysts based on ionic liquids

This new compound was characterized by elemental analysis and IR. The IR spectrum shows a broad absorption band at 3357 cm⁻¹ for the O-H stretching which is broadened and shifted toward lower frequency.

Although the ionic liquid has been known since 2010, its crystal structure has not been studied. Since interatomic distances and angles were important for us, we have grown single crystals of this ionic liquid. The structures of the 1 found to be in good agreement with the theoretical values. The colorless crystal of the compound [C₇H₁₅N₂OCl]₂Cl crystallizes in the monoclinic space group of P2(1).

The unit cell dimensions are $a = 4.90220 \text{ \AA}$, $b = 14.1086 \text{ \AA}$, $c = 7.29760 \text{ \AA}$. Its asymmetric unit contains two of the molecule, which has two-fold crystallographic symmetry that can be expressed as 2-fold screw axis with direction [0, 1, 0] at 0, y, 0 with screw component [0, 1/2, 0].

The distance between stereocenters of C(2)-C'(2) in packing structure is about 7.084 \AA and some of selected bond lengths are C(2)-C(3) 1.509 \AA , C(3)-N(1) 1.462 \AA , C(1)-Cl(1) 1.793 \AA , N(2)-C(7) 1.459 \AA , C(2)-O(1) 1.414 \AA . The ionic chloride which proves the ionic liquid structure of the compound is approximately 3.688 \AA to the stereogenic C(2) atom. The structure has also intramolecular O(1)-H(1)···Cl(2) hydrogen bond with distances 0.82 \AA and 3.075 \AA and the angle of 166.93°.

The comprehensive crystal data related about structure 1 is given in Table 1.

Table 1 - Crystallographic data and structure refinement for [C₇H₁₁N₂OCl]₂Cl.

Parameters	
Empirical formula	C ₇ H ₁₁ ClN ₂ O
M	175.0633 g/mol
Crystal system	Monoclinic
Crystal size(mm)	0.50×0.25×0.16

Since our next task was the synthesis of metal complexes, containing in the structure an ionic liquid, we needed to enclose into the ionic liquid a functional group

that can be easily coordinated to platinum group metals. We have used PR₂ group (R = Ph). Fixing this group into the structure of ionic liquid was performed by the reaction between the ionic liquid 1 and PR₂Cl with prior deprotonation of the OH group with butyl lithium.

As a result of ongoing research program for developing highly active catalysts, we synthesized ionic liquids based on phosphinite monodendate ligand. These phosphinite ligand [(Ph₂PO)-C₇H₁₄N₂Cl]Cl, 2 was synthesized from the starting material 1 and PPh₂Cl in CH₂Cl₂ solution, by the hydrolysis method.

The LiCl salt was separated by filtration and the ligands were obtained by evaporating the solvent in vacuum in good yields.

Our further task was the synthesis of homogeneous and heterogeneous catalysts based on ionic liquid 2 and 3. As the initial metal complex we can use dimer (for example: a dimeric complex of ruthenium chloride-[Ru(η⁶-benzene)(μ-Cl)Cl]₂), or a monomeric complex, containing labile ligand, in particular, 1,5-cyclooctadiene (for example monomeric complexes of platinum and palladium such as: [PtCl₂(cod)] and [PdCl₂(cod)]). Reactions of the ionic based monodendate phosphinite with metal precursor [Ru(η⁶-benzene)(μ-Cl)Cl]₂ is shown in Figure 8.

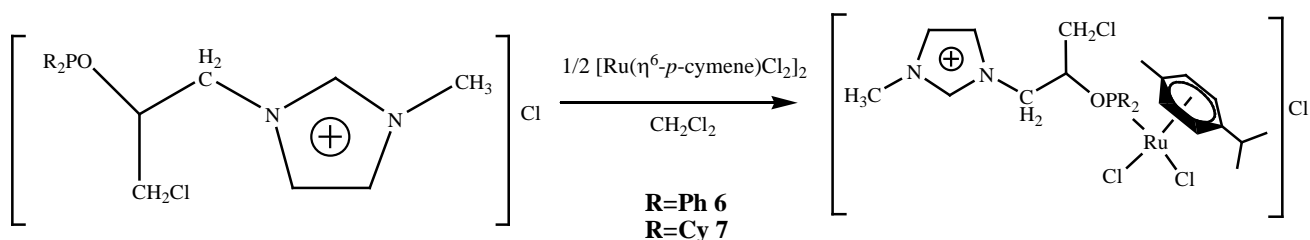


Figure 8 - Reaction of the ionic based monodendate phosphinite with metal precursor [Ru(η⁶-p-cymene)(μ-Cl)Cl]₂

The ability of dimers {[Ru(arene)(μ-Cl)Cl]₂} to form mononuclear complexes of general formula [Ru(η⁶-arene)Cl₂L] is well-known. As expected, the reaction of 2-3 with [Ru(η⁶-benzene)(μ-Cl)Cl]₂ gave corresponding complexes [Ru((Ph₂PO)-C₇H₁₄N₂Cl)(η⁶-arene)Cl₂]Cl {arene: benzene}, in high yields as air stable, red microcrystalline powder.

The phosphinite ligands were expected to cleave the [Ru(benzene)Cl₂]₂ dimer to give the corresponding complexes via monohapto coordination. The initial color change, i.e., from clear orange to deep red, attributed to the dimer cleavage most probably by the phosphinite ligand.

The reaction of stoichiometric amounts of [Ru(η⁶-benzene)(μ-Cl)Cl]₂ and [(Ph₂PO)-C₇H₁₄N₂Cl]Cl, 2 affords the [Ru((Ph₂PO)-C₇H₁₄N₂Cl)(η⁶-benzene)Cl₂]Cl, 3 in good yield as a dark red microcrystalline powders. These complexes are highly soluble in CH₂Cl₂ and slightly soluble in hexane and can be crystallized from CH₂Cl₂/hexane solution.

The starting Ru(II) complex was [Ru(η⁶-p-cymene)(μ-Cl)Cl]₂, which was prepared from the reaction of the commercially available α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) with RuCl₃ [246]. The whole reactions with [Ru(η⁶-p-

cymene)(μ -Cl)Cl₂ with ligand 2 is represented by Figure 8. The reactions of [Ru(η^6 -*p*-cymene)(μ -Cl)Cl₂] with equivalent of 2 in CH₂Cl₂ at room temperature gave the red compounds [Ru((Ph₂PO)-C₇H₁₄N₂Cl)(η^6 -*p*-cymene)Cl₂]Cl, 3 in high yield. The structures of the P-coordinated complex 3 is supported by elemental analyses, spectroscopic data (IR) (Figure 9).

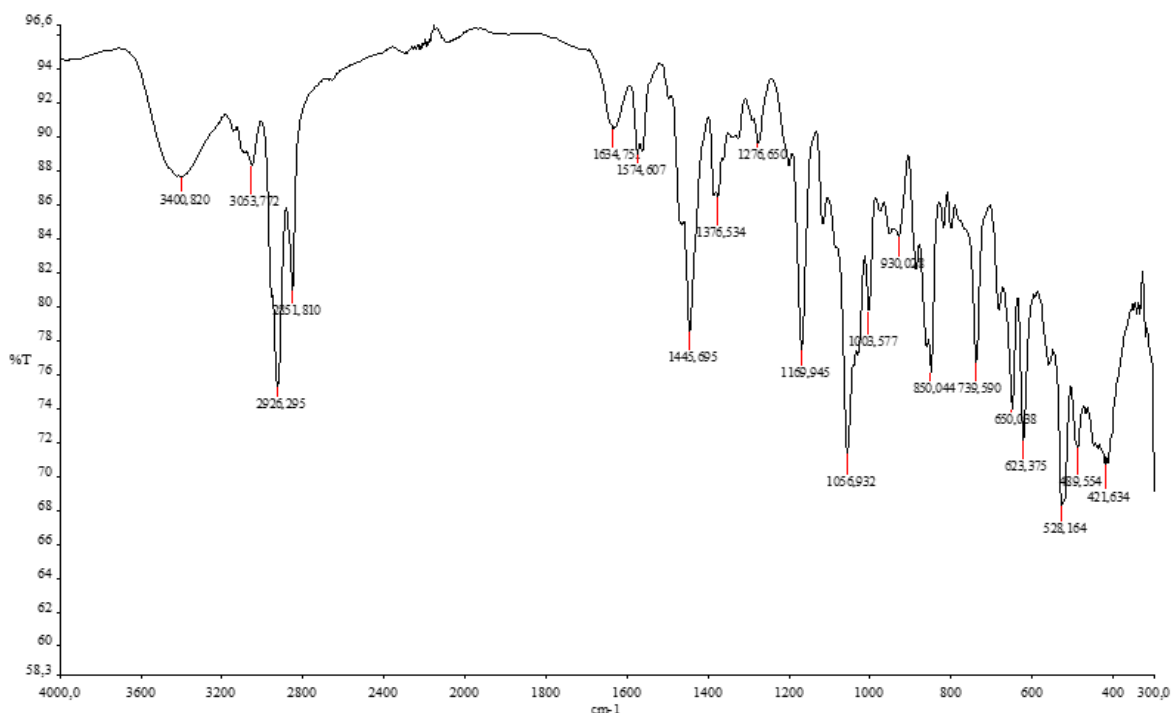


Figure 9 – IR spectroscopy of [Ru(η^6 -*p*-cymene)(μ -Cl)Cl]₂ complex

In conclusion, within this chapter the synthesis of 2 new ionic liquids and 4 ruthenium catalysts based on these new ionic liquids was described and their structures were discussed and confirmed with modern instrumental methods.

3.3 Denitrogenation using Ru-containing IL

The effect of the Ru content in ionic liquid 1 was evaluated for the desorption of a model fuel containing 5,000 ppm quinoline and 20,000 ppm n-octane as an internal standard in n-heptane.

As shown in Table 2, the extraction ability of [C₇H₁₁N₂OCl] Cl, expressed in KN value, increased from 3.34 to 46.8 when the equimolar amount of Ru was dissolved in [C₇H₁₁N₂OCl] Cl / Ru, although the KN value decreased with increasing molar ratio [C₇H₁₁N₂OCl] Cl / Ru, quinoline extraction was maintained above 80% in a molar ratio range of 1-20.

Table 2 - Effect of the molar ratio [C7H11N2OCl] Cl / Ru on the extraction of quinoline in model fuel

Molar ratio [C7H11N2OCl] Cl / Ru	DE^b (%)	K_N
d	40.6	3.34
20	81.6	21.5
10	84.6	27.9
5	85.3	28.7
Ru	42.3	5.44

Quinoline also was isolated at intensively high mass ratios of the model / IL = 20 and 30 (IL = [Ru (η 6-p-cymene) (μ -Cl) Cl]₂, 3) in order to obtain more significant results from an economic point of view. High K_N values of 44.7 and 42.9 were maintained even at higher molar ratios of 20 and 30, respectively, which indicates that Ru-containing IL can be used as promising N-extractants for practical use.

Ru-containing IL was also tested for the extraction of indole and acridine. As indicated in Table 3, 98.9% indole was extracted from model fuel containing 5000 ppm indole in n-heptane when treated with [Ru (η 6-p-cymene) (μ -Cl) Cl] 2, wt. fuel / mass models [Ru (η 6-p-cymene) (μ -Cl) Cl] 2 = 5).

Ru-containing IL, [Ru (η 6-p-cymene) (μ -Cl) Cl] 2 is also effective for denitrification of model fuel which contained 5000 ppm acridine, but the degree of extraction of acridines was lower than the extraction of indole and quinoline. To find the ease of extraction of nitrogen compounds, the mixture [Ru (η 6-p-cymene) (μ -Cl) Cl]₂ was mixed with a model fuel containing three nitrogen compounds: quinoline, indole, acridine (Table 3).

As expected during the extraction of one N-compound, the degree of extraction identified in the following order: indole > quinoline > acridine. The same tendency was observed for extraction with pure IL [C7H11N2OCl] Cl which indicates that the interaction of IL with the N-compound depends on the presence of the N-H bond, as well as on the steric thickness around the nitrogen atom or the basicity of the nitrogen compound. As shown in Table 4, more than 91% of indole was removed from the model oil using pure IL, 1 only with a fuel molar ratio / IL = 5, most likely due to the strong interaction between the H (N-H) atom and the main IL anion.

Table 3 - Denitrification of a model fuel containing indole or acridine with IL and Ru-containing IL

IL	indole		acridine	
	DE^b (%)	K_N	DE^b (%)	K_N
[C7H11N2OCl] Cl	91.8	328	35.4	3.01
[Ru (η 6-p-cymene) (μ -Cl) Cl] ₂	98.9	385	80.6	21.8

Table 4 - Denitrogenation of a model fuel containing quinoline, acridine and indole

IL	N compound	DE^b (%)	K_N
[C7H11N2OCl] Cl	indole	91.80	328
	quinolone	38.9	3.15
	acridine	35.4	3.01
[Ru (η^6 -p-cymene) (μ -Cl) Cl] ₂	indole	98.9	385
	quinolone	84.3	29.7
	acridine	80.6	21.8

This result convincing evidence that indole IL extraction mainly controls the interaction of N-H indole with -Ru. The effect of the interaction between indole and the center of IL, 1 through the N atom seems to be negligible.

3.4 Conclusions to the chapter

Ru-containing IL obtained by the interaction of [Ru (η^6 -p-cymene) (μ -Cl) Cl]₂ was effective extractant for the denitrogenation of model fuel containing quinoline, acridine and indole.

In particular, the effectiveness of ruthenium chloride with IL for the extraction of basic nitrogen compounds, such as quinoline and acridine, was significantly improved by more than two times due to the joint presence of Lewis acids of acidic RuCl₃.

CONCLUSION

The diploma work dedicated to the development of new extractive systems based on ionic liquids for the effective denitrogenation of diesel fuel.

In this diploma work has been considered the synthesis of monocationic metal-containing ionic liquids and the study of their extractive ability concerning nitrogen compounds contained in diesel fuels. The identification of metal-containing ionic liquids having the maximum affinity for nitrogen compounds was performed.

During the synthesis, the following conclusions were made:

- the interaction of 1-methylimidazole with hydrochloric acid and epichlorohydrin led to the formation of 1-chloro-3-(3-methylimidazolidine-1-yl)propane-2-ol chloride [C₇H₁₁N₂OCl]Cl viscous ionic liquid in 83% yield. The resulting compound was purified from the solvent;

- phenyl based phosphinite monodentate ligand [(Ph₂PO)-C₇H₁₄N₂Cl]Cl for further synthesis of metal-containing ionic liquid [Ru((Ph₂PO)-C₇H₁₄N₂Cl)(η⁶-p-cymene)Cl₂]Cl were synthesized. The mass ratio of IL / Ru ranged from 1 to 20;

- a model fuel containing quinoline, acridine and indole was prepared for subsequent denitrogenation;

- identified that Ru-containing IL obtained by the interaction of RuCl₃ with phenyl based IL-imidazolium is effective extractants for the denitrogenation of a model oil containing quinoline, acridine, and indole.

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