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Review

Ionic Liquids as Components of Systems for Metal Extraction

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Abstract: This review addresses research and development on the use of ionic liquids as extractants and diluents in the solvent extraction of metals. Primary attention is given to the efficiency and selectivity of metal extraction from industrial wastewater with ionic liquids composed of various cations and anions. The review covers literature sources published in the period of 2010–2021. The bibliography includes 98 references dedicated to research on the extraction and separation of lanthanides (17 sources), actinides (5 sources), heavy metals (35 sources), noble metals, including the platinum group (16 sources), and some other metals.

Keywords: extraction; extractant; ionic liquid; separation; purification

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1. Introduction

Extraction with ionic liquids (ILs) is a versatile method for the recovery and separation of metals, in which ILs can serve both as diluents and as extractants [1]. Owing to the possibility of combining different types of anions and cations, it is possible to synthesize ionic liquids with specific properties and characteristics [2,3].

Ionic liquids are a good alternative to organic solvents because of their low toxicity, thermal and chemical stability, non-flammability, the absence of vapor release, and good solvation capacity. Ionic liquids have high sensitivity and selectivity towards many types of analytes, which is due to different mechanisms of interaction, including electrostatic, hydrophobic–hydrophilic, dipole–dipole, and π–π interactions, ion exchange, and hydrogen bonding [4–7]. Therefore, ILs are being used more and more often in solvent extraction processes related to metal recovery [8–12]. ILs serve as selective extractants for heavy, rare earth, alkali, noble, and radioactive metals.

For example, it was demonstrated [13] that ionic liquids increase the efficiency and selectivity of metal extraction by several orders of magnitude. The potential of ILs as more environmentally benign substitutes for traditional organic solvents used to extract metals has been highly appreciated. Ionic liquids were considered for the hydrometallurgical extraction of metals, especially platinum-group metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum) from urban mines [14]. The benefits of ILs for the efficient separation of metal ions from aqueous solutions via electrostatic, van der Waals, and ion-pair interactions have been demonstrated [15]. Furthermore, ILs can be isolated by back extraction and reused for solvent extraction, adsorption, and membrane separation.

Ionic liquids allow for the efficient recovery of rare earth elements from magnets and luminophores [16], as well as various scraps and electronic waste [17]. In essence, with the appropriate selection of extraction systems and the chemical nature of ILs, it is possible to attain the isolation and separation of virtually all metals of the periodic table from Li(I) to Pu(IV) [18].

The chemical structure of ionic liquids is presented in the Supplementary Materials.

2. Ionic Liquids as Extractants in Extraction Systems

Despite the fact that ILs are more and more often considered as extractants for metals in hydrometallurgical processes [19,20], due to their high cost, they should provide better characteristics (high distribution ratios, selectivity, reusability, stability, etc.) than existing large-tonnage industrial extractants. Furthermore, a problem associated with the use of ILs as extractants is their high viscosity; therefore, they are dissolved in molecular solvents. This approach allows for producing highly efficient extraction systems for the recovery of indium(III) and gold(III) from electronic waste [21,22] and Mo(VI) in high (more than 99%) yields [23].

Although undiluted ILs have also been used as extractants in many studies, it is noted that they are saturated with water during extraction, which considerably decreases the viscosity. For example, tantalum(V) can be extracted in this way from aqueous solutions with high efficiency [24], and Pd(II) can be recovered [25] with an efficiency of more than 99%.

In view of their low melting points (below 100 °C) and environmental safety, IL extractants containing bulky cations with a positively charged heteroatom, such as phosphonium, ammonium, and imidazolium cations, are used most often. Below, we consider these types of extractants in more detail.

2.1. Ionic Liquids Based on Phosphonium Cations for Metal Extraction

According to published data, ionic liquids based on phosphonium cations are promising extractants for noble metals, rare earth elements, transition metals, and radionuclides; they can also be used to separate transition and rare earth metals.

Cyphos 104 and Cyphos 101 are the most popular and promising ILs. Cyphos 104 is an efficient extractant for the complete recovery of gallium(III), indium(III), zinc(II), and tin(II) from electronic waste, which is certainly important for both environmental and economic reasons. The extraction efficiency of gallium from 3 mol L^{-1} HCl can reach 99.8% [26], while the extraction of alkaline waste from LCD screen leach liquor resulted in indium(III), zinc(II), and tin(II) recovery with purities of 100%, 98.9%, and 100%, respectively [27]. The mechanism of indium extraction from chloride medium is described [27] by the following equation:

$$\mathrm{In^{3+}}_{\mathrm{aq.}} + 3\,\mathrm{Cl^{-}}_{\mathrm{aq.}} + 2\,[\mathrm{R_3R'P^{+}A^{-}}]_{\mathrm{org.}} \leftrightarrow [\mathrm{InCl_3{\cdot}2R_3R'P^{+}A^{-}}]_{\mathrm{org.}},$$

where $R_3R'P^+$ is trihexyl(tetradecyl)phosphonium, and A is bis(2,4,4-trimethylpentyl) phosphinate.

In a comparison of the extraction of europium(III) from a chloride medium with the organophosphorus D2EHPA extractant, the Cyphos 104 ionic liquid, and a mixture of the above extractants, a quantitative europium recovery was attained using only a mixture of 0.05 mol L^{-1} D2EHPA and 0.02 mol L^{-1} Cyphos 104. The authors also noted that Cyphos 104 has a higher loading capacity than D2EHPA; however, D2EHPA is a more appropriate extractant for the separation of yttrium(III) and europium(III). The highest separation factors β (Y(III)/Eu(III)) were 10,546 and 629.7 for extraction with D2EHPA and Cyphos 104, respectively [28].

The Cyphos 101 IL and its analogs can also be used for the separation of rare earth metals from transition metals such as iron(III), cobalt(II), copper(II), manganese(II), and zinc(II). This liquid is used without dilution and acts as both the organic phase and the extractant.

For example, $[P_{66614}][NO_3]$, an analog of Cyphos 101 with a nitrate anion, was used for highly efficient (with up to 99.9% purity) separation of samarium(III) and lanthanum(III) rare earth elements from cobalt(II) and nickel(II) in the processing of permanent magnets and nickel metal hydride batteries [29]. In addition, this ionic liquid can reduce the viscosity of the di(2-ethylhexyl) 2-ethylhexylphosphonate extractant and increase the extraction efficiency for rare earth elements, including yttrium(III), terbium(III), europium(III), and cerium(III), from waste luminophores to up to 90% due to synergistic effects [30].

Cyphos 101 in toluene is an efficient extractant for gold(III) from thiosulfate solutions, with an extraction efficiency of 99% [31]; undiluted Cyphos 101 provides quantitative recovery of platinum(IV) and palladium(II) from a leaching acidic solution of waste catalytic converters [32].

A functionalized ionic liquid, $[P_{66614}][MA]$, an analog of Cyphos 101 with the N,N,N′,N′-tetra(2-ethylhexyl)malonate anion, in combination with the $[P_{66614}][NO_3]$ IL as a diluent, is used to extract europium(III) and other trivalent rare earth elements from a nitric acid medium. The extraction behavior of europium was studied as a function of various parameters, such as the pH of the solution, temperature, concentrations of the extractant and salting-out agent, and metal content in the aqueous medium. It was found that this ionic liquid system can efficiently separate rare earth metal ions from transition metal ions, which are usually present together in luminophore lamps and magnets [33].

A group of researchers from the Netherlands proposed the use of a low-melting ionic liquid, tetraoctylphosphonium oleate $[P_{8888}]$[oleate], for the selective extraction of transition metals, e.g., cobalt(II), from chloride solutions. Owing to relatively low viscosity and good stability to environmental exposure, the process can be conducted in continuous mode at room temperature and occurs at a high rate and with high efficiency (96% within 15 min). However, the continuous-flow setup for extraction developed in this study is applicable only to the treatment of wastewaters containing low concentrations of metal ions. Furthermore, it is much more expensive than the currently used setup with ion exchange resins, since this requires additional membrane filters at the outlet of the settling tanks to minimize the leakage of the ionic liquid to the aqueous phase [34].

Lithium was extracted using tetrabutylphosphonium bis(2,4,4-trimethylpentyl) phosphinate $[P_{4444}]$[BTMPP] in toluene. The extraction efficiency of lithium with the synthesized ionic liquid was much higher (94.07%) than that for extraction with the molecular analog, bis(2,4,4-trimethylpentyl)phosphinic acid. One more advantage is that the $[P_{4444}]$[BTMPP] ionic liquid can be completely regenerated and reused without the deterioration of extraction properties [35].

Trihexyl(tetradecyl)phosphonium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate $[P_{66614}]$[hfac] in toluene can be used to recover the U(VI), Pu(IV), Am(III), and Eu(III) radionuclides from acidic waste solutions. Liu et al. [36] were able to back extract 98.99% of Am(III), 99.12% of Eu(III), 99.64% of U(VI), and 99.89% of Pu(IV) from 0.03 mol L^{-1} $[P_{66614}]$[hfac] into 1 M guanidine carbonate + 0.05 mol L^{-1} EDTA within 15 min.

Using the $[P_{1888}][C_6SAc]$ ionic liquid, it is possible to attain 90% recovery of zinc(II) from aqueous solutions within 2 h [37] and more than 80% recovery of high-purity cadmium and copper [38]. The extraction efficiency of cadmium(II) and copper(II) reached 30% as quickly as 30 min after the start of the process.

High rates of cadmium(II) and copper(II) extraction were also noted for the use of undiluted phosphonium ILs with thiosalicylate derivatives. It was found that $[P_{66614}]$[BTB] and $[P_{66614}]$[PTB] ILs extract copper, cadmium, and zinc from aqueous solutions with an efficiency of more than 90% [39].

2.2. Ionic Liquids Based on Ammonium Cations for Metal Extraction

Ionic liquids containing ammonium cations are promising extractants for Group 5 and 6 metals, period 4 transition metals, noble metals, alkali metals, and rare earth elements and for the separation of light and heavy rare earth elements or precious and base metals.

2.2.1. Group 5 and 6 Metals of the Periodic Table of Elements

The Aliquat 336 ionic liquid operating over a broad pH range proved to be efficient for the extraction of vanadium and molybdenum. For example, Wang et al. [40] used Aliquat 336 IL dissolved in sulfonated kerosene and thus attained complete recovery of trace amounts of vanadium(V) from an aqueous solution of ammonium tungstate. During the experiments, the authors [40] established the formation of a third phase when using 1 vol.% Aliquat 336 and 1 vol.% 2-octanol (modifying agent). However, when the 2-octanol concentration was increased to 5 vol.%, the formation of the third phase was not observed, and extraction was faster. However, simultaneously, the efficiency of the extraction of vanadium(V) decreased. The authors attributed the decrease in the extraction efficiency to the inhibitory effect of 2-octanol on ILs. As benefits of this method over vanadium precipitation by calcium(II) salts, the authors noted high selectivity and high speed.

A flow diagram for the separation of vanadium(V) and aluminum(III) using Aliquat 336 in sulfonated kerosene was developed [41]. It was found that when the initial pH is 0.78, the ratio of organic and aqueous phases is 1:2, the concentration of IL is 40 vol.%, and the time to establish equilibrium is 3 min, then the efficiency of extraction of vanadium is 99.06%, while that of aluminum is only 7.95%; thus, the separation factor β (V(V)/Al(III)) is 1221. Presumably, the mechanism of the extraction of vanadium(V) with Aliquat 336 from the oxalic acid leachate of shale is anion exchange between the $VO(C_2O_4)_2{}^{2-}$ anion and the chloride anion of the IL:

$$2[R_4N^+Cl^-]_{org.} + VO(C_2O_4)_2{}^{2-}{}_{aq.} = [(R_4N)_2VO(C_2O_4)_2]_{org.} + 2\,Cl^-{}_{aq.}$$

For the back extraction of vanadium, 8 mol L^{-1} HCl was proposed.

The authors concluded that this setup is environmentally safe; it does not require the control of pH and allows faster extraction of vanadium than systems containing inorganic acids. This setup can be used for the processing of vanadium-bearing shale.

Aliquat 336 diluted with kerosene can also be used to recover molybdenum(VI) from an alkaline solution containing aluminum(III), copper(II), and nickel(II) [42].

It was noted that the molybdenum extraction efficiency was increased to 98.5% by increasing the extractant concentration to 0.1 mol L^{-1}, while the process was virtually unaffected by changes in the temperature.

The authors pointed out [42] that Aliquat 336 can be used for the hydrometallurgical recovery of molybdenum from spent hydrotreating catalysts. However, they did not consider the separation of molybdenum from other elements contained in spent catalysts such as cobalt, rhodium, platinum, palladium, and vanadium.

2.2.2. Transition Metals of Periods 3 and 4 of the Periodic Table of Elements

Using the bifunctional ionic liquid [A336][Cy272] diluted with kerosene, complete recovery of Cu(II) from a solution containing other divalent metals, such as iron(II), zinc(II), cadmium(II), cobalt(II), and nickel(II), was attained [43,44].

In addition, Aliquat 336 ([A336]Cl) and its analogs with anions other than Cl^- are suitable for the recovery of period 4 metals and the separation of these metals from REEs, particularly from spent metal hydride batteries and Nd-Fe-B and Sm-Co permanent magnets.

For example, this extractant and its analogs with thiocyanate ([A336][SCN]) and nitrate ([A336][NO_3]) anions were used for the recovery and selective separation of cobalt(II), copper(II), and samarium(III) (the separation factor β (Co(II)/Sm(III)) was more than 7500), which are the major components of Sm-Co magnets [45]. More than 99.9% of cobalt and 99.7% of copper without samarium impurity were isolated using the [A336][SCN] extractant. However, due to the instability of the thiocyanate ion, the [A336][SCN] ionic liquid is thermally unstable and can also decompose in highly acidic and highly alkaline solutions. In this respect, the [A336][NO_3] ionic liquid is more stable.

However, [A336][SCN] and [A336][NO_3] ionic liquids were used without the addition of diluents; therefore, the extraction system had a fairly high viscosity. To decrease the viscosity, the reaction mixture was slightly heated (when the temperature was raised to 40–50 °C, the viscosity of the system decreased fourfold).

It is known that the classical design of liquid-liquid extraction includes an aqueous phase and an organic phase that is immiscible with the aqueous phase; however, in a study [46] devoted to the extraction of cobalt(II) and samarium(III) with Aliquat 336, water was replaced by ethylene glycol. Toluene was used as the diluent. To decrease the solubility of ILs in ethylene glycol, lithium chloride was added to the ethylene glycol phase. It was noted that cobalt was better extracted from ethylene glycol than from water, while samarium was not extracted from the organic phase. However, the authors did not provide an explanation for this fact. This system can also be used to separate metal pairs: nickel(II) and lanthanum(III), which are present in nickel metal hydride batteries, and Zn(II) and Eu(III). It can also be used to extract Fe(III) from magnets.

The drawbacks of using ethylene glycol as a polar phase include toxicity, the difficulty of regeneration, and higher viscosity (18 mPa·s at 25 °C) compared to that of water (0.89 mPa·s at 25 °C) and also the loss of extractant. The addition of lithium chloride also increases the viscosity of ethylene glycol.

Ionic liquids based on primary amines can also be used for metal extraction. For example, Alguacil et al. [47] studied the behavior of an ionic liquid based on the amine Primene JMT as the sulfate $PJMTH^+ HSO_4^-$ dissolved in Solvesso 100 for the extraction of indium(III) as functions of the time of the process, temperature, concentrations of the metal and sulfuric acid in aqueous solution, and the amount of extractant used. When the sulfuric acid concentration in aqueous solution decreased from 0.5 mol L^{-1} to 0.1 mol L^{-1}, and the $PJMTH^+ HSO_4^-$ concentration increased from 0.025 mol L^{-1} to 0.25 mol L^{-1}, the recovery of indium ions increased.

It was also noted that $PJMTH^+ HSO_4^-$ had the highest selectivity for In(III) over Zn(II), Mn(II), Cr(III), and Cr(VI).

The advantages of ionic liquids based on tetraalkylammonium (N_{8888}C18:1 and N_{8881}C18:2) oleate and linoleate over ILs based on phosphorus-containing anions were noted by researchers from the Netherlands [48] and included easy preparation, particularly from renewable feedstock, biocompatibility, and non-toxicity. These extractants showed high extraction efficiency for period 4 transition metals (>99%). Parmentier et al. [49] studied the mechanism of the extraction of zinc(II), cobalt(II), and nickel(II) from chloride solutions with the N_{8888}C18:1 IL. The mechanism of nickel and cobalt extraction is based on the formation of a metal–IL complex comprising three ionic liquid molecules. Zinc, in turn, interacts with only two extractant molecules. This fact is explained by the higher distribution ratio of zinc in comparison with nickel or cobalt.

2.2.3. Noble Metals

The Aliquat 336 IL is an efficient extractant for noble metals such as gold(III), platinum(IV), and palladium(II) [50]. Aliquat 336 allows recoveries of 100.0% of gold(III), 99.8% of platinum(IV), and 99.97% of palladium(II) from 0.1 M aqueous solutions of HCl within 5 min.

Vereycken et al. [51] proposed a one-stage separation method for the noble metals Pd(II), Pt(IV), and Au(III) from Fe(III), Cu(II), Ni(II), and Rh(III) impurities using undiluted Aliquat 336 IL and bromide and iodide Aliquat 336 derivatives, [A336][Br] and [A336][I]. Platinum(IV) and palladium(II) were quantitatively recovered upon extraction with Aliquat 336, [A336][Br], and [A336][I], while gold(III) was quantitatively extracted with Aliquat 336 and [A336][Br]. However, data on the efficiency of the extraction of gold with [A336][I] were not provided. In the authors' opinion, this is a promising method for the processing of electronic waste and for analytical purposes. The benefits of the proposed method include the use of only one extraction phase in the flow diagram, the absence of volatile and easily flammable organic diluents, and low contamination of the aqueous phase due to the low water solubility of Aliquat 336, [A336][Br], and [A336][I]. The drawbacks of the method are the need to use relatively small volumes of the aqueous phase; the high viscosity of the ILs and the low rate of mass transfer would be more pronounced when moving to large volumes.

By combining tetrahexylammonium $(C_6H_{13})_4N^+$ (THN) and tetraoctylammonium $(C_8H_{17})_4N^+$ (TON) cations with various anions, such as Br^-, SCN^-, and bis(trifluoromethylsufonyl) imide anion $[NTf_2]^-$, it is possible to obtain ionic liquids suitable for the extraction of the noble metals Au(III), Pt(II), and Pt(IV) from industrial wastewater.

For example, it was shown [52] that $[NTf_2]$-based ILs, $[TON][Tf_2N]$ and $[THN][Tf_2N]$, extract gold(III) with an efficiency of 95%; the highest recovery of platinum(II) is attained with ionic liquids containing dicyanamide or bromide anions: [THN][Br], [TON][Br],

[THN][Dca], and [TON][Dca] (extraction efficiency of more than 90%; distribution ratios above 200), while platinum(IV) is best recovered with liquids containing bromide and thiocyanate anions: [THN][Br] and [THN][SCN] (extraction efficiency of 100%, distribution ratios above 1000).

It was also shown that the [TON][Tf_2N] and [THN][Tf_2N] ILs do not extract Pt(II) or Pt(IV). This fact was attributed [52] to the higher charge density and higher Gibbs energy of the $PtCl_4{}^{2-}$ and $PtCl_6{}^{2-}$ anions in comparison with $AuCl_4{}^{-}$.

2.2.4. Lithium

The use of two ionic liquids, namely, tetrabutylammonium bis(2-ethylhexyl) phosphate [N_{4444}][DEHP] and tetraoctylammonium bis(2-ethylhexyl) phosphate [N_{8888}][DEHP], dissolved in toluene resulted in the extraction of lithium from hydrogen chloride solutions with more than 80% efficiency. Then, lithium was back-extracted from the organic phase with 0.5 mol L^{-1} hydrochloric acid via four stages with an efficiency of 95% [53].

Owing to the high extraction capacity for lithium inherent in tetrabutylammonium mono-2-ethylhexyl 2-ethylhexyl phosphate, [N_{4444}][EHPMEH], dissolved in methylbenzene, it was possible to separate lithium ions from other alkali metal ions such as sodium, potassium, and rubidium [54]. The distribution ratio of lithium was twofold higher (7) than those of Na, K, and Rb (3.5). According to the authors, this is due to the fact that the electrostatic interaction with the IL anion is stronger for the cation with a higher charge density. When the ionic liquid was used at a concentration greater than 0.6 mol L^{-1}, the lithium extraction efficiency was more than 90%. Zhao et al. [54] also studied the mechanism of lithium extraction. By performing slope analysis, the composition of the formed complex was found to be $3LiCl\cdot4[N_{4444}]$[EHPMEH].

Thus, the [N_{4444}][EHPMEH] IL is a promising extractant of lithium for the processing of lithium-ion batteries.

2.2.5. Rare Earth Elements

The use of mathematical models to describe the extraction of neodymium(III), terbium(III), and dysprosium(III) from chloride solutions with the [A336][oleate] ionic liquid comprising the Aliquat 336 cation and the oleate anion and dissolved in kerosene made it possible to attain the optimal stability constants in the aqueous phase and the equilibrium constants of extraction in the organic phase. The obtained values exactly corresponded to experimental results. Therefore, it became possible to predict the recovery for the simultaneous extraction of neodymium(III), terbium(III), and dysprosium(III) from an aqueous phase with this extractant [55].

During the liquid–liquid extraction of neodymium(III) from chloride solutions with [A336][oleate], it was found that neodymium recovery increased in the presence of high concentrations of Cl^- in the aqueous phase. Indeed, the percentage of Nd(III) extraction was 48.6% when the Cl^- concentration was 0.05 mol L^{-1} and increased to 82% in the presence of 4 mol L^{-1} Cl^- [56].

A new extraction system consisting of the ionic liquid trioctylmethylammonium dioctyl diglycolamate diluted in [A336][NO_3] was tested for the extraction of neodymium(III) and other rare earth elements from aqueous solutions. Almost 100% recovery of neodymium was attained under experimental conditions. It was also found that extraction from a nitrate solution far exceeds that from a chloride medium. A benefit of this system is its easy synthesis and the possibility of regeneration and reuse without the loss of efficiency [57].

It was indicated [58] that bifunctional ionic liquids based on the ammonium cation and bis(2,4,4-trimethylpentyl)phosphinate ([A336][Cy272]), di(2-ethylhexyl) phosphate ([A336][P204]), and 2-ethylhexyl 2-ethylhexylphosphonate ([A336][P507]) anions are suitable for the extraction of Ce(IV) and Ce(III) from 0.02 mol L^{-1} sulfuric acid and for their separation, with separation factors of 6.83×10^2, 1.29×10^3, and 1.33×10^3 for [A336][Cy272], [A336][P204], and [A336][P507], respectively. The extraction efficiency of

Ce(IV) from 0.1 mol L^{-1} H_2SO_4 was 98.36%, 97.36%, and 98.77%, respectively, for this series of extractants.

The ionic liquids trialkylmethylammonium di(2-ethylhexyl)orthophosphinate ([A336][P507]) and trialkylmethylammonium di-2-ethylhexyl phosphate ([A336][P204]) in *n*-heptane were used to extract trivalent rare earth elements from nitrate and chloride solutions [59]. It was noted that nitrate media are preferable for the separation of heavy rare earth elements, while light REEs are better separated using hydrogen chloride solutions. In particular, the separation factors for extraction with [A336][P507] from a nitrate solution were β (Tm/Er) = 3.36, β (Yb/Tm) = 7.92, and β (Lu/Yb) = 8.55, while those for a chloride solution and [A336][P507] extractant were β (Nd/Pr) = 9.52 and β (Sm/Nd) = 4.70.

The extraction properties of the undiluted ionic liquids trialkylmethylammonium sec-octylphenoxy acetic acid ([A336][CA-12]) and trialkylmethylammonium sec-nonylphenoxy acetic acid ([A336][CA-100]) towards rare earth elements in chloride solutions are higher than those of tri-n-butyl phosphate. The [A366][CA-12] and [A336][CA-100] ionic liquids were especially efficient for the separation of lanthanum(III) from other lanthanides: dysprosium(III), erbium(III), lutetium(III), yttrium(III), samarium(III), europium(III), and gadolinium(III). The separation factors were more than 5.0 [60].

A study [61] of the extraction properties of three ionic liquids, tetraoctylammonium oleate (N_{8888}C18:1), tetraoctylammonium dioctyl diglycolamate ([N_{8888}][DODGA]), and tetraoctylammonium di(2-ethylhexyl)oxamate ([N_{8888}][DEHOX]), dissolved in toluene towards lanthanum, cerium, neodymium, gadolinium, dysprosium, and ytterbium (nitrate and sulfate solutions) demonstrated that in the lanthanum–ytterbium series, the extraction efficiency with the N_{8888}C18:1 ionic liquid increases. In the opinion of the authors, this is due to an increase in the binding of REE cations to IL anions in the lanthanum–ytterbium series; this would enable the use of N_{8888}C18:1 for the separation of light and heavy lanthanides. However, as the IL-to-REE ratio decreases from 4:1 to 2:1, the REE extraction efficiency with these ILs decreases.

Ionic liquids based on ammonium cations are less water-soluble, less expensive, and less toxic than other nitrogen-containing ILs. However, the density of most ILs with ammonium cations is lower than 1 g cm^{-3}; this complicates the extraction, because it is more convenient when the organic phase is below the aqueous phase. In addition, these ILs should be diluted with molecular solvents or heated, because they have a higher viscosity than phosphonium or imidazolium ionic liquids. The use of toxic molecular organic diluents may be hazardous for human health and the environment.

2.3. Ionic Liquids Based on Imidazolium Cations for Metal Extraction

2.3.1. Transition Metals

Ionic liquids based on imidazolium cations can be used for the extraction and separation of transition metals.

For example, a study of zinc(II), cadmium(II), copper(II), and iron(III) extraction from a solution of hydrochloric acid using several imidazolium ionic liquids demonstrated that Zn and Cd can be selectively separated from Fe and Cu by using 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4]. In addition, the authors noted that 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([omim][NTf_2]) provide selective separation of Zn/Cd and Zn/Fe pairs [62].

Ionic liquids based on imidazolium cations with butyl ([bmim][NTf_2], [C_4C_1im][OTf], [C_4C_1im][$MeSO_4$], [C_4C_1im][Me_2PO_4], and [C_4C_1im][OAc]) and octyl ([C_8C_1im][Cl] and [C_8C_1im][OTf]) groups were used to extract zinc(II) and copper(II) from diesel fuel. It was shown that these compounds can recover up to 99.3% of zinc and up to 99.7% of copper when they are present in a fuel in amounts of only 2 mg kg^{-1} and 1 mg kg^{-1}, respectively [63]. The authors ascertained that ILs are slightly soluble in the fuel phase, which minimizes the loss of the extractant.

However, as compared with ILs based on ammonium and phosphonium cations, imidazolium-based ILs have high costs, are toxic, and poorly extract transition metals if the aqueous phase has low acidity. Quantitative extraction of transition metals can be attained using solutions with acid concentrations of no less than 5 mol L^{-1}.

2.3.2. Metals of Period 5 of the Periodic Table of Elements

Imidazolium ionic liquids containing a keto group in the cation, [EPipMIBK][NTf_2] and [MImMIBK][NTf_2], were used for the liquid–liquid extraction of tantalum(V) from a solution of sulfuric acid as an alternative to methyl isobutyl ketone, which is employed most often to separate these metals. These ionic liquids offer a number of advantages over methyl isobutyl ketone, which is highly soluble in water and is fire hazardous and explosive. Conversely, the ionic liquids are non-flammable and non-volatile; they have low viscosity and are poorly soluble in water and readily soluble in organic solvents (e.g., kerosene). The extraction efficiency of tantalum with ILs reached 96% [64].

An undiluted ionic liquid based on the imidazolium cation and diethyl phosphate anion, 1-ethyl-3-methylimidazolium diethyl phosphate [EMIM]-DEP, was proposed for the extraction of vanadium(V) from diluted oil sands (vanadium is present in oil as a porphyrin complex) [65]. For the displacement of the $VO_2{}^{2+}$ ion from the porphyrin anion, the ionic liquid was acidified with 37% hydrochloric acid. However, only 26% of vanadium could be recovered in this way. The authors did not provide an explanation for this fact.

2.3.3. Noble Metals and Platinum-Group Metals

Ionic liquids based on imidazolium cations can be used to extract gold(III) and platinum(IV) from electronic waste and to extract platinum-group metals from spent nuclear fuel. For example, 1,2-dimethyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ([OdMIM][NTf_2]) and 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ([OMIM][NTf_2]) were used to separate tetrachloroaurate and hexachloroplatinate complexes in two stages. First, gold was extracted with hydrophobic [OdMIM][NTf_2] as $AuCl_4{}^-$ from an aqueous solution containing 5 mol L^{-1} HCl, 0.8×10^{-3} mol L^{-1} $KAuCl_4$, and 0.4×10^{-3} mol L^{-1} H_2PtCl_6. Platinum that remained in the aqueous phase was extracted as $Pt(SCN)^{2-}$ with [OMIM][NTf_2] from a solution containing 0.1 mol L^{-1} HCl, 8.3×10^{-3} mol L^{-1} H_2PtCl_6, and 0.1 mol L^{-1} KSCN. The highest distribution ratios D for $AuCl^{4-}$ and $Pt(SCN)_6{}^{2-}$ were 1500 and 6000, respectively [66].

When the 1-hexadecyl-3-methylimidazolium chloride [C_{16}mim][Cl]/chloroform system was used to extract Au(III), high selectivity for gold extraction over other metals such as Cu(II), Co(II), Ni(II), Fe(III) Al(III), and Sn(IV) was observed. It was also noted that oxalic acid is an appropriate compound for the regeneration of [C_{16}mim][Cl] and the recovery of gold from the complex formed during extraction [67].

The introduction of kosmotropic (structuring) salts with a higher charge density and higher hydrophilicity compared to ionic liquids to the aqueous solution results in the formation of two aqueous phases and in the quantitative metal extraction from the phase rich in the ionic liquid. For example, a two-phase system consisting of an ionic liquid (1-alkyl-3-methylimidazolium bromide: [C_4mim][Br], [C_6mim][Br], and [C_8mim][Br]) and potassium hydrogen phosphate (K_2HPO_4) was used to recover gold(I) from alkaline solutions of aurocyanides. The use of this system allowed the recovery of up to 99.9% of gold [68].

Wu et al. [69] carried out the extraction of palladium(II), ruthenium(III), and rhodium(III) from nitric acid solutions with undiluted 1-methyl-3-dioctylaminopropylimidazolium bis(trifluoromethylsulfonyl)imide [DiOcAPmim][NTf_2]. When the nitric acid concentration was [HNO_3] < 1 mol L^{-1}, the extraction efficiency was >80%.

The authors believe that the mechanism of extraction of these metals from the aqueous phase at a nitric acid concentration of 0.1–1 mol L^{-1} is a cation-exchange reaction and is described by the equation:

$$n[\mathrm{DiOcAPmim}]^{+}{}_{\mathrm{IL}} + \mathrm{M}^{n+}{}_{\mathrm{aq.}} \leftrightarrow n[\mathrm{DiOcAPmim}]^{+}{}_{\mathrm{aq.}} + \mathrm{M}^{n+}{}_{\mathrm{IL}}$$

Thus, ionic liquids based on imidazolium cations are promising extractants for platinum-group metals from highly active liquid waste.

Moreover, ionic liquids based on imidazolium cations have a lower viscosity than ILs based on ammonium cations; therefore, they can be used in extraction processes without the addition of toxic and flammable organic diluents.

2.4. Ionic Liquids Based on Pyridinium, Piperidinium, Pyrrolidinium, Morpholinium, Benzimidazolium, Guanidinium, and Betainium Cations

2.4.1. Heavy Metals

Wojciechowska A. et al. [70] extracted lead(II) from chloride and nitrate solutions with 1-(3-pyridyl)undecan-1-one oxime 3PC10 and the corresponding pyridinium ionic liquids with chloride and bromide anions: 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium chloride (Ox-3PC10-PrCl) and 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide (Ox-3PC10-PrBr), respectively (using toluene as the diluent). The highest extraction efficiency, amounting to 70–75%, was attained in the case of Ox-3PC10-PrCl.

The same research team [71] extracted copper(II) with the following ionic liquids: Ox-3PC10-PrCl, Ox-3PC10-PrBr, 1-propyl-3-undecanoylpyridinium chloride K-3PC10-PrCl, and 1-propyl-3-undecanoylpyridinium bromide K-3PC10-PrBr (dissolved in toluene). The best results were observed when Ox-3PC10-PrCl was used. Good results were also obtained for K-3PC10-PrCl; however, in this case, the extraction efficiency was highly dependent on the concentration of chloride ions and the pH of the solution.

Three hydrophobic complexing agents, namely, 1-(3-pyridyl)undecan-1-one oxime 3PC10 and its quaternary salts Ox-3PC10-PrCl and Ox-3PC10-PrBr, were used to extract molybdenum(VI) from sulfate solutions. The high selectivity of extraction with these ILs was shown. However, quantitative recovery of the metal was attained only when using Ox-3PC10-PrCl at pH = 2.5 in toluene with the addition of 10 vol.% decan-1-ol. The oxime 3PC10, although proven to be a weak extractant for Mo(VI), formed more stable complexes than its quaternary salts [72].

2.4.2. Noble Metals

Nine ionic liquids containing pyridinium ($[4MBCNPYR]^+$), pyrrolidinium ($[MPS_2PYRRO]^+$, $[MPTPYRRO]^+$, $[MOPYRRO]^+$, and $[MBCNPYRRO]^+$), and piperidinium ($[MPS_2PIP]^+$, $[MPTPIP]^+$, $[MBCNPIP]^+$, and $[MOPIP]^+$) cations and the $[Tf_2N]^-$ anion were used to extract noble metals such as silver(I), palladium(II), and gold(III) from aqueous solutions at room temperature. It was found that ionic liquids containing a disulfide group ($[MPS_2PYRRO][Tf_2N]$ and $[MPS_2PIP][Tf_2N]$) or a nitrile group ($[MBCNPIP][Tf_2N]$, $[Tf_2N]$, and $[MBCNPYRRO][Tf_2N]$) exhibited good extraction properties towards silver and palladium ions. All of the considered ILs showed excellent selectivity for gold [73].

The $[C_6BIM_2][NTf_2]_2$ ionic liquid based on the benzimidazolium cation was used to extract gold(III) from hydrochloric acid solutions [74]. The gold extraction efficiency was 98.42%. This ionic liquid can be used to recover gold from multi-metal solutions containing Mg(II), Mn(II), Cu(II), Zn(II), Al(III), Co(II), Pd(II), Pt(IV), Rh(III), and Ru(III). The gold extraction rate from multi-metal solutions was more than 90%, whereas that for the extraction of other metals was less than 5%. A benefit of this study was the optimization of a number of extraction parameters: extractant concentration, acidity, and salinity. In addition, using data from UV, IR, and ^{13}C NMR spectroscopy of the extractant and the extracted species, it was found that the extraction of gold(III) proceeds according to the anion-exchange mechanism in accordance with the scheme:

$$[C_6BIM_2][NTf_2]_2 + 2\ AuCl_4^- \leftrightarrow [C_6BIM_2][AuCl_4]_2 + 2NTf^{2-}$$

Guanidine ionic liquids, the cations of which contain three nitrogen atoms, represent a new class of ionic liquids that are used for metal extraction. These ILs are more environmentally benign than commercial imidazolium ILs.

The ionic liquid 2,2-diheptyl-1,1,3,3-tetramethylguanidinium bromide dissolved in chloroform extracts platinum(IV) from chloride solutions over four cycles. The extractant shows a high selectivity (98.2%) for Pt(IV) over Mn(II) (4.2%), Al(III) (2.0%), Cu(II) (2.28%), Co(II) (4.7%), Fe(III) (1.0%), Mg(II) (4.3%), and Sn(IV) (7.8%) [75].

2.4.3. Rare Earth Elements and Actinides

Ionic liquids based on piperidinium, morpholinium, and pyrrolidinium cations and alkyl phosphite anions are promising extractants for rare earth elements and actinides from aqueous solutions.

A number of undiluted and low-viscosity ionic liquids based on 1-octyl-1-methylpiperidinium, 1-octyl-1-methylmorpholinium, and 1-octyl-1-methylpyrrolidinium cations and octyl phosphite anions were used for the quantitative recovery of neodymium(III) from nitric acid solutions with concentrations above 6 mol L^{-1} within only 30 min [76]. It was established that extraction with these ILs proceeds by a solvation mechanism, similar to the mechanism of extraction with neutral dioctyl phosphite. The authors proposed this extraction system for the recovery of neodymium from permanent magnets. However, data on the separation of neodymium from other components of the magnets, e.g., dysprosium(III) and cobalt(II), were not provided in this study. In addition, the ionic liquids are inefficient when the neodymium content in the aqueous phase is above 1.2×10^{-3} mol L^{-1}. This was attributed to the unavailability of the coordination sites of ILs.

Deactivation of uranium ores and nuclear waste by means of ionic liquids based on morpholinium cations and octyl phosphite anions showed that the distribution ratio and the efficiency of extraction of uranyl salts (UO_2^{2+}) depend on the acidity of the aqueous phase, time of extraction, the alkyl chain length in the IL, and the IL concentration. The highest distribution ratio (above 600) and extraction efficiency (98.6%) were attained when the nitric acid concentration was 7 mol L^{-1}, the initial concentration of [UO_2^{2+}] was not more than 10^{-2} mol L^{-1}, and the amount of IL was not more than 4 mmol. The equilibrium was established in 20 min. In addition, using the indicated extractants, uranium was quantitatively recovered (as UO_2^{2+} ions) from a mixture containing minor amounts of the transition metals Cu(II), Fe(III), Ni(II), Co(II), Zn(II), and Cd(II) in nitric acid [77]. Unfortunately, the authors did not investigate the effect of radionuclide impurities, which are always present in uranium nuclear waste, on the extraction. In particular, the presence of the most hazardous strontium ^{90}Sr and cesium ^{137}Cs ions in the waste was not considered.

ILs based on renewable natural raw materials, particularly betaine, an amino acid obtained from beets, are of considerable interest for the extraction of actinides and rare earth elements. These ILs can simultaneously act both as extractants and as diluents in extraction processes.

For example [78], betainium bis(trifluoromethylsulfonyl)imide [Hbet][NTf_2] was used to extract uranium(VI) from nitric acid media.

The authors of [79] showed that [Hbet][NTf_2] allows selectively extracting scandium(III) from chloride and nitrate media in the presence of lanthanum(III), cerium(III), neodymium(III), dysprosium(III), yttrium(III), iron(III), aluminum(III), titanium(IV), calcium(II), and sodium(I). The scandium(III) extraction efficiency was more than 95%.

Indium(III) was extracted from hydrochloric acid medium using [Hbet][NTf_2] [80]. The maximum values of the distribution ratios of In(III) and Tl(III) were 200 and 70, respectively, at low concentrations of hydrochloric acid. To improve the extraction, betaine was added to the hydrochloric acid solution before extraction.

2.4.4. Group 5 Metals of the Periodic Table of Elements

Ionic liquids based on piperidinium cations are promising extractants for recovering tantalum from electronic waste and separating it from other waste components, such as silicon and tin. Ionic liquids based on the piperidinium cations N-butyl-N-ethylpiperidinium bis(trifluoromethylsulfonyl)imide [EBPiP][NTf_2] and N-octyl-N-ethylpiperidinum bis (trifluoromethylsulfonyl)imide [EOPiP][NTf_2] can be used to extract tantalum(V) from a capacitor leaching solution and to separate Ta(V) from Cu(II), Si(IV), Sn(II), Ni(II), Cr(III), Al(III), and Fe(II), which are also present in the capacitor leaching solution. The density of [EBPiP][NTf_2] and [EOPiP][NTf_2] is above 1 g cm^3, which facilitates extraction. The efficiency of tantalum extraction was >90%, and the Ta/Me separation factor was >200 for [EBPiP][NTf_2] and [EOPiP][NTf_2] [81].

Thus, the extraction efficiency of tantalum with [EBPiP][NTf_2] and [EOPiP][NTf_2] does not depend on the hydrophobicity of the IL, which is determined by the alkyl chain length in the piperidinium cation. However, the authors believe that [EOPiP][NTf_2] is more promising for the recovery of tantalum than [EBPiP][NTf_2], which is due to its lower water solubility, resulting in lower loss of IL to the aqueous phase.

N-Octylpyridinium chloride ([OPy]Cl) and N-octylpyridinium tetrafluoroborate ([OPy][BF_4]) ionic liquids dissolved in 1-pentanol were used for vanadium(V) extraction [82]. It was shown that [OPy]Cl and [OPy][BF_4] recover vanadium from a vanadium slag leaching solution with an extraction efficiency of 95.42% and 93.52%, respectively. A benefit of this process is the fast recovery of vanadium (not more than 1 min). Using spectral methods (IR and UV spectroscopy) and slope analysis, it was shown that the extraction follows an anion-exchange mechanism and generates the adduct $[OPy]_2[HVO_4]$. The developed extraction system can be used in hydrometallurgy to extract vanadium from the vanadium slag leaching solution. However, the authors did not consider the presence of other metals in the solution, such as manganese(II) and chromium(III).

Thus, ILs based on pyrrolidinium, piperidinium, benzimidazolium, and morpholinium cations are promising extractants for metals, because they have low viscosity and, hence, do not require dilution. In turn, ionic liquids based on pyridinium cations have lower water solubility than imidazolium-based ILs.

However, ILs based on these cations are more expensive than ammonium and phosphonium ILs.

3. Ionic Liquids as Diluents in Extraction Systems

Of considerable interest is the use of ionic liquids of various classes as diluents for extractants. This may improve some characteristics of the extraction process.

3.1. Ionic Liquids Based on the Phosphonium Cation as Diluents

The Cyanex 272 extractant dissolved in the Cyphos 101 ionic liquid can be used for the selective extraction of cobalt(II) and nickel(II) from acidic chloride solutions. The Cyphos 101 diluent combines good selectivity, high extraction efficiency, and beneficial features of ionic liquids, such as low saturated vapor pressure and high thermal stability, which enhance the extraction efficiency.

For example, using a 0.5 mol L^{-1} solution of Cyanex 272 in Cyphos 101 at 323 K, fast and selective extraction of cobalt(II) from an aqueous chloride solution (pH = 6) that also contained Ni(II) was attained. The cobalt extraction efficiency reached 90%. The back extraction of cobalt amounted to 100% when 0.1 mol L^{-1} sulfuric acid and a temperature of 298 K were used [83].

Song et al. [84] used triethyl(pentyl)phosphonium bis(trifluoromethylsulfonyl)imide [P_{2225}][NTf_2] as a diluent for trioctylamine $(C_8H_{17})_3N$, an extractant for tungsten(VI) and cobalt(II). The authors indicated that the trioctylamine–[P_{2225}][NTf_2] system provides a higher efficiency and selectivity of separation and a higher distribution ratio than the trioctylamine–kerosene system. M. Matsumiya, a Japanese scientist, used a similar system with triethyl(hexyl)phosphonium bis(trifluoromethylsulfonyl)imide [P_{2226}][NTf_2] for the extraction of platinum(IV) from a chloride medium [85].

3.2. Ionic Liquids Based on the Imidazolium Cation as Diluents

Imidazolium ionic liquids are excellent diluents for metal extractants. For example, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][NTf_2] was used [86] as a diluent for 1,1,1-trifluoro-2,4-pentanedione, a β-diketone, for the supercritical fluid extraction of copper(II). It was found that the increase in the extractant concentration was accompanied by the increased efficiency of the process. Nevertheless, there was no need for high contents of β-diketone, since as the β-diketone concentration reached 60 mol L^{-1}, further increases in copper(II) extraction were insignificant. A semi-continuous process was developed for the isolation of the metal complex from the ionic liquid after extraction using carbon dioxide. The authors [86] stated that the process developed for the regeneration of the ionic liquid is markedly more efficient than the previously used batch processes.

The extraction of strontium(II) with a crown ether, 4′,4′(5″)-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6), using the ionic liquids $[C_n\text{mim}][\text{NTf}_2]$ (n = 2,4,6) as diluents was reported [87]. All extraction systems reached equilibrium within 10 min, with the strontium distribution ratio decreasing in the series $[C_6\text{mim}][\text{NTf}_2] > [C_4\text{mim}][\text{NTf}_2] > [C_2\text{mim}][\text{NTf}_2]$. It was also found that these ionic liquids cannot extract strontium ions by themselves, but they considerably increase the efficiency of the crown ether.

Ni^{2+}, Cu^{2+}, and Pb^{2+} ions were extracted with 2-aminothiophenol with an ionic liquid based on the imidazolium cation and the hexafluorophosphate anion $[\text{bmim}][\text{PF}_6]$ as the diluent [88]. It was shown that the optimal pH values for the extraction of nickel and lead are 4–6 and 5, respectively. The copper extraction efficiency did not depend on the pH of the solution. During the extraction of Ni^{2+}, Cu^{2+}, and Pb^{2+} ions, the extraction equilibria were attained within 120, 30, and 30 min, respectively. A comparison of the extraction efficiency of the indicated metals using 2-aminothiophenol in ionic liquid and in chloroform showed that the process is more efficient in the ionic liquid. It was also noted that competing ions such as Na^+, Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$, and Cl^- do not significantly affect the extraction efficiency of nickel, copper, and lead.

Quijada-Maldonado et al. [89] studied the selective extraction of molybdenum(VI) and rhenium(VII) from a synthetic highly acidic solution using [TOMA][D2EHP] diluted with $[\text{omim}][\text{Tf}_2\text{N}]$ and with kerosene. The authors showed that the replacement of kerosene as the diluent by $[\text{omim}][\text{Tf}_2\text{N}]$ can increase the selectivity of Mo(VI) and Re(VII) extraction by a factor of five.

In the extraction of REE from nitric acid solutions using DMDODGA, the replacement of the n-octanol/kerosene diluent by the $[\text{bmim}][\text{NTf}_2]$ IL results in a considerable increase in the distribution ratios of lanthanum(III), neodymium(III), samarium(III), gadolinium(III), and ytterbium(III). For example, in the case of neodymium(III), the distribution ratio was of the order of 10^2 with n-octanol/kerosene as the diluent [90] and of the order of 10^4 when the ionic liquid was used [91]. No explanation was proposed for this fact. It was also stated that an increase in the length of the alkyl chain in the imidazolium cation leads to a decrease in the distribution ratio. The authors attributed this trend to higher hydrophobicity and greater steric stability of long-chain ILs. The DMDODGA-$[\text{bmim}][\text{NTf}_2]$ extraction system was proposed for the processing of high-level nuclear waste.

A similar enhancement of the extraction capacity was observed when the $[\text{bmim}][\text{NTf}_2]$ IL was used as the diluent in comparison with molecular diluents such as N,N′-diethyl- and N,N′-ditolyl-2,9-diamide-1,10-phenanthrolines in the recovery of americium(III) from nitric acid solutions [92]. The distribution ratio of americium was approximately 10^4 when the extraction was carried out from a nitric acid solution using $[\text{bmim}][\text{NTf}_2]$, whereas in the case of a molecular diluent, cyclohexanone, the distribution ratio was reported [93] to be about 10.

In view of the foregoing observations, one can conclude that ILs are promising diluents for molecular extractants, which is due to the lack of toxicity and physicochemical stability in comparison with organic molecular diluents. However, the authors did not provide an explanation for why extraction systems containing ILs as diluents possess better extraction properties than those with organic solvents.

4. Solid-Phase Extraction of Metals with Ionic Liquids

Metal extraction with ionic liquids can also be conducted in the solid phase of a sorbent. Water-insoluble polymers are of interest as such sorbents, as they are environmentally benign, non-volatile, non-toxic, and easily separated from the liquid phase and regenerated.

Solid-phase extraction resins bearing a grafted extractant and extractant-impregnated resins are known. The latter are preferable because they are more easily prepared.

The principle of the modification of solid-phase sorbents by immobilizing liquid extractants to increase the efficiency of the extraction of mercury ions from aqueous solutions containing Hg(II), Pb(II), and Cu(II) was proposed by Zhang et al. [94]. The authors obtained a resin based on polyvinyl alcohol and sodium alginate in which an ionic liquid, tricapryl(methyl)ammonium 2-methylthiobenzoate [A336][MTBA], was used as the extractant. When the ratio of the ionic liquid volume (mL) to polyvinyl alcohol weight (g) was 0.5, the researchers were able to attain 100% recovery of Hg(II) from an aqueous solution with a mercury concentration of 50 mg/L. It was noted that an increase in the impurity ion concentrations in the solution did not significantly affect the extraction efficiency of mercury. The optimal pH of the solution was found to be 5.8. The developed sorbent was intended for removing mercury ions from wastewater. The authors also studied the regenerability and reusability of the extractant.

Two resins were obtained on the basis of tetrabutylammonium dihydrogen phosphate TBAH2P ionic liquid and natural cellulose and commercial Amberlite XAD-7 polymer as sorbents [95]. Both resins were tested as extractants for europium. The effects of pH, the time of contact, the initial concentration of Eu (III) in the solution, and temperature on the adsorption capacity of polymers were studied. The maximum adsorption efficiency of europium extractants occurred when the pH was below 6, while the optimal contact time was 30 min. Further increasing the time of contact did not have a significant effect on the adsorption capacity. Although both materials have good adsorption properties, experimental results led to the conclusion that functionalized Amberlite XAD-7 had higher selectivity (71.99 mg of Eu (III) per gram of the polymer) than modified cellulose. This fact was attributed to the chemical composition and the geometrical shape of particles of Amberlite XAD-7, which are more porous than cellulose.

For the removal of arsenic from aqueous solutions, new polyionic liquids were obtained by cross-linking poly-N-vinylimidazole and poly-4-vinylpyridine with 1,4-dichlorobutane ($[\mathrm{PVIm\text{-}(CH)_2)_4\ PVIm}][\mathrm{Cl}^-]_2$ and $[\mathrm{PVP\text{-}(CH_2)_4\text{-}PVP}][\mathrm{Cl}^-]_2$ ILs) and with 1,6-dichlorobutane ($[\mathrm{PVIm\text{-}(CH)_2)_6\text{-}PVIm}][\mathrm{Cl}^-]_2$ and $[\mathrm{PVP\text{-}(CH_2)_6\text{-}PVP}][\mathrm{Cl}^-]_2$ ILs). The gels were able to quantitatively remove As(V) when present in either low or high concentrations in water, thus demonstrating high affinity to the target ions. It is noteworthy that the gels $[\mathrm{PVIm\text{-}(CH)_2)_6\text{-}PVIm}][\mathrm{Cl}^-]_2$ and $[\mathrm{PVP\text{-}(CH_2)_6\text{-}PVP}][\mathrm{Cl}^-]_2$ showed higher extraction rates due to better accessibility of the active sites for As(V) ions [96].

The use of $\mathrm{Fe_3O_4}$ magnetic particles coated by a polymer shell containing ionic liquids facilitates the process of solid-phase extraction of metals, since these composites can be easily separated from the aqueous phase or soil using a magnet. Encapsulation of magnetic particles in polymers makes them stable in acid media.

Phosphonium-based ionic liquids are promising compounds for the functionalization of polymer sorbents. Mokhodoeva et al. [97] proposed magnetite nanoparticles obtained from PEG 4000 and Cyphos 101 IL to extract Pd(II) and Pt(IV) from wastewater. The platinum-group metals Pd(II) and Pt(IV) were extracted from multicomponent chloride solutions containing Cu(II), Ni(II), Au(III), and Rh(III). It was found that this system selectively recovers 98% of Pt(IV) and 99% of Pd(II) within 30 min. In the opinion of the authors, the PEG shell increases the hydrophilicity of nanoparticles and accelerates ion exchange. Among the achievements of this study is the possibility to extract minor concentrations of platinum-group metals (of the order of 10^{-5} mmoL L^{-1}). In addition, magnetite nanoparticles functionalized with ILs are stable in concentrated solutions of hydrochloric and nitric acids. However, the authors did not study the structure of the obtained sorbents. Is there a polymer in the structure? How does the polymer bind to components of the system? What is the mechanism of sorption? More studies are required to answer these questions.

It is noteworthy that the solid-phase extraction on an impregnated polymer support combines the advantages of liquid–liquid extraction and ion-exchange chromatography; however, on the other hand, impregnated resins are less resistant to washing out of the organic extractant from the polymer pores. Conversely, grafted extraction polymer resins are highly stable, which provides a rather long service life for these materials [98].

Thus, solid-phase extraction is a promising method for the extraction of metals from wastewater due to the reusability of the sorbent after desorption of the adsorbed metal and to the ease of operation. Moreover, there is no need to use toxic and combustible organic solvents or sophisticated equipment, such as mixer-settlers.

However, solid-phase extraction may face difficulties, e.g., the difficulty of dispersing the sorbent in the analyte solution. In addition, to quantitatively extract an analyte, the sorbent must have a set of certain properties, namely: a large specific surface area, suitable porosity, and ease of modification.

5. Conclusions

Ionic liquids have great prospects and potential for use in metal extraction. Ionic liquids can be used as extractants, diluents, or both, depending on the process conditions and particular metal ions to be separated. The low vapor pressure of ionic liquids makes them safer to use than commonly used molecular diluents. Furthermore, the high intrinsic electrical conductivity of ionic liquids prevents the accumulation of static charge, which is dangerous due to possible ignition.

However, the main drawbacks of ionic liquids, particularly those with long alkyl chains, are their significantly high viscosity, slower phase separation compared to that with molecular extractants, and high cost.

The generalizations and comparisons made in this review may suggest the future trends of research, development, and application of ILs for metal extraction.

For compliance with engineering requirements, the following IL characteristics should be comprehensively considered: cost, purity, acid stability, viscosity, solubility, density, electrical conductivity, electrochemical properties, extraction efficiency, selectivity, and the mechanism of extraction. Since there are quite a few types of ILs, experimental investigation of all ILs for the extraction is impossible. Chemoinformatics seems to be the most appropriate strategy for solving these complicated issues, and methods of chemoinformatics should be used for this purpose.

The investigation methods relevant to IL-based separation include quantitative structure–property relationships, molecular dynamics modeling, databases, combinatorial chemistry, and computer-aided molecular design. With the progress of IL-based extraction methods, functionalized ILs have become the focus of attention, and the work on functionalized ILs should be continued. Functional groups present in both cations and anions of ILs not only increase extractability and selectivity but also endow the ILs with excellent physicochemical properties for extraction.

Functionalized ILs obtained by the incorporation of functional groups into the cation have been extensively studied; the synthesis of functionalized ILs via modification of the anion has been less studied. The use of IL anions as carriers for functional groups offers advantages for the development of electron-rich compounds as efficient extractants for metal ions via Coulomb interactions.

The properties that are varied by the selection of the cation and the anion, e.g., density, viscosity, polarity, and water solubility, allow the preparation of ILs with the properties required for a particular task.

However, some studies have noted the shortcomings of using ILs, such as toxicity, poor biodegradability, the complexity of chemical processes in the system, and high cost, which limit their industrial use. IL synthesis and purification require standard synthetic methods to confirm their reproducibility. The large-scale yields of ILs for industrial applications and IL synthesis are the main challenges. The hydrophobicity of classical imidazolium ILs is due, in particular, to the presence of the fluorine-containing anions $[BF_4]^-$ and $[PF_6]^-$, the main drawback of which is instability to hydrolysis. The possible formation of HF is a severe hazard for the environment. However, insufficient hydrophobicity of ILs leads to the loss of IL components during extraction.

A relevant trend is related to less expensive and more readily available ILs with improved properties that are useful for extraction. A lot of additional studies will be required before the potential of ILs is fully evaluated.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/chemengineering6010006/s1, Table S1: Chemical structure and application of ionic liquids.

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Abbreviations

A	
[A336][Br]	trialkylmethylammonium bromide
[A336][CA-12]	trialkylmethylammonium sec-octylphenoxy acetic acid
[A336][CA-100]	trialkylmethylammonium sec-nonylphenoxy acetic acid
[A336][Cy272]	trialkylmethylammonium bis(2,4,4-trimethylpentyl)phosphinate
[A336][I]	trialkylmethylammonium iodide
Aliquat 336	a mixture of trioctylmethylammonium and tridecylmethylammonium chlorides
[A336][MTBA]	trialkylmethylammonium 2-(methylthio)benzoate
$[A336][NO_3]$	trialkylmethylammonium nitrate
[A336][oleate]	trialkylmethylammonium oleate
[A336][P204]	trialkylmethylammonium di-2-ethylhexyl phosphate
[A336][P507]	trialkylmethylammonium 2-ethylhexyl 2-ethylhexylphosphonate
[A336][SCN]	trioctylmethylammonium thiocyanate
B	
$[bmim][NTf_2]$	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[bmim][PF_6]$	1-butyl-3-methylimidazolium hexafluorophosphate
C	
Cyanex 272	di(2,4,4,-trimethylpentyl)phosphinic acid
Cyphos 101	trihexyl(tetradecyl)phosphonium chloride
Cyphos 104	trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate
$[C_4C_1im][OAc]$	1-butyl-3-methylimidazolium acetate
$[C_4C_1im][OTf]$	1-butyl-3-methylimidazolium trifluoromethanesulfonate
$[C_4C_1im][Me_2PO_4]$	1-butyl-3-methylimidazolium dimethyl phosphate
$[C_4C_1im][MeSO_4]$	1-butyl-3-methylimidazolium methyl sulfate
$[C_8C_1im][Cl]$	1-octyl-3-methylimidazolium chloride
$[C_8C_1im][OTf]$	1-octyl-3-methylimidazolium trifluoromethanesulfonate
$[C_2mim][NTf_2]$	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[C_4mim][Br]$	1-butyl-3-methylimidazolium bromide

[C_6mim][NTf_2]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C_6mim][Br]	1-hexyl-3-methylimidazolium bromide
[C_8mim][Br]	1-octyl-3-methylimidazolium bromide
[C_{16}mim][Cl]	1-hexadecyl-3-methylimidazolium chloride
D	
[DiOcAPmim][NTf_2]	1-methyl-3-dioctylaminopropylimidazolium bis(trifluoromethylsulfonyl)imide
D2EHPA	di(2-ethylhexyl) phosphonic acid
DMDODGA	N, N′-dimethyl-N, N′-dioctyl-3-oxadiglycolamide
E	
[EBPiP][NTf_2]	N-butyl-N-ethyl-piperidinium bis(trifluoromethylsulfonyl)imide
[EMIM]-DEP	1-ethyl-3-methylimidazolium diethyl phosphate
[EOPiP][NTf_2]	N-octyl-N-ethyl-piperidinium bis(trifluoromethylsulfonyl)imide
[EPipMIBK][NTf_2]	N-ethyl-N-(4-methyl-2-oxopentyl)-piperidinium bis(trifluoromethylsulfonyl)imide
H	
[Hbet][NTf_2]	betainium bis(trifluoromethylsulfonyl)imide
I	
IL	ionic liquid
K	
K-3PC10-PrBr	1-propyl-3-undecanoylpyridinium bromide
M	
[MBCNPIP]$^+$	1-butyronitrile-1-methylpiperidinium cation
[4MBCNPYR]$^+$	1-butyronitrile-4-methylpyridinium cation
[MBCNPYRRO]$^+$	1-butyronitrile-1-methylpyrrolidinium cation
[MImMIBK][NTf_2]	N-methyl-N-(4-methyl-2-oxopentyl)imidazolium bis(trifluoromethylsulfonyl)imide
[MOPIP]$^+$	1-methyl-1-octylpiperidinium cation
[MOPYRRO]$^+$	1-methyl-1-octylpyrrolidinium cation
[MPS_2PIP]$^+$	1-methyl-1-[4,5-bis(methyl sulfide)]pentylpiperidinium cation
[MPS_2PYRRO]$^+$	1-methyl-1-[4,5-bis(methyl sulfide)]pentylpyrrolidinium cation
[MPTPIP]$^+$	1-methyl-2-pentenepiperidinium cation
[MPTPYRRO]$^+$	1-methyl-2-pentenepyrrolidinium cation
N	
[N_{4444}][DEHP]	tetrabutylammonium bis(2-ethylhexyl)phosphate
[N_{4444}][EHPMEH]	tetrabutylammonium mono-2-ethylhexyl 2-ethylhexyl phosphate
N_{8888}C18:1	tetraoctylammonium oleate
N_{8888}C18:2	tetraoctylammonium linoleate
[N_{8888}][DEHP]	tetraoctylammonium bis(2-ethylhexyl) phosphate
[N_{8888}][DEHOX]	tetraoctylammonium di(2-ethylhexyl)oxamate
[N_{8888}][DODGA]	tetraoctylammonium dioctyl diglycolamate
O	
[OdMIM][NTf_2]	1,2-dimethyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide
[omim][NTf_2]	1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[OMIM][NTf_2]	1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide
[OPy][BF_4]	N-octylpyridinium tetrafluoroborate
[OPy][Cl]	N-octylpyridinium chloride
Ox-3PC10-PrBr	3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide
Ox-3PC10-PrCl	3-[1-(hydroxyimine)undecyl]-1-propylpyridinium chloride
P	
[P_{1888}] [C_6SAc]	methyltrioctylphosphonium S-hexyl thioglycolate
[P_{2225}][NTf_2]	triethylpentylphosphonium bis(trifluoromethylsulfonyl)imide
[P_{2226}][NTf_2]	triethylhexylphosphonium bis(trifluoromethylsulfonyl)imide
[P_{4444}][BTMPP]	tetrabutylphosphonium bis(2,4,4-trimethylpentyl)phosphinate
[P_{66614}][BTB]	trihexyl(tetradecyl)phosphonium 2-(benzylthio)benzoate
[P_{66614}][hfac]	trihexyl(tetradecyl)phosphonium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate

$[P_{66614}][MA]$	trihexyl(tetradecyl)phosphonium N,N,N′,N′-tetra(2-ethylhexyl)malonate
$[P_{66614}][NO_3]$	trihexyl(tetradecyl)phosphonium nitrate
$[P_{66614}][PTB]$	trihexyl(tetradecyl)phosphonium 2-(propylthio)benzoate
$[P_{8888}]$[oleate]	tetraoctylphosphonium oleate
3PC10	1-(3-pyridyl)undecan-1-one oxime
R	
REE	rare earth elements
S	
Solvesso 100	a mixture of aromatic hydrocarbons obtained by pyrolysis of oil fractions
T	
TBAH2P	tetrabutyl ammonium dihydrogen phosphate
THN^+	tetrahexylammonium cation
TON^+	tetraoctylammonium cation
[THN][Br]	tetrahexylammonium bromide
[THN][Dca]	tetrahexylammonium dicyanamide
[THN][SCN]	tetrahexylammonium thiocyanate
$[THN][Tf_2N]$	tetrahexylammonium bis(trifluoromethylsufonyl)imide
[TOMA] [D2EHP]	trioctylmethylammonium bis(2-ethylhexyl)phosphinate
[TON][Br]	tetraoctylammonium bromide
[TON][Dca]	tetraoctylammonium dicyanamide
$[TON][Tf_2N]$	tetraoctylammonium bis(trifluoromethylsufonyl)imide

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