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Improvement of Gd(III) Solvent Extraction by 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one: Non-Aqueous Systems

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Abstract: The study of the liquid–liquid extraction of gadolinium (Gd(III) ion) with a chelating compound, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP), and the determination of the process parameters are presented by employing two ionic liquids, namely, ($[C_1C_n\text{im}^+][Tf_2N^-]$, n = 4, 10) and $CHCl_3$, as diluents. Compared to $CHCl_3$, the ionic liquid offers increased distribution ratios in an aqueous medium. A step forward, enhanced solvent extraction, and improved separation upon the addition of ethylene glycol are demonstrated, i.e., a boost of two immiscible organic phases, compared to traditional aqueous solutions. However, this is noticeable when using $CHCl_3$, but unfortunately not with ionic liquid combination, $[C_1C_{10}\text{im}^+][Tf_2N^-]$. Several conclusions are given, highlighting the role of the ionic diluent in complexation processes and selectivity with an employment of the chelating agent HP for various metal s-, p-, d-, and f-cations, i.e., nearly 25 metals. A detailed evaluation of the selectivity between these metals was made when changing both the aqueous phase completely with ethylene glycol or partially with glycerol (1:1). Electron paramagnetic resonance (EPR) spectroscopy has been used to study the established chemical species in the obtained organic extracts, such as Gd^{3+}, Fe^{3+}, Cu^{2+}, and Cr^{3+}, with unpaired electrons.

Keywords: non-aqueous solvent extraction; gadolinium ion; chelating ligand; ionic liquids; separation; EPR

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1. Introduction

In reality, the intriguing alchemists' research on a "*Menstruum universal*" (universal diluent) somehow indicates the importance given to the diluent and the process of solubility in a larger scheme, with the development of the popular pronouncement nowadays in chemistry, i.e., "*Similia Similibus Solvuntur*" (similar solubilizes similar). The diluents (a solvent is a liquid phase containing more than one substance, i.e., solvent = diluent + extractant + modifier . . . IUPAC Gold Book) [1] usually used in all fields of chemistry are often classical ones and the choice can affect all solvent extraction processes as well as the separation effort. Thus, when planning the solvent system several factors can be taken into account choosing one, regarding its viscosity, polarity, solubility in water, a high flash point, a low freezing point, preferably a high boiling point, price, etc. [2]. Further, the main criteria for the choice include toxicity, chemical reaction hazard, etc. Another consideration when selecting an extraction diluent is, of course, its density. In other words, diluents that are denser than water will form the lower layer of the pair when mixing together, while diluents that are less dense than water will form the upper layer or "float" on water. However, it should contain preferably only carbon, hydrogen, nitrogen, and oxygen in order to be totally incinerable (the "CHON principle"). In fact, various diluents exist, both aromatic and aliphatic, and they range from straightforward molecules to complex mixtures.

As a whole, classical diluents are low molecular weight organic substances that belong to two different broad chemical families: hydrocarbons (aliphatic, cyclic, and aromatic hydrocarbons) and oxygenates (esters and ethers). Despite the fact that it is difficult to trace them far back in history, an enormous quantity of liquid organic compounds were synthesized since the early nineteenth century [3]. However, high water solubility in the organic phase is definitely a decreasing factor for the solvent extraction ability of the system in use [4]. Thus, the liquid–liquid extraction method has a significant drawback: the requirement of water-immiscible organic diluents that are often toxic, flammable, or volatile [5]. The growing awareness of safety and environmental impact related to the use of molecular diluents renders their replacement with less noxious alternatives desirable [6]. As a whole, the development of new types of diluents is likely an ongoing process in chemistry. One important idea under intensive research studies nowadays is, of course, the replacement of traditional organic diluents with ionic liquid (ILs) compounds [7–9]. In order to highlight the ionic character of these similar reagents, they are usually denoted as $[Cat^+][Ani^-]$ considering the ILs' bulky organic cations with a basic cyclic structure and smaller inorganic or organic anions. In particular, in the field of metal extraction, separation, and recycling by liquid–liquid processes, hydrophobic ILs of the imidazolium type $[C_nC_m im^+][Tf_2N^-]$ have already proved to be tremendously efficient media for a large variety of metals in the periodic table including lanthanoids (cations are denoted as $[C_nC_m im^+]$ for *n*-alkyl-*m*-alkylimidazolium, whereas they are denoted as the anion $[(CF_3SO_2)_2N^-]$ (bis(trifluoromethylsulfonyl) for imide, $[Tf_2N^-]$) [10–15]. However, in one way or another, the prediction of diluent effects is a challenging task in solvent extraction chemistry [16–18] or separation methods such as adsorption, biosorption, precipitation, reverse osmoses, ion exchange, [19–26], etc.

Furthermore, the innovative non-aqueous solvent extraction process, i.e., solvometallurgy with only several papers written by Prof. Binneman's group, is available at the moment [27–32]. Needless to say, an obvious advantage is the reduced use of water and the avoidance of wastewater treatment problems posterior. As no-aqueous solvent extraction systems often have two liquid organic phases, a distinction needs to be made between the more polar (MP) phase containing the target metal(s) to be extracted, and the less polar (LP) phase, comprising the extractant(s) as well as a diluent, but also in some cases a modifier. Therefore, the substitution of pure water by polar organic compounds used as diluents generally modifies the solvation of metals in this liquid phase, which in some way may alter the metal extraction sequence. Nevertheless, extractant molecules in these liquid−liquid extraction systems still reside in the typical LP phase, ex. $CHCl_3$ or another organic diluent. In general, extractant molecules are rarely used in pure form and are often mixed with an organic diluent. However, diluents may have a significant influence on the extracting behavior due to various possible interactions that may exist between them: dipole–dipole, π-electron, hydrogen bonding, cavity formation, polymerization of the ligand, etc. The formation of a third phase should be avoided; thus, diluents should not form third phases during experimental loading conditions [5].

In fact, the 4f-ions are outlined because they are rare and precious due to their unique mixture of chemical characteristics in combination with their physical properties and specific high-value applications, not to mention their recent high, volatile prices and demands. Thus, Gd(III) ion was selected for this investigation as a typical representative, i.e., situated in the middle of the 4f series. On the other hand, acylpyrazolone ligands have often been used in the field of solvent extraction and separation science of almost all metal ions as they can easily form stable chelate complexes in fairly acidic conditions due to their pK_a in the order of four or less [33–37]. However, the complex performance of this class of ligands towards metallic species has not been evaluated in two immiscible organic surroundings.

In this study, the use of switchable hydrophilicity phases is demonstrated mainly with the ethylene glycol compound in the role of a more polar (MP) phase between the two immiscible organic phases of the liquid−liquid extraction system incorporating a chelating agent, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP), in order to enhance or tune 4f-ions separations. Scientific results obtained in the comparative study, chloroform was chosen as a representative of widely used organic diluents in solvent extraction chemistry, in order to make a comparison with the data already acquired during years in the field. In addition, a few non-polar molecular organic diluents such as C_6H_{12}, n-hexane and n-heptane are also tested for comparison purposes. The results obtained from these scientific tests and the challenges encountered are further discussed in detail, including electron paramagnetic resonance analysis (EPR).

2. Materials and Methods

2.1. Reagents

All reagents were purchased from Aldrich, Merck, and Fluka and were used without further purification. The diluents were 1-butyl-, 1-decyl-3-methylimidazolium-bis(trifluoro methanesulfonyl)imides, (purity, 99.5%, average water content is ca. 200 ppm) purchased from Solvionic (Toulouse, France) and $CHCl_3$ (Merck, p.a.), C_6H_{12} (Merck, p.a.), $CH_3(CH_2)_4CH_3$, i.e., n-hexane (Merck, $\geq$95%), $CH_3(CH_2)_5CH_3$, i.e., n-heptane (Merck, 99%), ethylene glycol (Merck, 99.5%), glycerol (Thermoscientific, 99+%). The commercial products 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP, purity > 99%, Fluka) and 2-thenoyltrifluoroacetone (HTTA, Fluka, $\approx$ 99%) were used as received. All other commercially available analytical-grade reagents were used without any further purification.

Stock solution of gadolinium ion (3×10^{-3} mol/dm^3) was prepared from $Gd(NO_3)_3 \cdot 6H_2O$ (Fluka, puriss) by dissolving and diluting with distilled water or ethylene glycol to the required volume. Nitric acid, 65% was used (Merck, p.a.) to adjust the pH of the aqueous solutions or MP phase added to 0.1 mol/dm^3 2-morpholinoethanesulfonic acid (MES) buffer (Alfa Aesar, 98%).

2.2. Solvent Extraction Studies

Extraction experiments were carried out at room temperature by mixing the two immiscible phases in a 1:1 *v/v* ratio (1.5 mL) for 2 h (1500 rpm), which was sufficient for attaining equilibrium. After the separation of the liquid phases, the Gd(III) ion concentration in the aqueous or more polar organic phase was determined by using ICP-OES spectroscopy (“Prodigy” High dispersion ICP-OES, Teledyne Leeman Labs, Hudson, NH, USA). The concentration of the metal ion in the organic phase (less polar phase) was obtained by material balance. Extractant solutions in an IL were prepared by precisely weighted samples. The acidity of the aqueous phase at equilibrium was measured by a pH meter (pH 211 HANNA, Woonsocket, RI, USA) with an accuracy of 0.01 pH unit. The Gd(III) ion initial concentration was 6×10^{-4} mol/dm^3 in all experiments.

For competitive extraction tests, a volume of 2 mL of the prepared aqueous solution (or no-aqueous compound) containing various M^{n+} metal ions (the corresponding nitrate salts were used $M^{n+}(NO_3)_n/M^{n+}(NO_3)_n \cdot xH_2O$) was equilibrated for 3 h (1500 rpm) with 2 mL organic phase (LP phase), which includes the studied ligand molecule, HP. After phase separation, the metal ion concentrations in the aqueous solution were determined by ICP-OES (“Prodigy” High dispersion ICP-OES, Teledyne Leeman Labs, USA).

The distribution ratio (*D*) at equilibrium was calculated as follows:

$$D = \frac{[M^{n+}]_{aq,in} - [M^{n+}]_{aq,f}}{[M^{n+}]_{aq,f}} \times \frac{V_{aq}}{V_{IL}} \quad (1)$$

where $[M^{n+}]_{aq,in}$ is the concentration of M^{n+} ion in the aqueous phase (MP phase) before liquid–liquid extraction tests, and $[M^{n+}]_{aq,f}$ is the concentration of the same metal ion in the aqueous phase after extraction. In general, V_{aq} and V_{IL} are the volumes of aqueous and organic phases as well as the volumes of two immiscible phases used to perform experiments, herein a 1:1 *v/v* extraction. For instance, duplicate experiments showed that the reproducibility of *D* measurements was generally within 95%.

Extractability (%E) was evaluated as follows:

$$extractability = \frac{[M^{n+}]_{aq,in} - [M^{n+}]_{aq,f}}{[M^{n+}]_{aq,in}} \times 100. \quad (2)$$

The metal separation between elements in the periodic table can be estimated using separation factors (SF) determined as a ratio of distribution ratios of two metal ions, namely, the lighter and heavier ones:

$$\mathrm{SF} = D_{(\mathrm{Z})}/D_{(\mathrm{Z+n})}. \quad (3)$$

2.3. EPR Measurements

A Bruker EMX Premium X EPR spectrometer operating in the X-band at 9.4 GHz was used to perform the EPR analysis in the present study. The analysis of the extract solutions at room temperature was carried out with aqueous solution cell ER-160FC-Q, while for the measurements at 100 K a thermoregulatory system ER 4141 VTM was used. The concentration of Gd^{3+} ion was evaluated using a Bruker licensed software Spin count. As it is known, the Gd^{3+} ion adopts a $4f^7$ electronic configuration. In general, the EPR spectrum of Gd^{3+} displays many components due to transitions between Kramers doublets ($m_s = \pm 1/2$, $m_s = \pm 3/2$, m_s of $= \pm 5/2$ and $m_s = \pm 7/2$). For Gd^{3+} located in low-symmetry crystal field, the EPR spectrum is additionally complicated by zero-field splitting parameters (D, E).

All samples provided were recorded in the frozen state at a temperature of 120 K and in the liquid state at 295 K. The measurement conditions of the samples containing Fe and Cr at both temperatures were Modulation Amplitude, MA = 2 mT, and microwave power 1.796 mW (Att = 18). The measurement conditions of the samples containing Cu, at both temperatures, were Modulation Amplitude, MA = 1 mT, and microwave power 1.796 mW (Att = 20).

3. Results and Discussion

3.1. Investigation of Gd(III) Solvent Extraction: Comparison of Molecular Diluent and IL as Well as Aqueous and Non-Aqueous Systems

The main goal of this study is to develop a non-aqueous process for switchable separation of 4f-ions, which is to be competitive over conventional aqueous solvent extraction systems, and to test this process further with other switchable hydrophilicity diluents. It is worth noting that preliminary tests with ethanol amine and ethyl lactate showed the impossibility of being used for these research purposes. Unlike conventional solvent extraction chemistry, the new approach uses two immiscible organic phases: more polar (MP) as well as less polar (LP). The influence of the ligand HP concentration on the extraction of Gd(III) ions was studied with $CHCl_3$/EtG and $[C_1C_{10}im^+][Tf_2N^-]$/EtG solutions in order to assess the advantages of non-aqueous chemical process and IL compounds as well as to check the difference in 4f-ion extraction behavior. The results are shown in Figure 1. D_P is the distribution ratio due to the gadolinium extraction with HP alone under the experimental conditions, applying various concentrations of the chelating ligand. It is evident that when EtG solutions are used, the organic diluent $CHCl_3$ somehow clearly excels the IL compound $[C_1C_{10}im^+][Tf_2N^-]$. In fact, the opposite picture is usually seen, i.e., ionic liquids outperforming typical organic diluents during metal solvent extraction. It should be noted that all physical and chemical diluent properties, including gaining more insight into the solvation of metal ions in a non-aqueous environment, contribute to the extraction mechanism, resulting in higher efficiency for a similar molecular system. The obtained two plots for HP concentration (when two different, less polar organic phases were applied to $CHCl_3$ and the hydrophobic IL) give a good linear log–log confidence with a slope of 0.48 but strongly deviate from the value of one. This means that no more than one molecule of the acidic ligand is involved in the extraction process under the applied experimental conditions and the rest of the charge of Ln^{3+} ion could be compensated probably by $[Tf_2N^-]$ anions present in the organic phase [38–41]. It is very likely that the reaction mechanism in both cases is the same and it can be said that there is no transfer of the IL cation ($[C_1C_{10}im^+]$) in the second organic phase, i.e., ethylene glycol:

$$Gd^{3+}_{(MP)} + ½\,HP_{(LP)} + n[Tf_2N^-]_{(LP)} \rightleftharpoons Gd(P)_{½}{}^{z+}(Tf_2N^-)_{n(LP)} + H^+_{(MP)} \quad (4)$$

where the subscripts "MP" and "LP" denote the two organic phases, more and less polar, respectively.

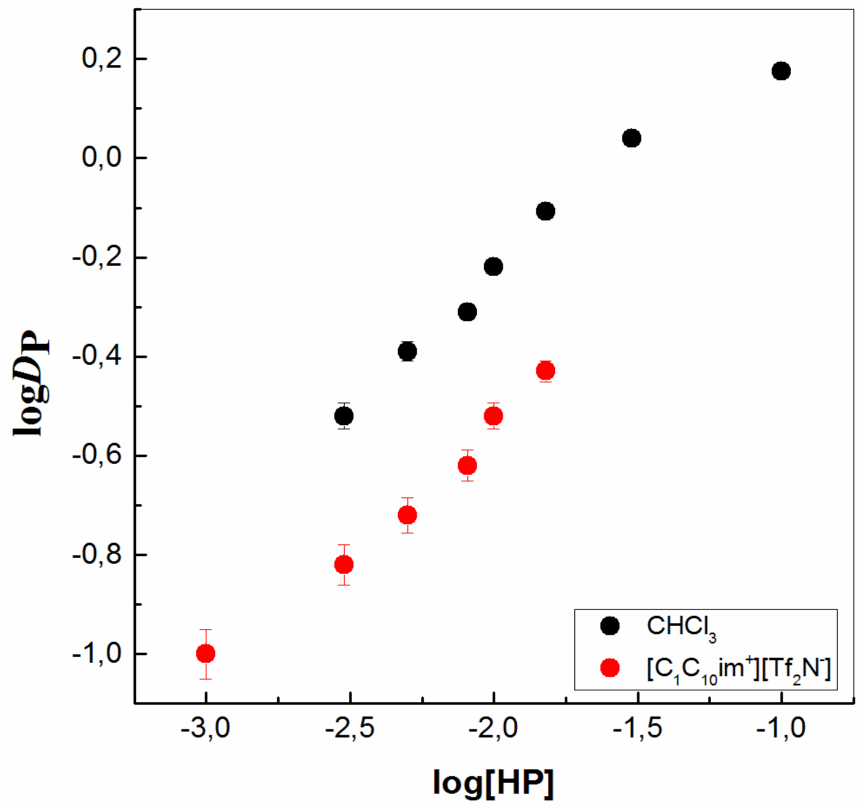


Figure 1. LogD_P vs. log[HP] for Gd(III) liquid–liquid extraction at pH_{in} = 3.30 from EtG solutions.

In order to investigate the role of ionic liquid on the traditional solvent extraction process, a set of experiments was performed under conditions of the aqueous phase comparable with those carried out in $CHCl_3$. The distinct extraction behavior of the corresponding two systems towards Gd(III) ions was described in Figure 2. As a whole, the higher extraction efficiency of various extractants diluted in ILs compared to traditional molecular diluents is a common feature and different stoichiometries of the extracted metal species are usually, but not always, found [10,34,41,42]. Therefore, as expected, the solvent extraction of Gd(III) ion increased rapidly when $CHCl_3$ was changed with the IL compound. Furthermore, as shown in Figure 2, linear relationships between log$D$ and log[HP] with a slope close to one (1.05 (IL) and 0.98 ($CHCl_3$)) were obtained for investigated two systems. Consequently, the possible extraction mechanism can be elucidated by applying the following equations:

$$Gd^{3+}_{(aq)} + HP_{(o)} + n[C_1C_{10}im^+][Tf_2N^-]_{(o)} \rightleftharpoons Gd(P)^{2+}(Tf_2N^-)_{n(o)} + H^+_{(aq)} + n[C_1C_{10}im^+]_{(aq)} \quad (5)$$

$$Gd^{3+}_{(aq)} + HP_{(o)} + \rightleftharpoons Gd(P)^{2+}_{(o)} + H^+_{(aq)} \quad (6)$$

where the subscripts "aq" and "o" denote aqueous and organic phases, respectively.

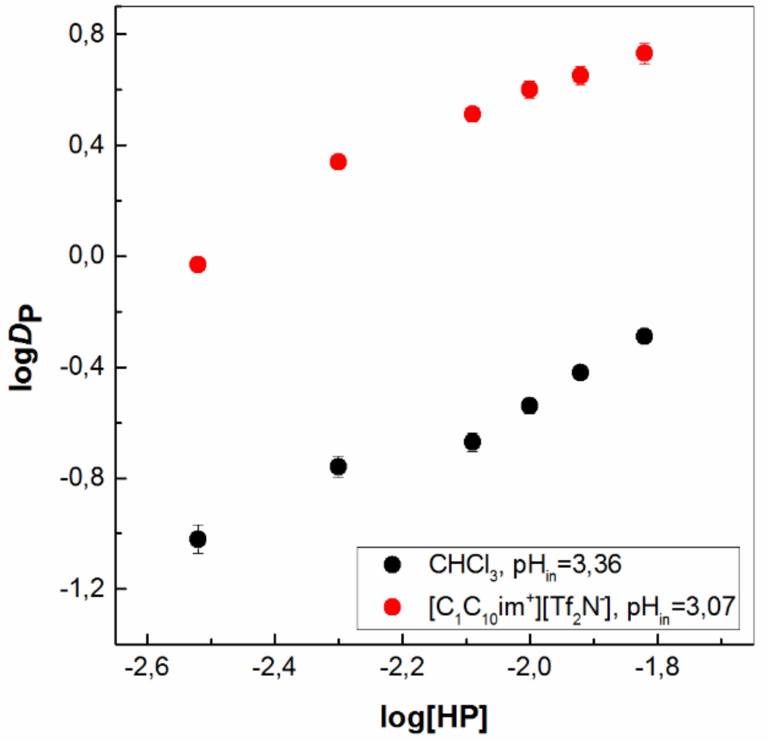


Figure 2. LogD_P vs. log[HP] for Gd(III) liquid–liquid extraction from aqueous solutions.

It is certain that under other experimental conditions, i.e., changing the acidity of the aqueous phase would produce a different result for the system involving chloroform, usually with the participation of three or four molecules of the chelating ligand in the reaction mechanism [43]. However, several general conclusions can be drawn from the information obtained herein. First, when using an ionic liquid, water is preferable to be used as the second phase containing the target metal for solvent extraction, rather than ethylene glycol. Thus, in other words, unsatisfactory results were obtained precisely with this second organic phase compared to water. Second, as a whole, the exact opposite trend can be seen with the use of $CHCl_3$ as a less polar phase; i.e., in an ethylene glycol medium, the metal extraction is much more efficient than when water is applied as a medium (MP).

Another noteworthy point is that the process is not so affected by pH (0.1 mol/dm^3 MES and HNO_3/NaOH):

(a) The solvent system EtG/[C_1C_{10}im$^+$][Tf_2N^-] has a pH in the range of 1.60 to 4.45 at [HP] = 2.5 × 10^{-2} mol/dm^3 produce log$D$~0.52;

(b) The H_2O/[C_1C_{10}im$^+$][Tf_2N^-] system has a pH in the range of 1.90 to 3.04 at [HP] = 4 × 10^{-2} mol/dm^3, leading to log$D$ > 1.4; i.e., 100% extraction was achieved.

What happens when the diluent is chloroform in combination with water (1.855 D) and ethylene glycol (EtG has a zero-dipole moment) can be seen in Figure 3. The solvent system in used EtG/$CHCl_3$ is superior to H_2O/$CHCl_3$.

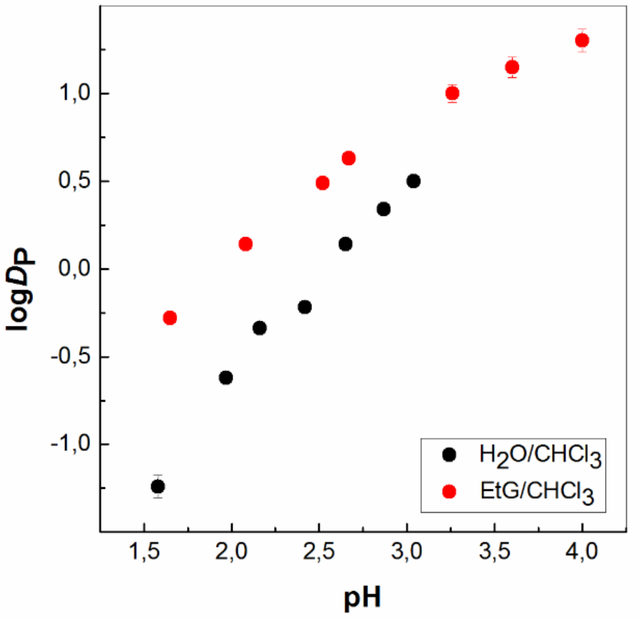


Figure 3. LogD_P vs. pH of the more polar phase at [HP] = 4 × 10^{-2} mol/dm^3 (slopes 0.67 and 1.15 for EtG and H_2O, respectively).

Another interesting fact, however, is that a similar trend is not observed when non-polar diluents are used instead of investigated $CHCl_3$ (dipole moment, 1.15 D) such as C_6H_{12} (0.0 D), n-hexane (0.08 D), or n-heptane (0.0 D). From the experiments carried out with various concentrations of the chelating ligand (HP), it can be seen that the aqueous phase gives extremely good results and as a consequence is preferable (MP) than ethylene glycol in these cases, Figure 4. Thus, the superiority of the non-aqueous solvent system such as EtG/n-heptane is emphasized compared to H_2O/n-heptane, changing the pH values, as shown in Figure 5.

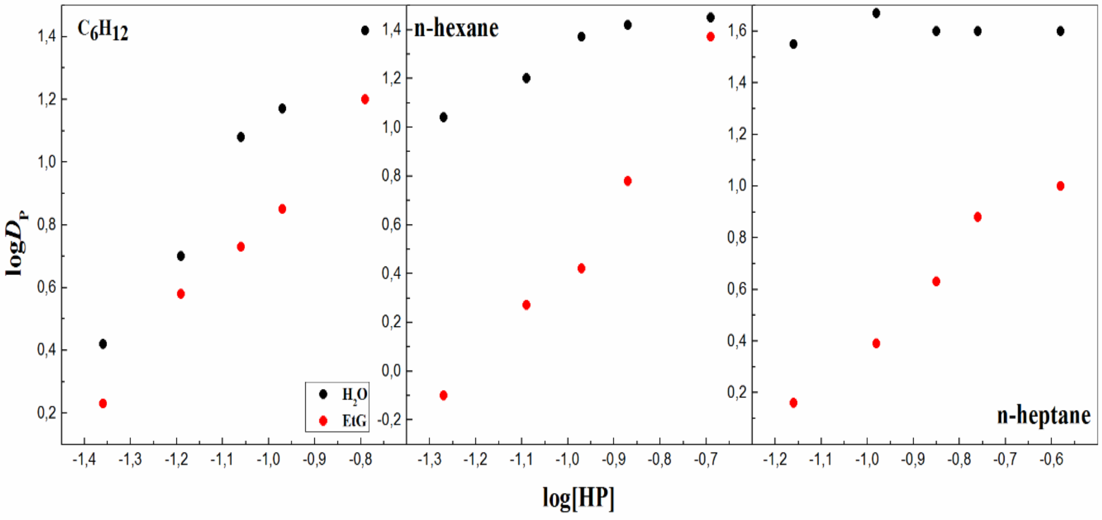


Figure 4. LogD_P vs. log[HP] at constant pH (C_6H_{12}, pH = 2.16 and 0.43; n-hexane, pH = 2.70 and 1.26; n-heptane, pH = 2.19 and 0.51, respectively, H_2O and EtG).

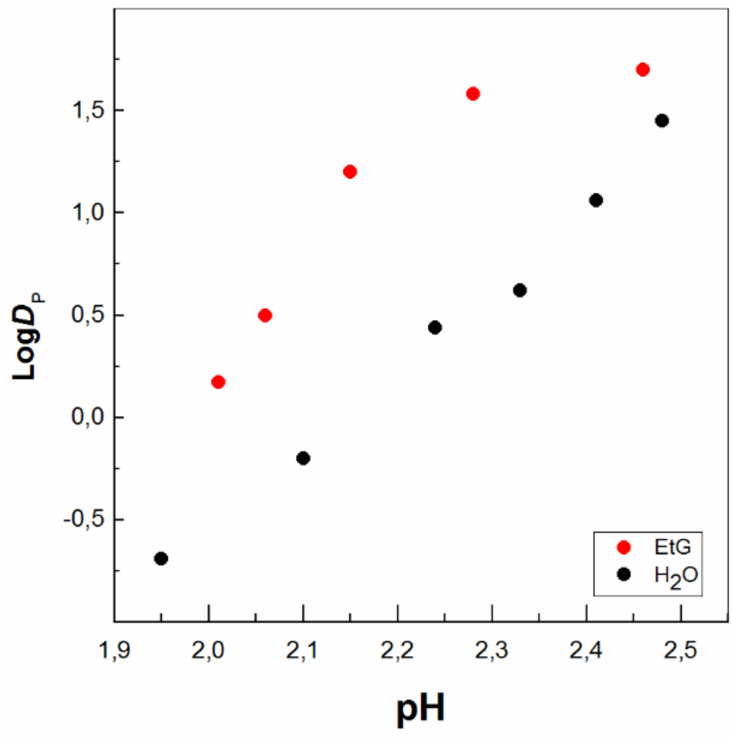


Figure 5. LogD_P vs. pH of the more polar phase at [HP] = 4.2×10^{-2} mol/dm^3 using n-heptane as a diluent.

3.2. Solvent Extraction and Selectivity across the Periodic Table and 4f Series

It is a known fact in coordination chemistry that different metal ions show a different affinity towards a given specific extractant molecule, so they will probably distribute differently over both immiscible liquid phases and metal separation can be easily achieved. The competitive solvent extraction test of almost 25 metal ions by the chelating ligand HP diluted in two ILs and $CHCl_3$ has also been conducted in order to evaluate the switchable hydrophilic diluent, EtG as a more polar liquid phase, Figure 6.

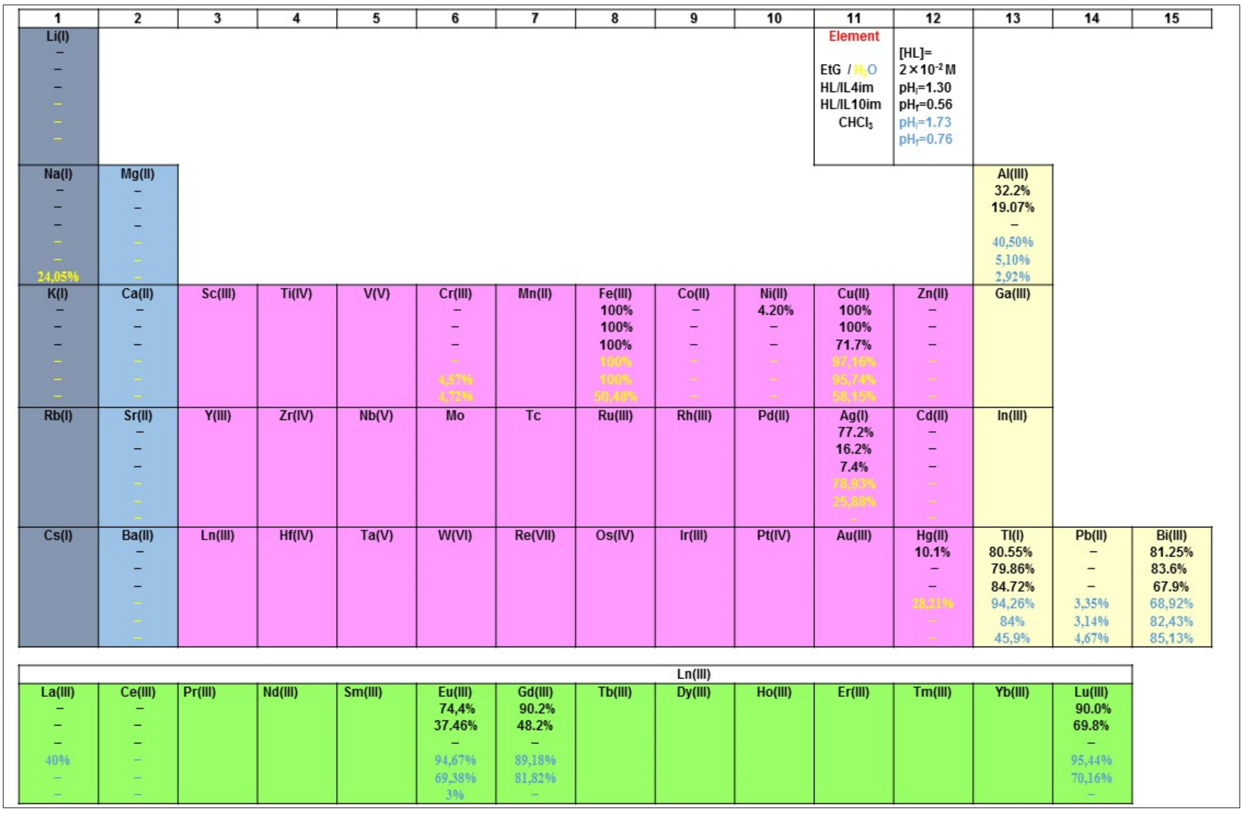
In summary, the studied 25 metal ions could be classified into the two groups listed below, according to the degree of HP extraction performance in an IL media applying EtG:

(1) Unextractable metal ions, %E < 1: Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Zn^{2+}, Cd^2+, Cr^{3+}, Co^{2+}, La^{3+}, Ce^{3+};

(2) Overall extraction %E $\leq$ 50: Al^{3+} as well as Ni^{2+} and Hg^{2+} with only $[C_1C_4im^+][Tf_2N^-]$ as a diluent.

Overall extraction %E > 50: Fe^{3+}, Cu^{2+}, Tl^+, Bi^{3+}, Lu^{3+}, while Ag^+, Eu^{3+}, Gd^{3+} only with the participation of the $[C_1C_4im^+][Tf_2N^-]$ compound in the system.

Therefore, metal cations such as Hg^{2+} and Ni^{2+} could be removed from the ion mixture by applying only 1 butyl homolog of the imidazolium IL, and, at the same time, it is not at all possible to extract them with the more hydrophobic IL $[C_1C_{10}im^+][Tf_2N^-]$. What is noticeable about the f-elements is the obtained zero extraction for lanthanum and cerium, which can be explained by the relatively low acidity of the environment. If we compare the two ionic compounds, a negligible difference is observed for Ag^+, Eu^{3+}, and Gd^{3+} ions, about two times lower solvent extraction with $[C_1C_{10}im^+][Tf_2N^-]$ compared to its short-chain analog. When using chloroform as a diluent, the picture is the same in parts above or equal to 50% extraction, but only for d-elements, i.e., Fe^{3+}, Cu^{2+}, Tl^+, and Bi^{3+}. Unfortunately, lanthanoids are not extracted under these experimental conditions by applying EtG/$CHCl_3$. A lack of affinity towards the chelating agent HP in this organic medium was observed for all metal cations examined, with one exception: silver ions. For the first time, the advantage of ionic liquids as an extractant diluent leading to better extraction, which can be used successfully in the separation chemistry for various metal cations, has been observed herein, of course in combination with EtG, i.e., non-aqueous processes.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Li(I) – – – – – –										Element EtG / H_2O HL/IL4im HL/IL10im $CHCl_3$	[HL]= 2×10^{-2} M pH_i=1.30 pH_f=0.56 pH_i=1.73 pH_f=0.76			
Na(I) – – – – – 24,05%	Mg(II) – – – – – –											Al(III) 32.2% 19.07% – 40,50% 5,10% 2,92%		
K(I) – – – – – –	Ca(II) – – – – – –	Sc(III)	Ti(IV)	V(V)	Cr(III) – – – – 4,57% 4,72%	Mn(II)	Fe(III) 100% 100% 100% 100% 100% 50,48%	Co(II) – – – – – –	Ni(II) 4.20% – – – – –	Cu(II) 100% 100% 71.7% 97,16% 95,74% 58,15%	Zn(II) – – – – – –	Ga(III)		
Rb(I)	Sr(II) – – – – – –	Y(III)	Zr(IV)	Nb(V)	Mo	Tc	Ru(III)	Rh(III)	Pd(II)	Ag(I) 77.2% 16.2% 7.4% 78,93% 25,88% –	Cd(II) – – – – – –	In(III)		
Cs(I)	Ba(II) – – – – – –	Ln(III)	Hf(IV)	Ta(V)	W(VI)	Re(VII)	Os(IV)	Ir(III)	Pt(IV)	Au(III)	Hg(II) 10.1% – – 28,21% – –	Tl(I) 80.55% 79.86% 84.72% 94,26% 84% 45,9%	Pb(II) – – – 3,35% 3,14% 4,67%	Bi(III) 81.25% 83.6% 67.9% 68,92% 82,43% 85,13%
Ln(III)														
La(III) – – – 40% – –	Ce(III) – – – – – –	Pr(III)	Nd(III)	Sm(III)	Eu(III) 74,4% 37.46% – 94,67% 69,38% 3%	Gd(III) 90.2% 48.2% – 89,18% 81,82% –	Tb(III)	Dy(III)	Ho(III)	Er(III)	Tm(III)	Yb(III)	Lu(III) 90.0% 69.8% – 95,44% 70,16% –	

Figure 6. Solvent extraction performance of HP ligand (2 × 10^{-2} mol/dm^3) diluted in two ILs, i.e., $[C_1C_4im^+]/[C_1C_{10}im^+][Tf_2N^-]$ and $CHCl_3$ for 25 metal ions. Extraction data with the more polar organic phase consisting of EtG or water were also involved, in the first three and the second three positions, respectively, in the cells (see the explanation under NO.11 cell). The reported extractability values (%) represent the average of three measurements with a deviation of less than 5%.

When using the immiscible system H_2O/ILs, the grouping of metal ions is as follows according to the data presented in Figure 6:

(1) Unextractable metal ions, %E < 1: Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Cd^2+, Co^{2+}, Ni^{2+}, Ce^{3+};

(2) Overall extraction %E ≤ 50: Cr^{3+}, Pb^{2+}, Al^{3+} but Hg^{2+} and La^{3+} only when the $[C_1C_4im^+][Tf_2N^-]$ compound is a diluent;

(3) Overall extraction %E > 50: Fe^{3+}, Cu^{2+}, Tl^+, Bi^{3+}, Eu^{3+}, Gd^{3+}, Lu^{3+}, but Ag^+ only reacts with the $[C_1C_4im^+][Tf_2N^-]$ compound.

Of interest is the chemical element lead, which, although below 5%, it is extracted, while in an ethylene glycol medium, it is not. The same is true for the lighter member of the 4f series, La^{3+}. Under certain experimental conditions, however, this simplification is perhaps unjustified. Understanding could be achieved by analyzing the exact parameters of the process. The water environment turns out to be favorable for another metal cation, such as chromium, Cr^{3+}, but not with the IL having n = 4 ($[C_1C_nim^+][Tf_2N^-]$), so the hydrophobic diluents are favorable in this case, i.e., n = 10 and $CHCl_3$. Again, the advantage of the $[C_1C_4im^+][Tf_2N^-]$ compound for both solvent extraction and separation processes of metal cations is worth noting, and this is particularly evident for ions such as Al^{3+}, Ag^+, Eu^{3+}, and Lu^{3+}. On the other hand, the advantage of ILs has been demonstrated for the umpteenth time in this water system as well, in comparison to the organic molecular diluent $CHCl_3$. Among the lanthanoids, only Gd^{3+} is extracted at ~3%, while the s-ion, Na^+

is about 24%. More than 50% extraction efficiency is observed as usual in similar studies for Fe^{3+}, Cu^{2+}, and the heavy Bi^{3+} [44,45], while less than 50% solvent extraction from water to chloroform medium could be seen for Al^{3+}, Pb^{2+}, and Cr^{3+}.

It is a known fact that the good selectivity of metal ions during liquid−liquid extraction process largely relies on the affinity of metals to the ligands, which normally reside in the organic (less polar) phase because of their high hydrophobicity. We follow a different route herein to apply a typical and well-known chelating extractant in coordination chemistry such as 4-acylpyrazolones in order to see the influence of the organic (more polar) phase on separation chemistry. The first thing that is noticeable from the obtained selectivity data is the absence of the solvent extraction process for nickel in aqueous environments (see Tables S1 and S2 in the Supplementary Material). However, the calculated values for the separation coefficient of nickel with all heavier ions are extremely high when using ethylene glycol. For example, the SFs for Ni/Cu pair is 324, while for the Ni/Gd pair, this value is ca. 211. This is also a characteristic feature of Al^{3+}, whose selectivity is more pronounced in EtG than in water. However, the opposite is observed for Fe^{3+}, Hg^{2+}, as well as Cu^{2+} in a non-aqueous environment, wherein their separation from other metal ions is extremely weak. The calculated SF values for Fe/Hg and Cu/Hg pairs are 1×10^{-2} and 7×10^{-3}, while in a water environment, these values reach up to 525 and 88, respectively. It should be emphasized that lanthanoids, in general, have a poorer separation with Hg^{2+} in EtG (approximately over 1000 times). For instance, it is very difficult to draw a similar conclusion for the ion Tl^{+} and Bi^{3+} as well, but water seems to be the preferred medium, like a polar phase, in this case. What can be said about the 4f-ions is that they are better separated into EtG. In other words, a conclusion that deserves further research investigations of different non-aqueous phases. However, the 4f separation from heavier ions such as Hg^{2+}, Bi^{3+} and Tl^{+} is likely much better in the system $H_2O//[C_1C_4im^+][Tf_2N^-]$, in contrast to $EtG//[C_1C_4im^+][Tf_2N^-]$. However, the results indicate that 4f-ions were recovered efficiently from the aqueous phase. Thus, the employment of the EtG compound, i.e., a non-aqueous solvent extraction system, appears to be a versatile scientific approach when the intragroup 4f selectivity is searched for.

Moreover, since ethanol amine, ethyl lactate, and glycerol did not prove to be suitable to replace water 100%, and the last compound was not able to dissolve a sufficient amount of MES to achieve the desired concentration, a test was carried out to investigate the influence of glycerol in a ratio of 1 to 1 with water (*v/v*). The obtained results are presented in Figure 7. It can be concluded on the basis of obtained results that the influence is particularly pronounced in a very positive way, especially referring to the solvent extraction of s-elements, something that was not noticeable in the previous solvent system combinations, as well as for d-elements such as Co, Ni, Zn, and Cd. In addition, the typical good extraction of metals such as Fe, Hg, Al, Tl, Bi, and, of course, the 4f series is achieved again. If we look at a Table S3 (Table S4) in the Supplementary material, where the separation coefficients for the studied metal ions from the periodic table, whole number 25, and the various ion pairs are placed, it can be seen that the selectivity in the 4f series is reasonably good above ca. 0.3. The high values of SFs calculated for Zn and Sr with other metals ranging from Li to Cu must be noted. The high values obtained for SFs between cobalt and lanthanoids could be useful and could be further used in recycling processes, while it is low for nickel and Lns [46]. We cannot skip the high selectivity obtained also for K and Al ions as forming pairs with other chemical elements with an atomic number after 29, i.e., Cu. In general, the obtained data herein show that the addition of this compound, glycerol, to the aqueous phase can be cleverly exploited in the future in separation chemistry.

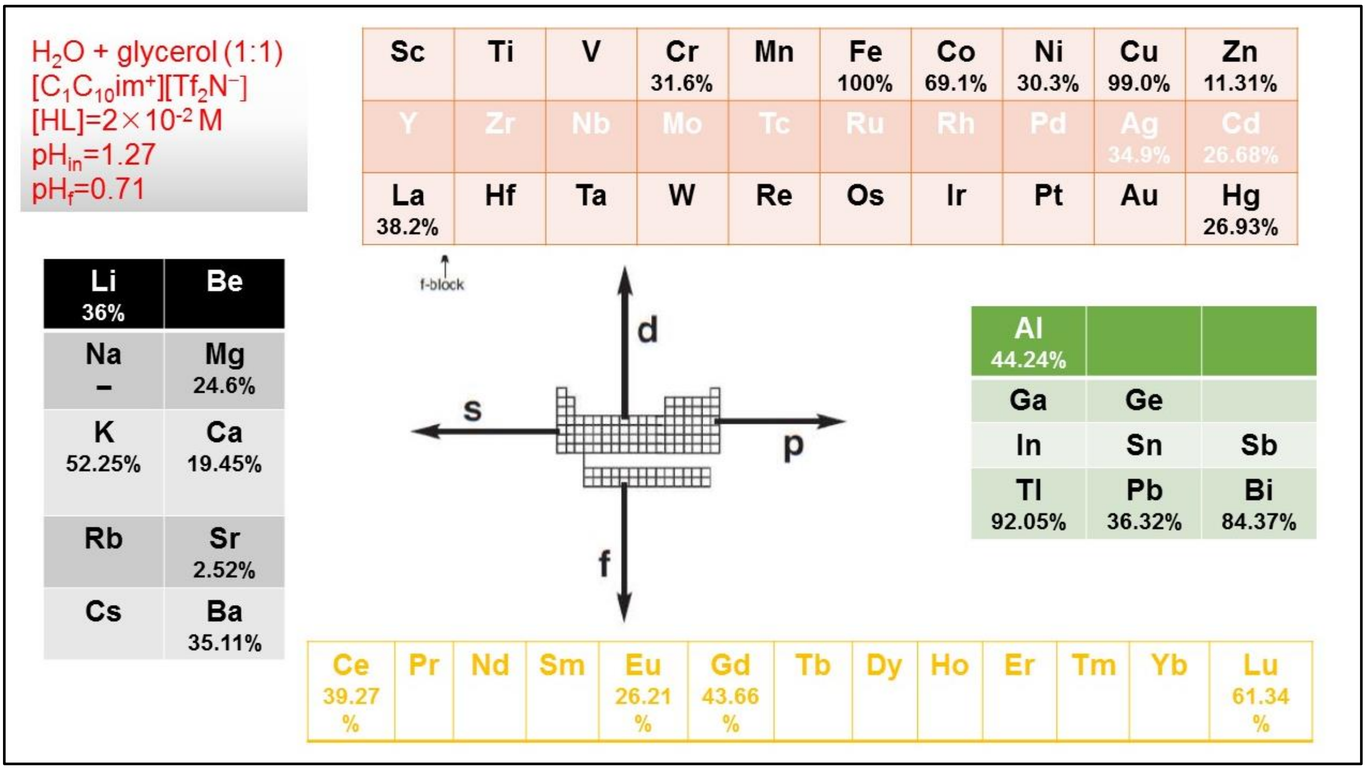


Figure 7. Extraction performance of HP ligand (2 × 10^{-2} mol/dm^3) diluted $C_1C_{10}im^+$][Tf_2N^-] for 25 metal ions. Extraction data with the more polar organic phase consisting of glycerol and water (1:1, *v/v*). The reported extractability values (%) represent the average of three measurements with deviation of less than 5%.

Further, from the obtained results, general rules mainly within the IL phase [$C_1C_nim^+$][Tf_2N^-] could be derived: first, whatever the extracting compound, its ability in the IL phase is always largely above that in the traditional organic diluent. However, as a whole, the chelating compounds do not provide improved SFs between two lanthanoids in an IL media as compared to molecular diluents, i.e., $CHCl_3$. On that account, the results from solvent extraction are clear advantages of the IL media compared to molecular, while the selectivity might be considered likely as rather disappointing at first glance. Nevertheless, it is worth explaining that the extraction ability and selectivity are almost always a pair of contradictory elements (*videlicet*, frequently high extraction efficiency was not accompanied by marked selectivity with any change in the solvent system, i.e., the nature of the two liquid phases or extracting moiety). This statement is demonstrated once again herein based on the data obtained from various investigated solvent systems, as shown in Figure 8.

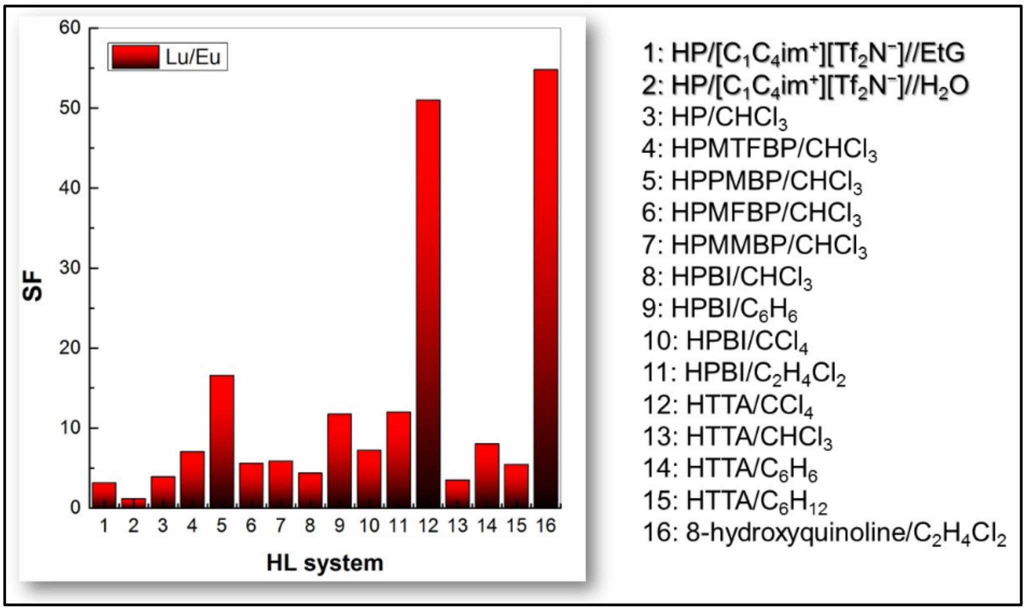


Figure 8. SFs for Lu/Eu pair using various solvent systems including chelating ligands: 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (HTTA), 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (HPMTFBP), 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one (HPPMBP), 3-methyl-4-(4-methylbenzoyl)-1-phenyl-pyrazol-5-one (HPMMBP), 4-(4-fluorobenzoyl)-3-methyl-1-phenyl-pyrazol-5-one (HPMFBP), and 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) [47–50].

Hence, the type of the used diluent usually has only a pronounced qualitative effect on the solvent extraction efficiency of 4f-ions without a noticeable influence to such a degree on the reaction mechanism, Figure S1. For a given metal, the values of the equilibrium constant increase in the following order $CHCl_3 < C_6H_6 < C_2H_4Cl_2 < CCl_4 < C_6H_{12}$ [51–53]. In many cases, spectrophotometry shows that the coordination of the metal chelate is invariant from one traditional organic diluent to another. As a starting assumption, the molecular diluent is usually considered inert, since it does not appear further in the extraction equilibrium expression, unlike ILs. It may be concluded that, as a whole, the increase in the diluent solvating ability hinders the extraction process [54]. Thus, it seems that the diluent effect on solvent extraction follows the general schematic behavior described in the solvation process of a solute in a liquid. Nevertheless, as a whole, based on our previous investigations and other research studies, while the selectivity decreases, the lanthanoid solvent extraction increases in the following order: β-diketone < 4-acylpyrazolone < 4-acyl-3-phenyl-5-isoxazolone. Another appropriate way to evaluate the solvent extraction power of the chelating ligands is to compare the corresponding values of pH_{50} [44]. Evidently, the values of pH_{50} for the liquid–liquid extraction of 4f-elements obtained when the chelating compound is the typical β-diketone, thenoyltrifluoroacetone (HTTA) are more than one pH unit larger compared to when 4-acylpyrazolone is in use, as well as approximately three pH units larger compared with 4-benzoyl-3-phenyl-5-isoxazolone reagents (see Figure S1). In addition, the difference of calculated ΔpH_{50} values decreases with increasing the atomic number of the investigated lanthanoids. Moreover, the sequence of the pH_{50} is in the following order: Lu < Ho < Eu < Nd < La. Consequently, the value of pH_{50} rises as the ionic radius of the lanthanoid element increases, as shown in Figure S2.

3.3. EPR Investigation of the Extracting LP Phases

In this investigation concerning the complexation of Gd(III) ion in the organic phase (LP), two chelating ligands have been chosen for parallel EPR analysis 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP) as well as thenoyltrifluoroacetone (HTTA). The data in Figure 9 indicates that the EPR spectrum of solutions **c** (ligand—HTTA in $CHCl_3$) consists of a slightly asymmetric signal with the following EPR parameters: g = 1.99 and

ΔH_{pp} = 3.0 mT. In samples **a** and **b**, in which the ligand HTTA was used for complexation, respectively, in $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_{10}im^+][Tf_2N^-]$, signals with $g \approx 1.99$ were also detected; however, they were extremely weak (Figure 9, narrow range). The spectra in a wide range of the magnetic field (Figure 9, left) do not show additional signals of interest. The signal with $g \approx 1.99$ corresponds to a transition between energy states with $m_s -1/2 \leftrightarrow +1/2$ and is attributed to Gd^{3+} located in a ligand field with high symmetry. In order to clear up the origin of all registered signals in the spectrum, we have to mention that the asterisk-marked signals are probably due to the well-resolved hyperfine structure of Cu^{2+} ions found as impurities in ILs.

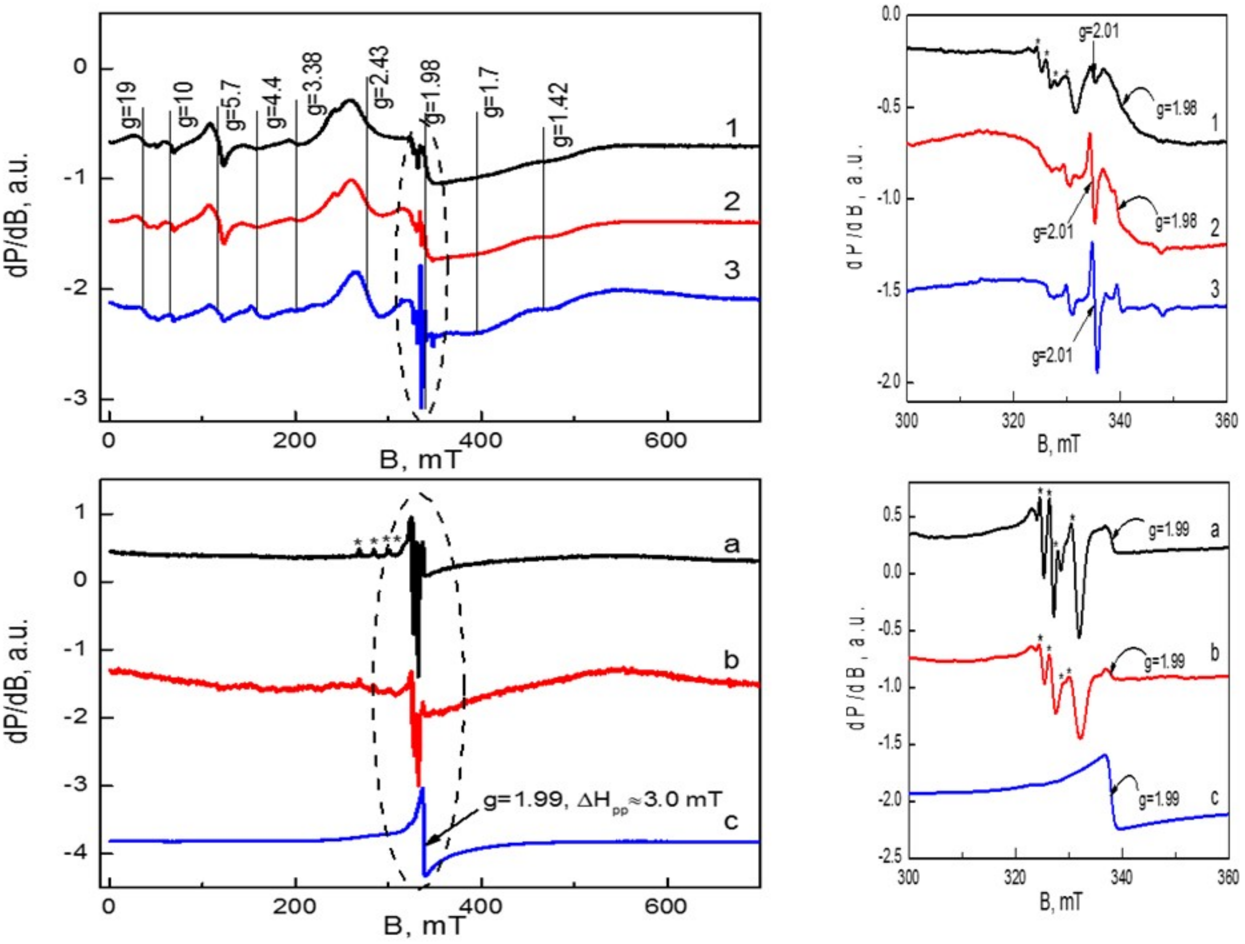


Figure 9. EPR spectra of frozen solutions of complexes of Gd^{3+} ($[Gd^{3+}]_{in} = 6 \times 10^{-4}$ mol/dm^3) with ligands [HP] = 8×10^{-3} mol/dm^3 (1, 2 and 3) and [HTTA] = 8×10^{-3} mol/dm^3 (a, b, and c) obtained after solvent extraction from EtG, respectively, in the following diluents $[C_1C_4im^+][Tf_2N^-]$ (1: pH_{eq} = 1.90 and a: pH_{eq} = 3.18), ($[C_1C_{10}im^+][Tf_2N^-]$ (2: pH_{eq} = 1.80 and b: pH_{eq} = 2.76), $CHCl_3$, (3: pH_{eq} = 2.32 and c: pH_{eq} = 5.81). On the left: range of the magnetic field 0−700 mT, on the right: range of the magnetic field 300−360 mT. Calculated $\log D_L$ are 0.27, 0.12, and −0.37 for samples 1-2-3 as well as −0.59, −0.06, and −0.92 for samples a-b-c.

The wide magnetic field EPR spectra of solutions one, two, and three (HP as a ligand, respectively, in $[C_1C_4im^+][Tf_2N^-]$, $[C_1C_{10}im^+][Tf_2N^-]$, and $CHCl_3$) consist of multiple signals located in the range from 0 to 600 mT and at least nine lines are clearly visible. In Figure 9, the effective values of the g-factors of the observed signals are indicated within a wide range. These signals could be assigned to the Gd^{3+} fine structure, as the existence of some forbidden transition could not be excluded. The presence of multiple signals with $g >> 2.0$ and $g < 2.0$ is associated with Gd^{3+} ions in a low-symmetry crystal field with large zero-field splitting parameters (D~hν) [55]. In the spectra registered in the narrow magnetic field range (300–360 mT), the signal with g = 1.98 could be seen as a constituent of the fine structure. A signal with g = 2.01 and ΔH_{pp} = 0.9 mT was also registered, on both sides of which two symmetrically located less intense signals were observed. Most likely, the narrow signal with g = 2.01 and the two satellite lines originate from the presence of a free radical in the ligand. Using the SpinCount program, part of the Bruker Xenon software, concentrations of Gd^{3+} ions in the investigated frozen solutions at 120 K were found (see Table S5). Results were obtained directly from the analysis without further experiments and quantitative EPR sample measurements such as those described by Yordanov in 1994 [56]. Thus, despite that the same analyses are performed with a higher concentration of the chelating extractants, In general, there is no particular change in the obtained spectra, although the amount of extracted gadolinium is different, as shown in Figure S4 and Table S6 (see as well Figure S3 for information).

On the other hand, from the conducted tests of simultaneous extraction of different metal ions, the established relatively high extraction of copper and iron is really striking. So, this led to the thought of studying the corresponding organic phases obtained after their solvent extraction using the EPR technique. As the reader can see, Figure 10 shows the EPR spectra of Cu^{2+} complexes extracted from EtG solution with HP dissolved in two iLs (n = 4 and 10) as well as their simulations. The EPR spectra were recorded both in a liquid state at room temperature and in frozen solutions at 100 K. As seen in Figure 10, all recorded EPR spectra show similar signals composed of parallel and perpendicular components with $g_{\|} > g_{\perp}$. Such spectra are usually attributed to Cu^{2+} ions in tetragonally distorted octahedral symmetry, with an unpaired electron occupying the $d_z{}^2$ orbital ($d_x{}^2{}_{-y}{}^2$ ground state of Cu^{2+}). The frozen solutions spectra are characterized with clearly resolved hyperfine structure (hfs) lines in parallel and perpendicular components, while liquid spectra show only resolved hfs lines in their parallel part. The performed simulation reveals the existence of hyperfine structure lines that belong to two kinds of Cu^{2+} ions in slightly different environments (Table 1). The described spectra with well-separated hfs lines are characteristic of the presence of well-isolated Cu^{2+} ions. In addition, no substantial differences in parameters for liquid and frozen samples were established. Taking into account the EPR results, we could summarize that Cu^{2+} ions possess similar coordination with HP ligand, regardless of the used ionic diluent ($[C_1C_4im^+][Tf_2N^-]$ or $[C_1C_{10}im^+][Tf_2N^-]$). The quantitative analysis performed on the frozen solutions showed that the concentration of Cu^{2+} ions in the investigated quantity of LP phases $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_{10}im^+][Tf_2N^-]$ are 2.00×10^{-3} mol/dm^3 and 1.17×10^{-3} mol/dm^3, respectively.

Further, the EPR spectra of the corresponding frozen samples containing Fe^{3+} are presented in Figure 11. As seen, the two spectra consist of a signal with g~4.23 and line width ΔH_{pp} = 15 mT. Such a signal is characteristic of isolated Fe^{3+} ions located in highly distorted symmetry. The Fe^{3+} concentrations calculated from the EPR analysis of frozen solutions for Fe^{3+} applying both ILs (n = 4 and n = 10) are 3.7×10^{-4} mol/dm^3 and 4.8×10^{-4} mol/dm^3, respectively.

Table 1. Values of EPR parameters of Cu^{2+} ions established after HP complexation in ILs.

$Cu^{2+}-[C_1C_4im^+][Tf_2N^-]$ 100K	$Cu^{2+}-[C_1C_{10}im^+][Tf_2N^-]$ 100K	$Cu^{2+}-[C_1C_4im^+][Tf_2N^-]$ 295K	$Cu^{2+}-[C_1C_{10}im^+][Tf_2N^-]$ 295K
g_1 = 2.0575, g_2 = 2.0636 g_3 = 2.3034 $A_{\|}$ = 17.62 mT	g_1 = 2.0583, g_2 = 2.0645 g_3 = 2.2980 $A_{\|}$ = 17.66 mT	g_1 = 2.0746, g_2 = 2.0596 g_3 = 2.2975 $A_{\|}$ = 14.45 mT	g_1 = 2.0692 g_2 = 2.0560 g_3 = 2.2952 $A_{\|}$ = 15.00 mT
g_1 = 2.0526, g_2 = 2.0662 g_3 = 2.31057 $A_{\|}$ = 15.53 mT	g_1 = 2.0625, g_2 = 2.0663 g_3 = 2.3155 $A_{\|}$ = 15.16 mT		

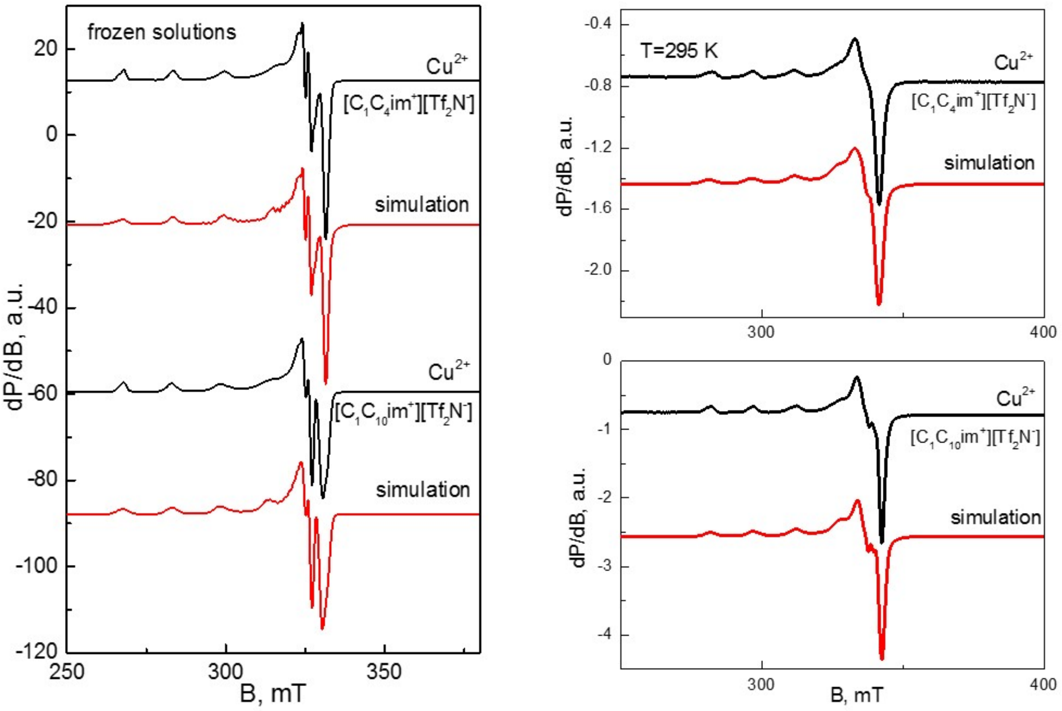


Figure 10. EPR spectra of Cu^{2+} obtained after solvent extraction with HP = 2 × 10^{-2} mol/dm^3 in $[C_1C_4im^+][Tf_2N^-]$ (1) and $[C_1C_{10}im^+][Tf_2N^-]$ (2) recorded in frozen solutions (left) and at room temperature (right): MP phase—$[Cu^{2+}]_{in}$ = 6 × 10^{-4} mol/dm^3 and 0.1 mol/dm^3 MES in EtG. Calculated %E is 98.66% and 99.53%—ICP-OES based on an average of three parallel determinations.

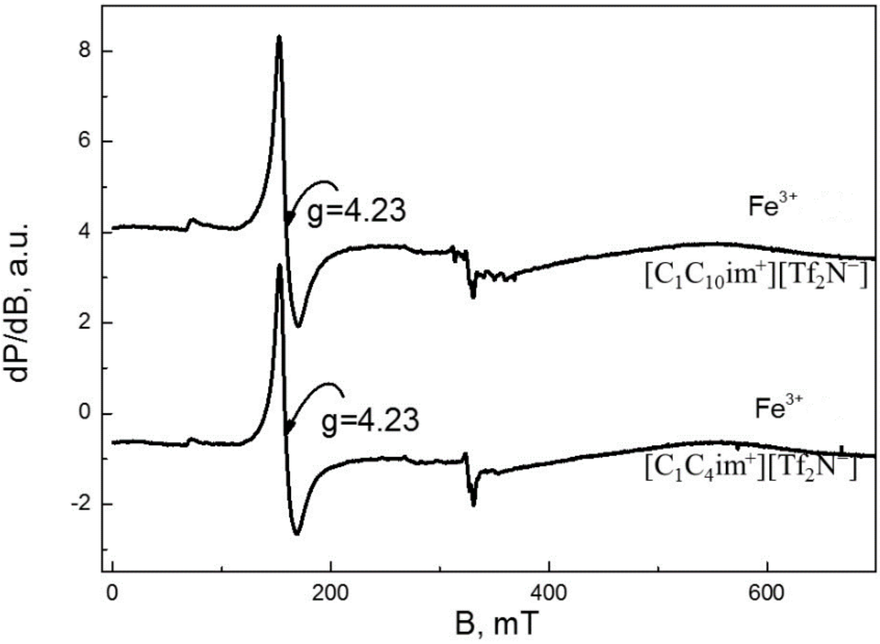


Figure 11. EPR spectra of Fe^{3+} obtained after solvent extraction with HP = 2 × 10^{-2} mol/dm^3 in $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_{10}im^+][Tf_2N^-]$ recorded in frozen solutions: MP phase—$[Fe^{3+}]_{in}$ = 6 × 10^{-4} mol/dm^3 and 0.1 mol/dm^3 MES in EtG. Calculated %E is 95.82% and 96.12%—ICP-OES based on an average of three parallel determinations.

Since chromium (III) compounds (d^3) are paramagnetic (S = 3/2), EPR spectroscopy provides an additional analytical method. However, the attempt to obtain an EPR spectrum of Cr^{3+} complexes with HP ligand extracted in both ionic liquids brought about difficulties.

Both registered spectra are shown in Figures S5 and S6 (Supplementary material). In fact, the EPR spectrum of Cr^{3+} in EtG consists of several lines that could be set in two groups according to their line width: one set of narrower lines (g = 5.7, 2.08, 1.92, 1.98) (ΔH_{pp} = 5 mT) and one set of broader signals (g = 4.7, 2.4, 2.2, 1.5) (Figure S7). The narrow line set is ascribed to well-isolated Cr^{3+} ions, while the broad line set is ascribed to Cr^{3+} ions that experience some exchange interaction. In the central part of the spectrum (g~1.98) is visible a broad signal of exchanged coupled Cr^{3+} ions, on which are superimposed the narrow signals with g = 2.08, 1.92, 1.98. Taking into account the standard spectrum (Figure S7), it seems that the signals with g = 5.7, 2.4, and 2.2 in samples that have undergone extractions into IL could be related to Cr^{3+} ions in ligand fields with distorted symmetry and large zero-field splitting constants. However, their extremely low intensities should be outlined.

4. Conclusions

An environmentally sound solvent extraction process of Gd(III) ions was developed in the present study, changing the chemical nature of the two liquid phases. In order to improve the process efficiency, the substitution of typical organic diluents with ILs as well as pure water with ethylene glycol or partly with glycerol (1:1) was considered. Overall, the results obtained from the investigation are as follows:

1. As a general rule, our results indicate that “green media” such as ILs have fantastic solvent extraction potential, which usually results in less selectivity. This phenomenon can be changed by changing the nature of the opposite liquid phase: replacing the water.
2. All 4f-ions could be recovered in higher yield when HP is used as an extractant with ILs combined with both MP organic phases: aqueous or non-aqueous. However, the process is not so efficient with the $CHCl_3/H_2O$ solvent system. When EtG solutions are used, the organic diluent $CHCl_3$ somehow clearly expels the IL compound $[C_1C_{10}im^+][Tf_2N^-]$.
3. The metals with the highest competitive impact on rare earth recovery from mixed e-waste extracted by chelating ligand HP are almost always Fe, Al, Cu, and Ag, while Pb could only be extracted from the aqueous phase.
4. Improvement of the solvent extraction process was observed with a small addition of glycerol (1:1, *v/v*) in the aqueous phase. After this ploy, the elements whose competitive effect increased the most are those in two s-blocks, Co and Ni. Therefore, this switchable separation is relevant to the recycling demands nowadays. In other words, the leveling of separation factors as obtained usually in IL mediums, at values around or below 1, together with the very high distribution ratios normally seen, would be an interesting property of such diluents to be further explored in non-aqueous solvent systems.
5. Unfortunately, EPR analysis could give good informative results in solvent extraction chemistry when the process is efficient, i.e., only above 50–60% metal extraction.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/separations10050286/s1, Figure S1: Log*K* vs. Z.; Figure S2: pH_{50} in the solvent extraction of lanthanoids with HL in $CHCl_3$ as a function of the ionic radius. Figure S3: EPR spectra of Gd^{3+} ion in ethylene glycol at room temperature and in the frozen state at 120 K: $[Gd^{3+}] = 3 \times 10^{-3}$ mol/dm^3. Figure S4: EPR spectra of frozen solutions of complexes of Gd^{3+} ($[Gd^{3+}]_{in} = 6 \times 10^{-4}$ mol/dm^3) with ligands [HP] = 2.5×10^{-2} mol/dm^3 (A, B, and C) and [HTTA] = 3×10^{-2} mol/dm^3 (1, 2 and 3) obtained after solvent extraction from EtG, respectively, in the following diluents $[C_1C_4im^+][Tf_2N^-]$ (A: pH_{eq} = 1.98 and 1: pH_{eq} = 2.60), ($[C_1C_{10}im^+][Tf_2N^-]$ (B: pH_{eq} = 2.02 and 2: pH_{eq} = 2.57), $CHCl_3$, (C: pH_{eq} = 1.98 and 3: pH_{eq} = 2.21). On the left: the range of the magnetic field (0−700 mT). On the right: range of the magnetic field (300−360 mT). Figure S5: EPR spectra of Cr^{3+} obtained after solvent extraction with HP = 2×10^{-2} mol/dm^3 in $[C_1C_4im^+][Tf_2N^-]$ and $[C_1C_{10}im^+][Tf_2N^-]$ recorded in frozen solutions: MP phase—$[Cr^{3+}]_{in} = 6 \times 10^{-4}$ mol/dm^3 and 0.1 MES in EtG. Calculated %E is 71.23% and 54.60%—ICP-OES based on an average of three parallel determinations. Figure S6: EPR spectra of Cr^{3+} obtained after solvent extraction with HP = 2×10^{-2} mol/dm^3 in $[C_1C_{10}im^+][Tf_2N^-]$//EtG (1), $[C_1C_4im^+][Tf_2N^-]$//EtG (2) and $[C_1C_4im^+][Tf_2N^-]$//H_2O (3) recorded in frozen solutions: MP phase—$[Cr^{3+}]_{in} = 1 \times 10^{-3}$ mol/dm^3 and 0.1 MES in EtG. Calculated %E is 99.04% (1) and 99.57% (2) and below 0.5% (3)—ICP-OES based on an average of three parallel determinations. Figure S7: EPR spectra of Cr^{3+} ion in ethylene glycol at room temperature and in the frozen state at 120 K: $[Cr^{3+}] = 3 \times 10^{-3}$ mol/dm^3. The Cr^{3+} concentration in the so-called "standard sample" was found to be about 4×10^{-4} mol/dm^3 (the spectra were integrated from 0 to 500 mT.). Table S1: Separation factors of M^{n+} metal ions extracted with HP = 2×10^{-2} mol/dm^3 ligand in $[C_1C_4im^+][Tf_2N^-]$ applying EtG and H_2O. Table S2: Initial concentrations of metal ions used in competitive extraction after 7 and 6.3-fold dilution. Table S3: Separation factors of M^{n+} metal ions extracted with HP = 2×10^{-2} mol/dm^3 ligand in $[C_1C_{10}im^+][Tf_2N^-]$ applying H_2O and glycerol, 1:1. Table S4: Initial concentrations of metal ions used in competitive extraction test applying H_2O and glycerol, 1:1. Table S5: Concentrations of the investigated Gd^{3+} ions using the SpinCount program, part of the Bruker Xenon software. Table S6: Concentrations of the investigated Gd^{3+} ions using the SpinCount program, part of the Bruker Xenon software.

Author Contributions: Conceptualization, M.A.; methodology, M.A.; validation, M.A. and R.K.; investigation, M.A. and R.K.; writing—original draft preparation, M.A.; writing—review and editing, M.A.; visualization, M.A. and R.K.; project administration, M.A.; funding acquisition, M.A. All authors have read and agreed to the published version of the manuscript.

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