

Article

Aliquat 336 in Solvent Extraction Chemistry of Metallic ReO_4^- Anions

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Abstract: A study of the liquid–liquid extraction of ReO_4^- anions from hydrochloric acid solutions using the ionic liquid Aliquat 336 (QCl: trialkyl($\text{C}_8\text{--}\text{C}_{10}$)methylammonium chloride) via the well-known method of slope analysis along with the determination of the process parameters is presented. This study employs CCl_4 , CHCl_3 and C_6H_{12} as diluents. This study was carried out at room temperature (22 ± 2) °C and an aqueous/organic volumetric ratio of unity. The ligand effect on the complexation properties of ReO_4^- is quantitatively assessed in different organic media. The organic extract in chloroform media is examined through ^1H , ^{13}C and ^{15}N NMR analysis as well as the HRMS technique and UV-Vis spectroscopy in order to view the anion exchange and ligand coordination in the organic phase solution. Final conclusions are given highlighting the role of the molecular diluent in complexation processes and selectivity involving ionic liquid ligands and various metal s-, p-, d- and f-cations. ReO_4^- ions have shown one of the best solvent extraction behaviors compared to other ions. For instance, the Aliquat 336 derivative bearing Cl^- functions shows strongly enhanced extraction as well as pronounced separation abilities towards ReO_4^- .

Keywords: liquid–liquid extraction; Aliquat 336; ReO_4^- ; organic diluents; selectivity



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1. Introduction

Rhenium is classified as a critical metal of significant industrial importance due to its valuable physicochemical properties including the high melting point (3182 °C) and a large number of stable valence states, and consequently, it is an integral component in so-called specialist materials such as high-performance alloys, catalysts, nanomaterials, etc. [1]. In the world, its distribution today like all others is evaluated as critical and so valuable metals present an uneven situation. Currently, thirty-four elements of the periodic table have been designated by the European Union as “critical” raw materials of strategic importance to the European economy and of high supply risk. As a matter of fact, the average concentration of rhenium in the Earth’s crust is just one part per billion (ppb) and is not included this list [2,3]. On the other hand, the maintenance and development of the European economy and the implementation of a smooth transition to renewable energy sources and waste-free technologies are highly dependent on a number of mineral raw materials. Despite partial successes in recycling, the only source unfortunately remaining is mining and extraction from deposits. Therefore, it is necessary to emphasize and draw attention in the scientific research field to the issue of the separation and extraction of rhenium from its associated minerals or related secondary solutions. In general, rhenium is mostly contained in copper sulfide, molybdenum minerals, rare earth ores or niobium–tantalum-containing ores. At present, the method of recovering this metal mainly includes solvent extraction techniques and separation to obtain over 50% of rhenium produced globally [2,3]. As an example, Muruchi et al. have proposed a sustainable and flexible approach for the extraction and separation of rhenium and molybdate species based on a polymeric aqueous two-phase

system, in which the high metal content in concentrated copper effluents is directly used as the driver of phase demixing [4]. Moreover, it was found that the resulting process achieves very high separation yields and relies exclusively on cheap chemicals with relatively low toxicity. Thus, it could serve as a more sustainable alternative for the extraction of both metals Re and Mo from copper mine effluents.

In fact, metals and metalloids with high oxidation states exist as oxoanions in water [5]. Thus, the design of functional ligands with a suitable size, shape, electronegativity and hydrophobicity which can reorganize these oxoanions, especially toxic ones, is a significant task to attain effective extraction from the viewpoints of environmental monitoring and protection. Rhenium is known to be a non-radioactive congener of Tc and is applicable as its substitute owing to their similar electronic configuration, stereochemistry and thermodynamic properties as well [6,7]. In essence, studying the technology for separating and extracting rhenium is significant for promoting its industrial applications and the safe disposal of spent fuel [8–10]. Therefore, perrhenate anions have adsorption characteristics like those of perchlorate and perthechnate anions (contaminants that cause major environmental concerns), so they can serve as their surrogates. Further, rhenium(VII) is usually present in real technology solutions containing a rather high concentration of sulfuric acid in the form of the perrhenate ion ReO_4^- [11,12]. The equilibria and dynamics of rhenium uptake from innovative materials with anion exchangers have also been studied [13,14]. On the other hand, rhenium(VII) could be recovered from solutions of this kind with anion-exchange extraction agents (aliphatic amines and their salts) or neutral reagents [15,16]. The degree of efficiency of metal ions extracted at the same experimental conditions using amine-based extractants usually follows the order as follows: quaternary > tertiary > secondary > primary. For example, Gerhardt et al. have investigated for the solvent extraction of rhenium various organic extractants, namely tri-*n*-octylamine, bis-isododecylamine, pyridine, Aliquat 336, tributyl phosphate, trioctylphosphine oxide, ethyl xanthate and mesityl oxide [17]. Undoubtedly, among the ionic liquid compounds scientifically investigated the most intensively in the last two decades not only in the field of the liquid–liquid extraction and separation chemistry of metallic species, the one that stands out is Aliquat 336 [18,19]. This colorless viscous liquid compound (0.884 g/cm³ density) is a water-insoluble quaternary ammonium salt (Q^+Cl^- : Q^+ is the cation) based on the tricaprilmethylammonium cation [$\text{C}_{25}\text{H}_{54}\text{N}^+$] combined with the chloride [Cl^-] anion. Nowadays, focusing on the employment of more benign and sustainable technological processes, this fascinating liquid chemical has already found a large-scale application in the field of solvent extraction chemistry: extracting a compound, additive, modifier or organic phase (2 in 1) [20]. For example, the synergistic extraction of lanthanoids with a chelating ligand like thenoyltrifluoroacetone (HTTA) or 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HP) in combination with Aliquat 336 in the role of a synergistic agent has been studied in detail by Atanassova and Dukov [21–27]. It has been reported that lanthanoids form anionic complexes of the type $\text{Q}^+[\text{Ln}(\text{TTA})_4]^-$ in the organic phase. The role of the quaternary ammonium salt anion is important because anionic complex formation depends on the breaking of the bond between the cation and anion of the liquid salt during the extraction process. Taking into account that the bond energy between the cation and anion increases in the order $\text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^-$ [28,29], it is clear why lanthanoid extraction decreases in that order exactly. It has been established that the change in chloride with a perchlorate anion in Aliquat 336 causes a significant decrease in the overall equilibrium constant (3–4 orders). This fact was explained by the authors again with the stronger bond between the cation and the anion in the QClO_4 molecule which makes the formation of anionic complexes $\text{Q}^+[\text{Ln}(\text{PMBP})_4]^-$ more difficult. It was found that the synergistic extraction increases in the sequence $\text{CHCl}_3 < \text{C}_6\text{H}_6 < \text{CCl}_4 < \text{C}_6\text{H}_{12}$. As a whole, the increase in the diluent solvating ability hinders the extraction process. Further, the values of the thermodynamic functions have been determined for the extraction of Pr, Gd and Yb with HTTA and Aliquat chloride in CCl_4 , C_6H_6 and CHCl_3 in the interval 288–318 K [25]. The values of ΔH , ΔS and ΔG have been established to be negative for the organic phase synergistic reaction. So, the formation

of the anionic complex in the organic phase is favored by the negative enthalpy changes. Perhaps the main disadvantage of this liquid compound, which must be noted, is that it is very viscous; for that reason, it inevitably requires the use of an organic diluent influencing the greenness of the process.

The object of the scientific work undertaken is to present the investigation on the solvent extraction of ReO_4^- ions by the ionic liquid Aliquat 336 diluted in three diluents, CHCl_3 , CCl_4 and C_6H_{12} , with the goal to elucidate the nature of the extracted complexes into the organic phase as well as to clarify the role of the diluent when its polarity decreases. In addition, the selectivity of Re(VII) and 37 other chemical elements in the periodic table is also studied in detail.

2. Results and Discussion

2.1. Solvent Extraction Study of ReO_4^- Anions Applying Aliquat 336: Effect of pH, Ligand Concentration and Organic Diluent

In fact, one ideal representative of ionic liquid compounds is the quaternary ammonium salt, having an industrial nickname of Aliquat 336 (trialkyl($\text{C}_8\text{--}\text{C}_{10}$)methylammonium chloride, m.p.: $-20\text{ }^\circ\text{C}$; viscosity: $1500\text{ mPa}\cdot\text{s}$). Over and above that, it is an intensively investigated molecule from the broad family of IL compounds in academic fundamental research, with essential application for ion-pair complexation in the mining industry for the role of the extractant [19]. Therefore, it is not a surprise that numerous scientific articles dealing with the evaluation of its coordination ability towards f-elements have also appeared [18,30,31]. However, due to its high viscosity, this IL is mostly used as dissolved in organic molecular diluents, as already mentioned. Additionally, it was found that the solvent extraction mechanism is based on anion exchange and hence strongly depends on the composition of the aqueous phase as well [27,32,33]. The extraction behavior of QCl (Q^+ is the quaternary ammonium salt cation) towards ReO_4^- as a function of the pH in the aqueous phase using the studied three organic diluents is shown in Figure 1. In all three investigated solvent systems, the extractability of ReO_4^- reaches a maximum value in the pH range from 1.2 to 2.3, i.e., 100%. What is good to pay attention to is that a diluent like CCl_4 likely prefers a more acidic extraction (aqueous) medium than the other two diluents. Shimojo et al. have recently found that the tripodal ligand N,N,N',N',N'',N'' -hexa-*n*-octylnitriltriacetamide, composed of three amide groups and a tertiary amine in isooctane medium, quantitatively extracted TcO_4^- and ReO_4^- anions in the pH range from 1.0 to 2.5 [8]. Moreover, it was reported that after five cycles of both forward and back extraction, the ligand retained its high extraction ability for ReO_4^- in the aqueous phase, and the presence of or increase in NO_3^- anions in the aqueous phase unfortunately inhibited the ReO_4^- transfer. The effect of the composition of the organic and aqueous phases on the recovery of rhenium(VII) by triisooctylamine dissolved in 1-octanol or 2-ethyl-1-hexanol was analyzed by Kasilkov and Petrova [34]. Furthermore, the established decrease in D_{Re} on passing from weakly acidic to more concentrated solutions is found to be probably due to a change in the state of the ligand salt in the organic phase under conditions of an increasing concentration of H_2SO_4 from 0.1 to 9 mol/dm^3 in the aqueous phase. The observed effect was accounted for by the competing extraction of the mineral acid by the amine, which hinders the rhenium(VII) solvent extraction. The effect of salt (Na^+) or acid anions was investigated by Zhou and co-researchers that indicated a weaker competition of SO_4^{2-} or Cl^- over ReO_4^- than that of NO_3^- attributed to the largest ΔG_{h} (standard Gibbs hydration energy) value of NO_3^- among the three anions [9]. Thus, the inhibition of D_{Re} caused by other competitive anions followed the order as follows: $\text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} \approx \text{Cl}^-$. Accordingly, this shows that exactly the chosen chloride anion investigated herein is an ideal candidate and the most suitable for an ion exchange with metal anion species like ReO_4^- .

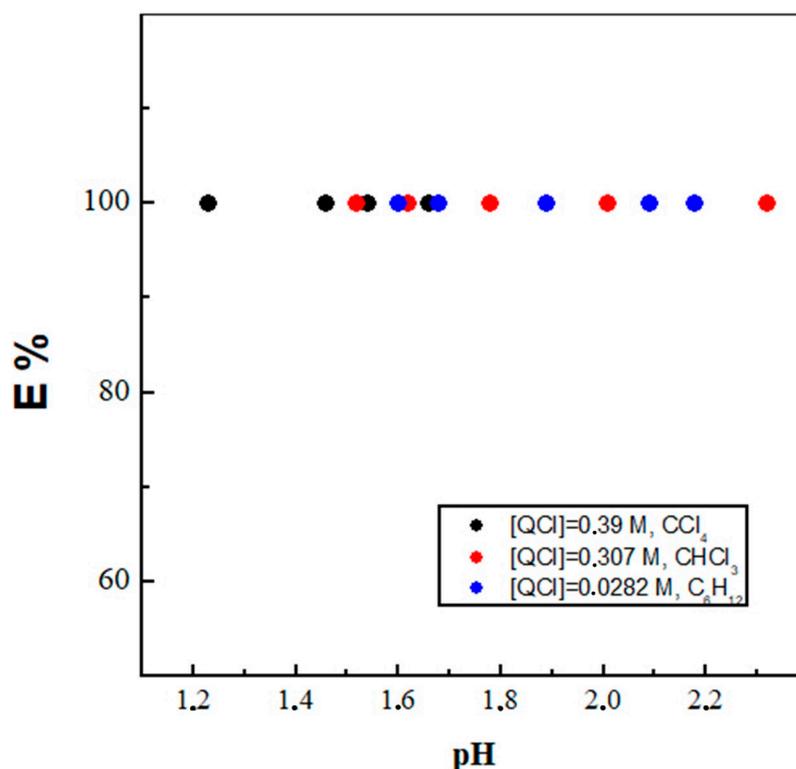


Figure 1. The extraction behavior of ReO_4^- as a function of pH_{eq} in the aqueous phase.

Further, the mechanism of ReO_4^- solvent extraction with QCl was investigated using the known slope analysis method [27]. In this respect, Figure 2 represents logarithmic plots of the distribution ratio (D) of ReO_4^- using QCl as a function of the logarithmic extractant concentrations at a constant pH of the aqueous phase in three different organic diluents. It is evident from the obtained results that this liquid compound is quite a strong extractant for metal anions. Therefore, an indisputable advantage is that very small concentrations of the applied extractant QCl completely extract the metal Re(VII) particles from the aqueous to the organic phase. Thus, it is unnecessary for the ligand to be in excess or at a concentration greater than a 1:1 ratio to the metal. Unfortunately, only in a diluent like C_6H_{12} is it possible to report and calculate an approximate slope, i.e., ca. 0.88. Of course, the concentration selected for analysis when using this diluent is also smaller. This result implies that one molecule of QCl ($[\text{R}_3\text{CH}_3\text{N}^+][\text{Cl}^-]$) participated in the ReO_4^- extraction and 1:1 QCl: ReO_4^- complexes are formed in the organic phase with possible stoichiometry Q^+ReO_4^- . Thus, the reaction mechanism in the organic phase is via ion-exchange mode, and the solvent extraction of metallic anions is much more efficient in solvent systems with chlorine-containing diluents. That is, the whole body of the data obtained, combined with previously published evidence, makes it possible to represent the extraction of Re(VII) with a new formation connected with breaking of the bond between the cation ($[\text{R}_3\text{CH}_3\text{N}^+]$) and the anion ($[\text{Cl}^-]$) of the IL salt.

Therefore, the solvent extraction process of the metallic anionic species ReO_4^- can be expressed with equilibrium as follows:



where $[\text{R}_3\text{CH}_3\text{N}^+][\text{Cl}^-]$ denotes the ligand Aliquat 366, and the subscripts "aq" and "o" denote aqueous and organic phases, respectively.

In general, the solvent extraction mechanism involving the Aliquat 336 molecule alone is based on the anion exchange or ion association reaction mode of behaviors with metal

chloride or sulfate species and somehow strongly depends on the chemical composition and pH of the aqueous phase (formation of different metal species) [18,35].

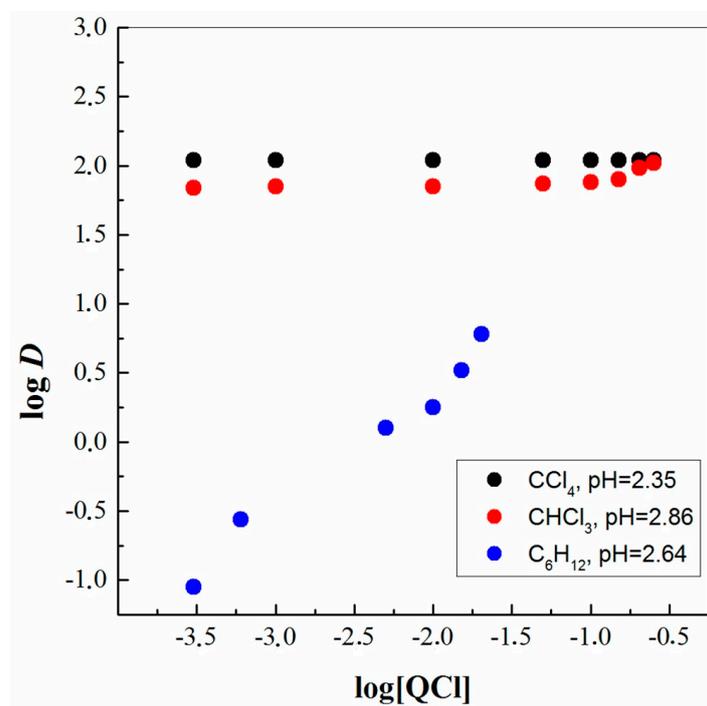


Figure 2. Slope analysis of ReO_4^- extraction by QCl: dependency on extractant concentration.

An additional analysis is undertaken to estimate the degree of anion exchange upon solvent extraction (ligand to metal species concentration ratio 1:1); the latter was performed in deuterated chloroform, and the solutions before and after the extraction of ReO_4^- with the QCl ligand are analyzed by proton, carbon and nitrogen NMR spectra. The signals for methyl and methylene groups neighboring nitrogen are shifted downfield in proton spectra upon anion replacement, 3.211 and 3.342 vs. 3.304 and 3.421, respectively (Figure 3a). The opposite shifting is observed in carbon spectra (Figure 3b), while nitrogen chemical shifts are almost identical (Table 1). Therefore, the fact that these particular chloride signals are not detected in the organic perrhenate spectra indicates that the anion is completely exchanged during the solvent extraction process.

Table 1. Selected signals in ^1H and ^{13}C spectra and ^{15}N chemical shifts (extracted from ^1H - ^{15}N HMBC experiment) of QCl and QReO_4 in CDCl_3 .

Compound	$\text{CH}_3\text{-N}^+$	$\text{CH}_3\text{-N}^+$	$\text{CH}_2\text{-N}^+$	$\text{CH}_2\text{-N}^+$	^{15}N
$[\text{A336}^+][\text{Cl}^-]$	3.211	61.65	3.342	62.97	60.2
$[\text{A336}^+][\text{ReO}_4^-]$	3.304	61.42	3.421	62.83	60.4

In fact, Aliquat 336 is typically specified by the supplier to be a trialkylmethylammonium ion consisting of a mixture of C_8 and C_{10} chains regarding the three alkyl residues with C_8 predominating. As can be seen from the spectrum in Figure 4, the analysis of the supplied Aliquat 336 by positive ion mode HR-MS disclosed its actual composition. Therefore, four groups of signals with different m/z ratios and varying intensities could be clearly distinguished and assigned to trioctylmethylammonium ($\text{A336}^+_{\text{C}_{25}}$), dioctyldecylmethylammonium ($\text{A336}^+_{\text{C}_{27}}$), didecylmethylammonium ($\text{A336}^+_{\text{C}_{29}}$) and tridecylmethylammonium ($\text{A336}^+_{\text{C}_{31}}$). Note the increasing carbon number in this order from C_{25} to C_{31} as indicated by the subscripts. The observed signal pattern aligns with previously reported ESI-MS data in the literature [36]. The new anion component of the quaternary

ammonium cation after the solvent extraction process is shown in Figure 5. It can be seen that the anion ReO_4^- is present approximately in equimolar amounts to the cation Q^+ (molar ratios close to 1) indicating a quantitative exchange of the chloride counterion of the ligand by the target metallic anion in the course of the solvent extraction process.

In addition, the UV-Vis absorption spectra of the loaded organic phase (CHCl_3) after the solvent extraction process and the organic liquid phase before extraction were both measured as well. The representative peak for the ReO_4^- anion at wavelength 246 nm [14] was clearly observed (Figure 6), indicating its quantitative transfer from the aqueous phase through an anion exchange mechanism also confirmed by this analysis.

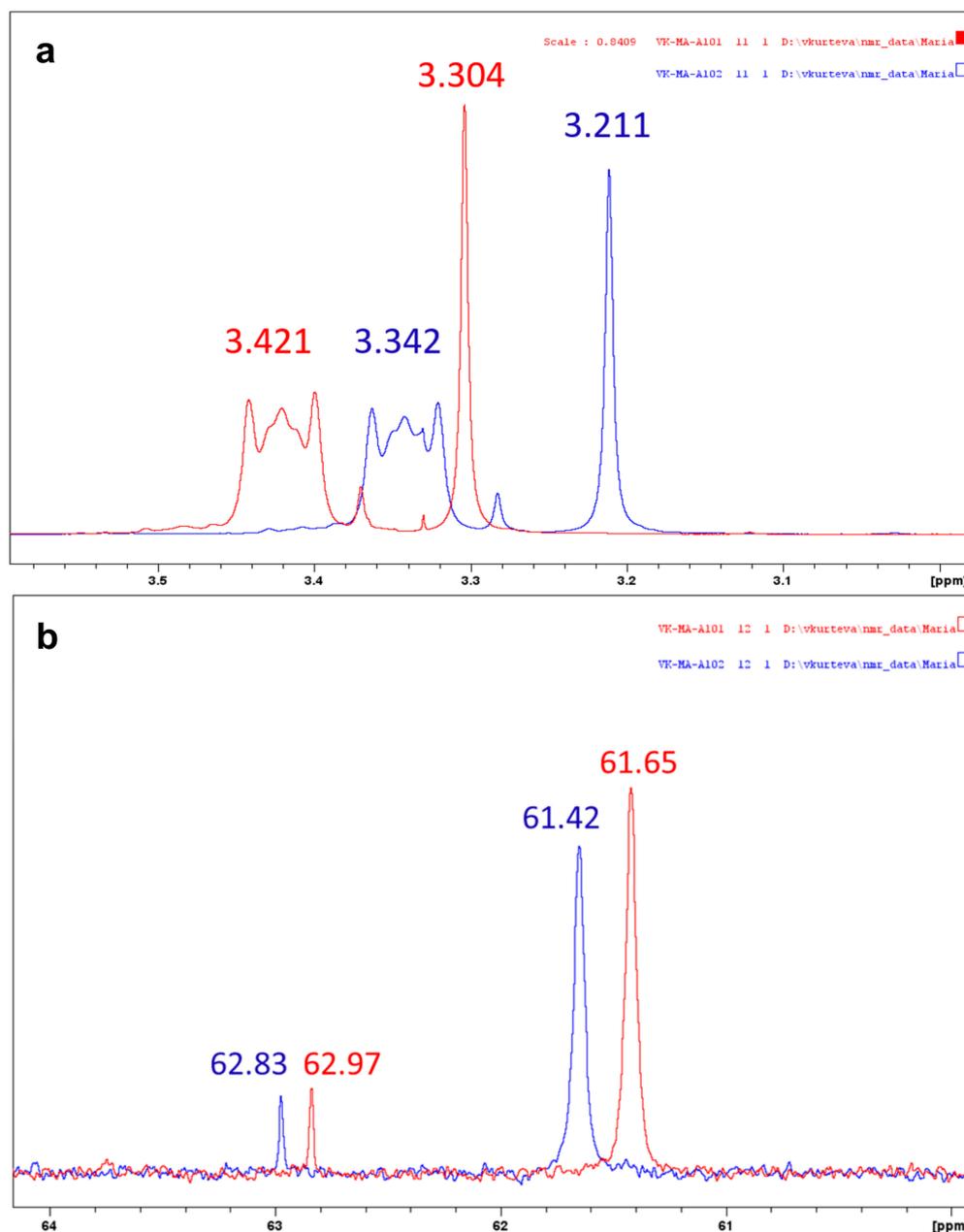


Figure 3. The signals for *N*-methyl and *N*-methylene groups in proton (a) and carbon (b) spectra of QCl (blue) and QReO₄ (red) in CDCl₃.

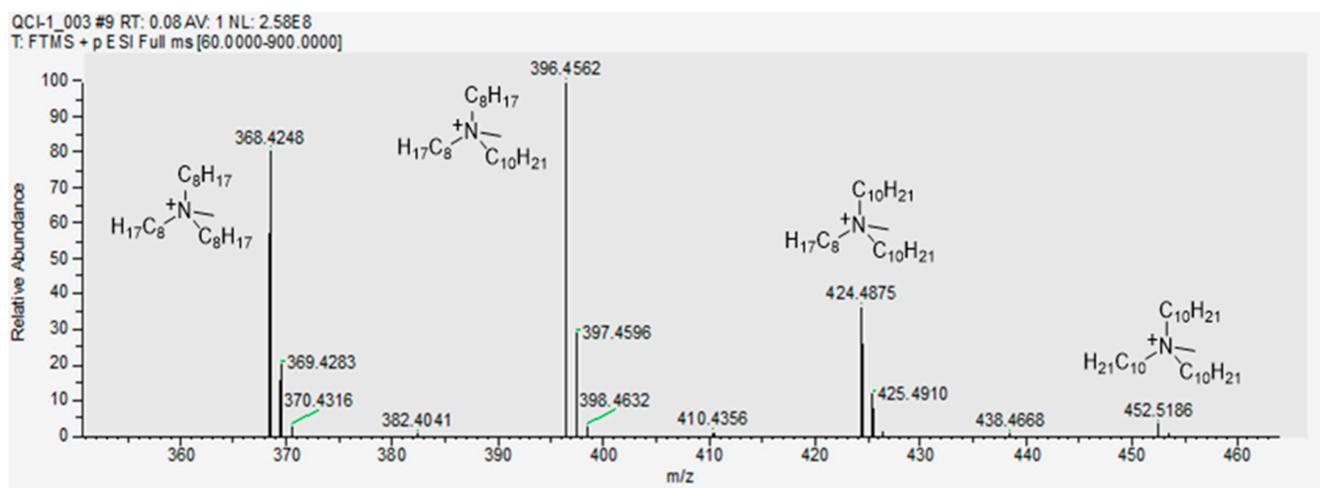


Figure 4. HR-MS (ESI⁺) m/z calcd. for $C_{25}H_{54}N^+ [M]^+$ 368.4251, found 368.4248, $\Delta = -0.3$ mDa; calcd. for $C_{27}H_{58}N^+ [M]^+$ 396.4564, found 396.4562, $\Delta = -0.2$ mDa; calcd. for $C_{29}H_{62}N^+ [M]^+$ 424.4877, found 424.4875, $\Delta = -0.2$ mDa; calcd. for $C_{31}H_{66}N^+ [M]^+$ 452.5190, found 452.5186, $\Delta = -0.4$ mDa.

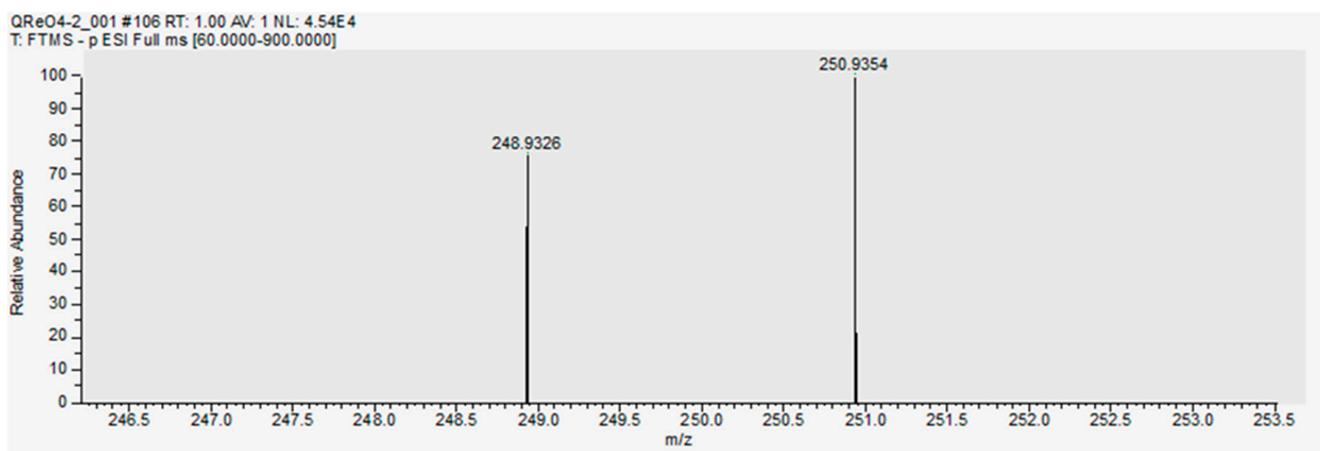


Figure 5. HR-MS (ESI⁻) m/z calcd. for $O_4Re^- [M]^-$ 250.9349, found 250.9354, $\Delta = 0.5$ mDa.

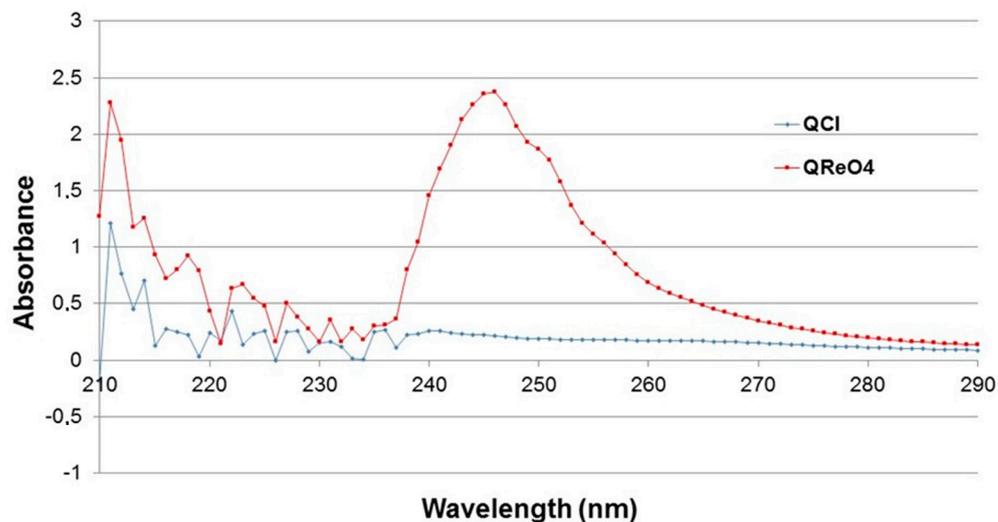


Figure 6. UV-Vis absorption spectra of the formed $Q^+ReO_4^-$ species extracted by Aliquat 336 from the aqueous solution and the ligand.

2.2. Solvent Extraction and Selectivity across the Chemical Elements in the Periodic Table Applying Aliquat 336

Generally, as already mentioned, rhenium is present in very low concentrations in the Earth's crust ($0.4 \text{ mg}\cdot\text{t}^{-1}$) [37]. Additionally, it is produced primarily as a byproduct of molybdenum and copper solvent extraction regardless of the great environmental costs [38]. It is recovered during the pyrometallurgical processing of molybdenum sulfide and copper sulfide ores. This process traditionally involves removing rhenium (VII) oxide, Re_2O_7 , from the sulfurous gas phase generated during hearth roasting (in molybdenum processing) and smelting (in copper processing) [39–41]. The low-grade molybdenite concentrate (20–45%) is also associated with approximately 0.01% Re values, in addition to a number of impurity elements such as Si (7.45%), Fe (1.62%), Ni (0.17%) and Cu (0.35%) [42]. Therefore, it would be interesting to study the behavior of more metals during their simultaneous solvent extraction and to compare the obtained results with the target metal, i.e., rhenium. In general, the extraction efficiency diminishes in competitive extraction tests with respect to the single species extraction, which is probably due to a multi-ion competition, or crowding effect or both of them [43]. From the research study aimed at evaluating the solvent extraction ability of the Aliquat 336 molecule towards various metal cations, it can be seen that it is not a suitable extractant for alkali, alkaline earth metals, Cr, Fe, Al or, of course, lanthanoids [27,44], as shown in Figure 7. The lanthanoid solvent extraction with the quaternary ammonium salt Aliquat 336 in perchlorate form alone is negligible under the experimental conditions applied in the previous study by Atanassova as well [27]. Secondly, regardless of the diluent used, ligand concentration or cation charge, complete quantitative extraction was achieved in all three solvent systems for ions such as Re, Hg, Bi and Ag (Figure 7). Unfortunately, when using Aliquat 336, the increases in metal extraction percentages decreased selectivity regardless of the diluent, since the obtained extraction percentages are very close. This indicates a decrease in the separation factors and, consequently, selectivity between target metals. However, for two of the cations in group 12, viz. Zn^{2+} and Cd^{2+} , changing the diluent leads to a reduction in their extraction process by five times or a lack of it. Moreover, one cannot fail to emphasize the commonly observed better capabilities of the diluent CCl_4 in extraction systems compared to CHCl_3 [45,46], as seen for metals such as Co^{2+} , Ni^{2+} , Cu^{2+} and light 4f-ions. Thus, the efficient and selective leaching of specific metals from minerals or wastes is feasible by using the Aliquat 336 compound. In addition, it can be concluded that the proposed solvent extraction system exhibits highly selective extraction for ReO_4^- in the presence of a large number of diverse ions, as shown in Table 2. The corresponding values of separation factors (SFs) for one solvent system are presented only.

Table 2. Separation factors between Re(VII) and various s-, p-, d- and f-ions extracted with $\text{QCl} = 0.39 \text{ mol}/\text{dm}^3$ in CCl_4 .

SF	Li	Na	Al	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Re	9×10^3	1×10^4	3×10^3	4×10^4	1×10^5	2×10^4	1×10^5	8×10^3	5×10^3	4×10^3	1×10^3	6.7	
SF	Sr	Ag	Cd	Ba	La	Ce	Eu	Gd	Lu	Hg	Tl	Pb	Bi
Re	5×10^5	1.09	0.86	5×10^3	3×10^3	1×10^4	7×10^5	2×10^4	8×10^5	2.4	2×10^3	106	4.5

In summary, the 26 studied metal ions could be classified approximately in the following four groups according to the degree of their separation with Re(VII):

- (1) Very difficult to separate, $\text{SF} < 5$: Zn, Ag, Cd, Hg and Bi;
- (2) Difficult to separate, $\text{SF} < 100$: Pb;
- (3) Overall selectivity $\approx 10^3$: Li, Al, Fe, Co, Ni, Cu, Ba, La and Tl;
- (4) Overall selectivity $\approx 10^4$ – 10^5 : Na, K, Ca, Cr, Mn, Sr, Ce, Eu, Gd and Lu.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Li(I)										mol/dm ³ CCl ₄ 0.39 CHCl ₃ 0.3 C ₆ H ₁₂ 0.028	QCl pH _{in} =0.15			
-														
-														
-														
Na(I)	Mg(II)												Al(III)	
-													-	
-													-	
-													-	
K(I)	Ca(II)	Sc(III)	Ti(IV)	V(V)	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ga(III)		
-	-				-	-	-	1.4%	2.2%	5.4%	92.6%			
-	-				-	-	-	-	-	-	89.6%			
-	-				-	-	-	-	-	-	-			
Rb(I)	Sr(II)	Y(III)	Zr(IV)	Nb(V)	Mo		Ru(III)	Rh(III)	Pd(II)	Ag(I)	Cd(II)	In(III)		
-	-									100%	100%			
-	-									100%	100%			
-	-									100%	20.9%			
Cs(I)	Ba(II)	Ln(III)	Hf(IV)	Ta(V)	W(VI)	Re(VII)	Os(IV)	Ir(III)	Pt(IV)	Au(III)	Hg(II)	Tl(I)	Pb(II)	Bi(III)
-	-					100%					100%	4.7%	43%	100%
-	-					100%					100%	5%	47%	100%
-	-					100%					100%	2.5%	-	100%
La(III)	Ce(III)	Pr(III)	Nd(III)	Sm(III)	Eu(III)	Gd(III)	Tb(III)	Dy(III)	Ho(III)	Er(III)	Tm(III)	Yb(III)	Lu(III)	
2.4%	1%				-	-							-	
-	-				-	-							-	
-	-				-	-							-	

Figure 7. The extraction performance of the Aliquat 336 ligand towards 26 metal ions. The reported extractability values (%) represent the average of three measurements, with deviations of less than 5%.

From the additional analysis carried out to investigate the selectivity between rhenium and 12 refractory elements, it is seen that only the C₆H₁₂ diluent and low extractant concentrations are suitable for this scientific purpose separation except only the Re/Ta pair, as shown in Figure 8. Regarding the environmental pressure today in terms of green chemistry, the C₆H₁₂ system may play a role in these efforts so as to create eco-friendly organic solutions, i.e., halogen-free. The solvent system QCl/CCl₄ is obviously quite effective for the competitive extraction of metal ions, like Re, Ta, Mo and Sn, and their pronounced separation from the rest of the ions in the studied mixture, i.e., Si, Ti, Ge, Sb, Te, Zr, Nb, Hf and W. On that account, the obtained extractability followed the following order: Re ≈ Ta > Mo ≈ Sn > Nb > Sb ≈ W > Ti > Hf > (Zr ≈ Ge ≈ Te ≈ Si). It is worthy to mention as well that when changing the diluent CCl₄ with polar one CHCl₃, a sensitive difference is noticed as the extraction ability of the ligand molecule remains at 100% only for Re and Ta ions and sharply decreases for the other ions in the series. Therefore, this know-how could be used in order to obtain a certain selectivity among refractory metals. The diluent in use can influence the solvent extraction efficiency through both chemical and entrainment effects. The use of CCl₄ as a diluent increases the solvent extraction of Mo and acts more effectively than CHCl₃ or the influence of aromatic diluent components on the selectivity of the extractant, i.e., C₆H₁₂.

Moreover, in hydrometallurgy, the separation between rhenium and molybdenum ions in aqueous solution is a difficult task owing to their relatively adjacent positions in the periodic table and being in possession of similar chemical properties. One example is the recovery of rhenium and molybdenum from a sulfuric acid leaching solution of molybdenite roasting dust performed by tri-octyl-amine dissolved in kerosene. The extraction efficiency of rhenium and molybdenum was obtained and reported by Kang et al. as 99 and 30%, respectively, using 5 vol% TOA at the solution equilibrium pH of 0 and an O/A ratio of 0.4 [47]. So, the published result clearly shows that a pH equal to 0 is somehow a better experimental condition to separate both metals with the highest separation factor. Further, the extraction of some oxonium anions, TcO₄⁻, ReO₄⁻, Cr₂O₇²⁻, MoO₄²⁻ and WO₄²⁻, from 1 mol/dm³ HNO₃ was performed by a new neutral, tridentate ligand, 2,2'-

(methylimino)bis(*N,N*-dioctylacetamide) in *n*-dodecane with a reported trend of *D* in the order $Tc > Re > W > Mo > Cr$ [48]. The masking effects of 16 S-, O- and N- donor water-miscible multidentate ligands showing a five- or six-membered ring formation on the solvent extraction of Pd, Ru, Mo and Re from 2 mol/dm³ HNO₃ were studied using the same ligand as well as NTAamide dissolved in *n*-dodecane. However, no masking agent for Re was found in the cited work, contrary to other metals tested [49].

4	5	6	7	14	15	16
		Aliquat Cl	pH_{in}=0.15			
		CCl₄ 0.39 CHCl₃ 0.3 C₆H₁₂ 0.028 mol/dm³		Si		
				-		
				-		
Ti				Ge	Sb	Te
3.1%				-	22.09%	-
-				-	5.0%	-
-				-	-	-
Zr	Nb	Mo		Sn		
-	28.4%	65.3%		63%		
-	4.3%	31.5%		41%		
-	-	-		-		
Hf	Ta	W	Re(VII)			
1.4%	100%	21.7%	100%			
-	100%	2.7%	100%			
-	89.5%	-	92.8%			

Figure 8. The extraction performance of Aliquat 336 towards 13 metal ions. The reported extractability values (%) represent the average of three measurements, with deviations of less than 5%.

The selectivity of Re(VII) and the twelve refractory ions is studied for the best system, i.e., QCl/CCl₄, and the results are displayed in Table 3. As a whole, the calculated separation factors obtained for all pairs are extremely high with one exception Re/Ta and are not significantly lower for Mo and Sn combinations. In general, the observed strong selective extractant's behavior could be discussed as two possible reaction mechanism effects: an anionic, which, in this case, seems to be the determinant, or cationic extraction process followed by a solvation. In other words, this ionic liquid ligand presents a higher selectivity due to its different extraction force towards s-, p-, d- or f-ions. The quaternary ammonium salt, an economically advantageous class of industrial compounds known for decades, will rest a favorable anion-exchange extraction agent in the field of chemical and environmental engineering.

Table 3. Separation factors between Re(VII) and 12 refractory ions extracted with QCl = 0.39 mol/dm³ in CCl₄.

SF	Si	Ti	Ge	Sb	Te	Zr	Nb	Mo	Sn	Hf	Ta	W
Re	7.3×10^4	4×10^3	3.3×10^4	464	4.2×10^4	3.8×10^4	332	70	77.4	9.2×10^3	4.6	475

3. Materials and Methods

3.1. Reagents

All reagents were purchased from Aldrich, Merck and Fluka and were used without further purification. The commercial product Aliquat 336 was obtained from Fluka (Bern, Switzerland). The quaternary ammonium salt was purified before use according to the procedure suggested by Goto [29]. The diluents were CHCl₃ (Merck, p.a. (Darmstadt, Germany)), C₆H₁₂ (Merck, p.a.) and CCl₄ (Merck, p.a.). Re standard for ICP 999 mg/dm³ ± 4 mg/dm³ (Sigma-Aldrich (St. Gallen, Switzerland)) and ICP-MS refractory elements standard—12 components: 10 mg/dm³ ± 0.022–0.059 mg/dm³ each of Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W and Zr (CPAchem Ltd., Bogomilovo, Bulgaria). All other commercially available analytical-grade reagents were used without any further purification.

A stock solution of rhenium ions ($2 \times 10^{-3} \text{ mol/dm}^3$) was prepared from KReO_4 (Fluka, puriss) by dissolving and diluting with distilled water to the required volume. Hydrochloric acid 37% was used (Merck, p.a.) to adjust the pH of the aqueous solutions added to 0.1 mol/dm^3 2-morpholinoethanesulfonic acid (MES) buffer (Alfa Aesar, 98% (Karlsruhe, Germany)).

3.2. Solvent Extraction Studies

Extraction experiments were carried out at room temperature by mixing the two immiscible liquid phases in a 1:1 v/v ratio (1.5 mL) for 1.5 h (1500 rpm), which was sufficient for attaining equilibrium. After the separation of the liquid phases, the concentration of rhenium in the aqueous phase was determined by using ICP-OES spectroscopy ("Prodigy" High-dispersion ICP-OES, Teledyne Leeman Labs, Hudson, New Hampshire, USA). The concentration of the metal ion in the organic phase was obtained by material balance. The reproducibility of distribution ratio (D) measurements was generally within 95%. The acidity of the aqueous phase at equilibrium was measured by a pH meter (pH 211 HANNA, Hanna, Smithfield, RI, USA) with an accuracy of 0.01 pH unit. The Re(VII) ion initial concentration was $2.6 \times 10^{-4} \text{ mol/dm}^3$ in all experiments.

For competitive extraction tests, a volume of 2 mL of the prepared aqueous solution containing various M^{n+} metal ions ($\sim 3 \times 10^{-4} \text{ mol/dm}^3$ including $3 \times 10^{-4} \text{ mol/dm}^3$ Re(VII)) or various refractory elements (9 mg/dm^3) including $2 \times 10^{-4} \text{ mol/dm}^3$ Re(VII) was equilibrated for 2 h (1500 rpm) with a 2 mL organic phase, which includes the studied ligand molecule, Aliquat 336. After phase separation, the metal ion concentrations in the aqueous solution were determined by ICP-OES.

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

$$D = \frac{[M^{n+}]_{aq,in} - [M^{n+}]_{aq,f}}{[M^{n+}]_{aq,f}} \times \frac{V_{aq}}{V_o} \quad (2)$$

where $[M^{n+}]_{aq,in}$ is the concentration of the M^{n+} ion in the aqueous 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_o are the volumes of the aqueous and organic phase as well as the volumes of two immiscible phases used to perform experiments, herein always a 1:1 v/v extraction. For instance, duplicate experiments showed that the reproducibility of D measurements was generally within 95%.

The extractability (% E) was evaluated as follows:

$$\text{extractability} = \frac{[M^{n+}]_{aq,in} - [M^{n+}]_{aq,f}}{[M^{n+}]_{aq,in}} \times 100 \quad (3)$$

The metal separation between chemical elements in the periodic table can be estimated using separation factors (SFs) determined as a ratio of the distribution ratios of the two studied metal ions:

$$\text{SF} = D_1/D_2. \quad (4)$$

3.3. NMR, UV-Vis and HRMS Measurements

The NMR spectra of the extract solutions at room temperature are recorded directly after Re(VII) solvent extraction ($3 \times 10^{-2} \text{ mol/dm}^3$ Re(VII)) and QCl , $\text{pH}_{\text{eq}} = 1.4$) on Bruker Avance NEO 400 spectrometers (Rheinstetten, Germany) in CDCl_3 medium. The chemical shifts are quoted in ppm in δ -values against tetramethylsilane (TMS) as an internal standard. The ^{15}N chemical shifts are extracted from two-dimensional ^1H - ^{15}N HMBC experiments. The spectra are processed with the Topspin 3.6.3 program.

The mass spectra are recorded (Aliquat 336 and organic phase after Re(VII) solvent extraction ($1 \times 10^{-2} \text{ mol/dm}^3$ Re(VII)) and QCl in CHCl_3 , $\text{pH}_{\text{eq}} = 1.4$) using a Q Exactive Plus Hybrid Quadrupole-Orbitrap Mass Spectrometer from Thermo Scientific (HESI HRMS)

in both positive and negative modes. The spectra are processed with the Thermo Scientific FreeStyle program version 1.8 SP1 (Thermo Fisher Scientific Inc., Waltham, MA, USA).

The UV–vis spectra of the extract solution at room temperature is recorded directly after Re(VII) solvent extraction (8×10^{-4} mol/dm³ Re(VII) and QCl in CHCl₃ at pH_{eq} = 1.4) using an Analytic Jena Specord 200 Plus spectrophotometer (Jena, Germany) and 10.0 mm path length quartz cuvettes.

4. Conclusions

The extraction behavior of Re(VII) by an ionic liquid ligand Aliquat 336 indicates a rapid and spontaneous anion exchange reaction at room temperature. The established stoichiometric ratio in the formed extracted compound in the organic phase is 1:1, with the structure [R₃CH₃N⁺][ReO₄[−]]. The investigation of the effect of the organic diluent on the extracting properties of the ligand revealed that the efficiency of Aliquat 336 dissolved in CCl₄ was higher than its solutions in CHCl₃ or C₆H₁₂. Based on the evaluated SF values, it was concluded that Aliquat 336 demonstrated a higher extraction performance and a better separation characteristic particularly with respect to ReO₄[−]. This study clearly showed the high potential of the investigated affordable ionic liquid compound for the selective separation–recovery of metals such as Re, Ta, Mo, Ag, Hg, Bi, Zn and Cd from multi-component solutions.

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