

Evaluation of a Phosphinate Functionalized Ionic Liquid for the Separation of Nb and Ta from Nitric Acid Feed Conditions

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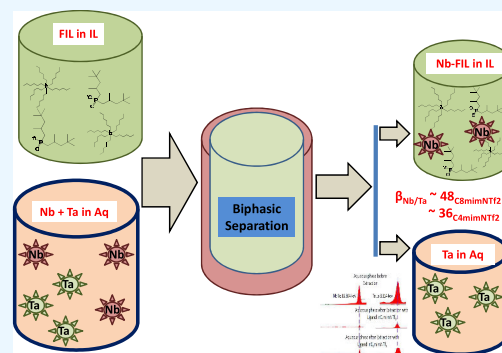


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Supporting Information

ABSTRACT: A 'green' single-step separation process, involving a phosphonium phosphinate functionalized ionic liquid (FIL) in $C_8\text{mim}\cdot\text{NTf}_2$, has been developed for highly encouraging improvements in the mutual separation of Nb and Ta with a maximum separation factor of ~ 48 at 2 M nitric acid. The separation factor in $C_4\text{mim}\cdot\text{NTf}_2$ was found to be somewhat lower compared to that seen in $C_8\text{mim}\cdot\text{NTf}_2$. In $C_8\text{mim}\cdot\text{NTf}_2$, the extraction proceeded via the neutral $\text{NbOF}_3(\text{R}_4\text{P}^+)(\text{R}_2\text{POO}^-)$ and $\text{TaOF}_3(\text{R}_4\text{P}^+)(\text{R}_2\text{POO}^-)$ species predominated by a 'solvation' mechanism at 2 M HNO_3 , where both the cationic and anionic parts of the FIL took part in the metal ion extraction. However, in the case of $C_4\text{mim}\cdot\text{NTf}_2$, the extraction proceeded via a cation exchange mechanism involving the mono-positive species viz. $[\text{NbO}(\text{R}_2\text{POO}^-)_2]^+_{\text{IL}}$, $[\text{TaO}(\text{R}_2\text{POO}^-)_2]^+_{\text{IL}}$. Only the phosphinate group of the FIL was directly involved in the binding to the metal ion. The charge neutrality was maintained by the exchange of the $C_4\text{mim}^+$ ion from the ionic liquid phase to the aqueous phase. The processes were spontaneous, exothermic involving outer sphere complexation. The radiolytic stabilities of the $C_8\text{mim}\cdot\text{NTf}_2$ -based solvent systems were poorer than those of the solvents based on $C_4\text{mim}\cdot\text{NTf}_2$. Aqueous solutions of EDTA-guanidine carbonate or DTPA-guanidine carbonate showed promising back extraction ability though three contacts of these organic phases were required for more than 99.99% stripping of the metal ion. The reusability of these solvent systems was evaluated. After four consecutive cycles, a maximum of only 8% reduction in the extraction efficiency of Ta was noticed, while for Nb it was less than 4% for Nb.



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INTRODUCTION

Due to modernization, there is a high demand of niobium and tantalum globally in superalloy materials applied in superconductors, energy, electronics, cell phones, and energy-related fields.^{1–3} These two elements along with tellurium, indium, silver, dysprosium, neodymium, and molybdenum are declared as critical metals by the European Union (EU) due to their potential strategic and sustainable energy applications including nuclear, solar, wind, carbon capture and storage.^{4,5} Due to high melting point and other metallurgical properties, Nb is being used in steel to improve the latter's mechanical strength, corrosion resistance, reduction in grain boundary, and brittleness.^{6,7} The high-strength low alloy steel is largely applied in the manufacturing of vehicle bodies, railway tracks, ship hulls, and oil and gas pipelines. Due to the nontoxicity and physiological inertness, Nb and its compounds exhibit large biomedical applications related to medical implantations, pacemakers, etc.^{8–10} Nb-Ta-based alloy materials have largely been utilized in the manufacturing of superconducting and magnetic materials.^{11,12} The biocompatibility of the Ta-based compounds have also been explored for the production of surgical clips, metal plates, screw, and support for bone growth and joining.^{13,14}

Due to very low neutron absorption cross section for thermal neutron (1.1 barns/atom), Nb is introduced (less than

or equal to 2.5%) to form Zr-based alloys to improve their mechanical strength in cladding materials of normal as well as heavy water-based nuclear reactors.^{15,16} The presence of elements with a high neutron absorption cross section is not at all desirable. Ta has a neutron absorption cross section that is ca. 20 times higher (21.3 barns/atom) compared to Nb. Therefore, the presence of Ta in the Zr–Nb-based alloy beyond a certain level (0.1%) should be avoided to achieve its desired performance inside the nuclear reactors. On the contrary, Ta has been introduced as control rods in nuclear reactors to restrict nuclear fission as and when it is required.^{17,18} Due to their similar atomic radius (147 and 146 pm), chemical properties (identical ionic species), and natural co-existence in ores there is a requirement for the efficient mutual separation of Nb and Ta from their mixtures. Acid and alkaline leaching was reported to induce some selectivity in the dissolution of Nb and Ta, whereas the

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differences in the density of the ores can be utilized for their gravimetric separations.^{19,20} Solvent extraction methods, involving amines, phosphates, phosphonates, phosphinates, phosphine oxides, phosphoric acids, etc., have also been exploited for their mutual separation as well.^{21–23} However, for most of the reports, the separation factors were not really exciting (i.e., less than 10).

Ionic liquids have been considered as a class of “green” diluents alternative to the volatile organic diluents and have extensively been exploited for the separation of actinides, lanthanides, and long-live fission and activation products from different aqueous acidic streams obtained during different activities of the closed nuclear fuel cycle.^{24–27} The unique properties of tunable extraction mechanism, speciation, high radiation, and thermal stabilities, and wide liquidous range with a large degree of solubility resulted in its wide range of applications including possibility of those in the nuclear industry as an extracting media for actinide separations in aqueous reprocessing or as direct dissolving media in nonaqueous reprocessing.^{28–30} The extraction mechanism of metal ions was reported to be tuned from ‘cation exchange’ to ‘solvation’ by changing the length of alkyl groups in alkyimidazolium-based ionic liquid.^{24–27} Hence, it is of interest to vary the alkyl group of alkyimidazolium-based ionic liquid from *n*-butyl to *n*-octyl to see any mechanistic tuning resulting in improved separation between Nb and Ta.

In functionalized ionic liquids (FILs), the desired functional groups have been covalently attached to the ionic liquid (either cationic or anionic part of it) to be exploited for task-specific applications to improve the efficiency as well as selectivity.^{31,32} Phosphine oxide and phosphate functionalities covalently attached to the imidazolium cations were utilized for efficient separation of uranyl ions from aqueous acidic streams.^{33,34} Diglycolamide (DGA)- and carbamoyl methyl phosphine oxide (CMPO)-based FILs exhibited drastic improvements in the extraction efficiency toward trivalent actinides (Am^{3+} , Cm^{3+} , etc.) compared to the combination of a conventional ionic liquid with a ligand with a similar functional group.^{35–37} Ammonium-based task-specific ionic liquid, *N,N*-dioctyl-(4-trihexylammonium)butyramide bis(trifluoromethanesulfonyl)-imide has also been used for the efficient extraction of the Am^{3+} ion.³⁸ Rout et al. reported amide-based task-specific ionic liquid, *N,N*-dioctyl-2-(3-methylimidazolium)acetamide bis(trifluoromethanesulfonyl)imide for the extraction of UO_2^{2+} , Pu^{4+} , and Am^{3+} from the aqueous phase.³⁹ Three FILs viz. tetrabutylammonium di(2-ethylhexyl)phosphate (TBA-D2EHP), trioctylmethylammonium di(2-ethylhexyl)phosphate (TOMA.D2EHP), and trihexyl(tetradecyl)phosphonium di(2-ethylhexyl)phosphate ([THTP][D2EHP]) exhibited better extraction efficiencies for the rare earth elements as compared to D2EHPA (di-2-ethylhexyl phosphoric acid) in an ionic liquid.⁴⁰ Though there are several reports on cationic FILs, examples of anionic FILs are very few. Among the rare lot, Dai et al. reported the trioctylmethylammonium di(2-ethylhexyl)phosphate ([TOMA][D2EHP]) for the extraction of rare earth elements.⁴¹ Anionic FILs have also been reported for the separation of carbon dioxide (trihexyl(tetradecyl)phosphonium methioninate [P66614][Met] and prolinatate [P66614][Pro] and SO_2 (acylamido-based anion-functionalized ILs).^{42,43} β -Diketonate-based FILs showed promise in the efficient extraction of actinides and Li^+ from aqueous acidic and alkaline streams, respectively.^{44,45}

In view of the requirement of improvement in the mutual separation of Nb and Ta in the nuclear industry and the importance of environmentally benign separation technology based on FILs, an attempt was made to achieve a “green” and efficient mutual separation of Nb and Ta by the use of a phosphonium phosphinate-based anionic FIL. The extraction mechanism, speciation, kinetics, thermodynamics, radiation-induced performance deterioration, and stripping characteristics have been investigated. The separation efficiency was compared with different processes reported in the literature.

EXPERIMENTAL SECTION

Materials. All reagents used in the present investigation were of analytical grade. The aqueous stock solutions of Nb and Ta were prepared from the Specpure solutions obtained from E-Merk, Germany, after suitable dilution. Milli-Q (Millipore, USA) water was used throughout the study for dilution purposes. Suprapur nitric acid procured from E-Merk was used in the present investigations. Sodium carbonate, formic acid, citric acid, oxalic acid, hydrazine hydrate, ethylene diamine tetra acetic acid (EDTA), diethylene triamine penta acetic acid (DTPA), and lithium bis(trifluoromethylsulfonyl)-imide ($\text{Li}\cdot\text{NTf}_2$), etc., were purchased from Sigma-Aldrich. The ionic liquids, 1-butyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)-imide ($\text{C}_4\text{mimNTf}_2$), 1-butyl-3-methylimidazolium-bromide ($\text{C}_4\text{mim}\cdot\text{Br}$), 1-octyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)-imide ($\text{C}_8\text{mim}\cdot\text{NTf}_2$), and 1-octyl-3-methylimidazolium-bromide ($\text{C}_8\text{mim}\cdot\text{Br}$), were procured from IoliTec, Germany. The FIL trihexyl tetradecyl phosphonium bis (2,4,4) trimethylpentyl phosphinate of analytical grade, used in the present investigations, was procured from Aldrich. The FIL was used as it is without further purification. The chemical structures of the FIL and ionic liquids are shown in Figure 1.

Instrumentation. The determination of Nb and Ta was carried out using energy-dispersive X-ray fluorescence (EDXRF) spectrometry using a Jordan Valley EX-3600 M model spectrometer procured from Xenometrix, Israel. Six filter

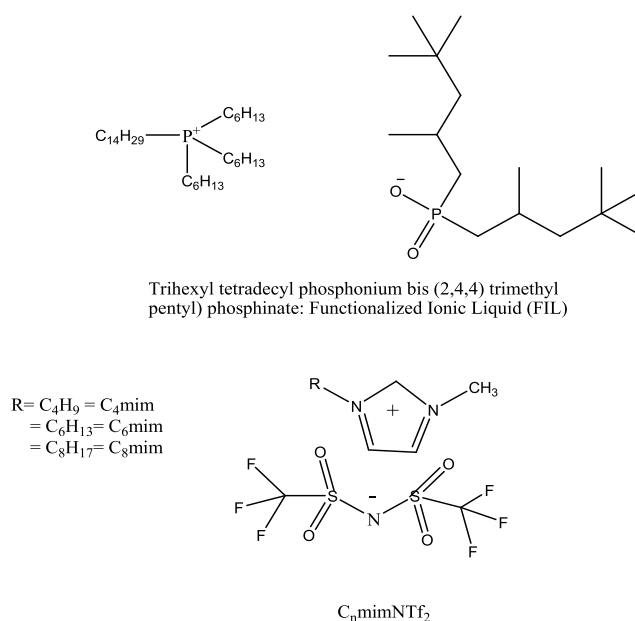


Figure 1. Chemical structures of FIL, $\text{C}_4\text{mim}\cdot\text{NTf}_2$, and $\text{C}_8\text{mim}\cdot\text{NTf}_2$.

assemblies (Cu, Fe, Mo, Rh, Sn, and Ti) with 10 sample introduction slots were used. A Teflon cup with mylar foil at the bottom was taken to pour suitable aqueous aliquots for X-ray excitation.

Method. For liquid–liquid extraction, 1 mL of aqueous phase containing 1 mg mL⁻¹ of Nb and Ta solution individually, in 2 M nitric acid (only in the case of acid variation, the nitric acid concentration was varied as specified later). It was allowed to equilibrate with 1 mL of ionic liquid phase containing FIL in C_nmimNTf₂ (where *n* ~ 4 and 8). All the solvent extraction experiments were performed using 100 mM FIL in C_nmimNTf₂. However, for ligand concentration variation experiments, the concentration of FIL was varied as specified below. The studies were performed in leak-tight Pyrex glass tubes and equilibrating those in a thermostated water bath operated in the range of 5–80 °C with temperature stability of 0.1 °C for a duration of 3 h. The tubes were subsequently centrifuged at 3000 rpm for 5 min to achieve complete phase separation. Subsequently, 500 μL of an aliquot from the aqueous phase was collected for EDXRF analysis for the determination of Nb or Ta using the K_α and the L_α lines, respectively. The initial concentration of the metal ions in the feeds was also determined by EDXRF technique using the same procedure. The distribution ratio was calculated using the equation below:

$$D = \frac{C_i - C_a}{C_a} \quad (1)$$

where *C_i* and *C_a* are the concentration of metal ions before and after extraction in the aqueous phase, respectively. The separation factor of Nb over Ta was calculated using the equation below:

$$\beta_{\text{Nb/Ta}} = \frac{D_{\text{Nb}}}{D_{\text{Ta}}} \quad (2)$$

where, *D_{Nb}* and *D_{Ta}* are the distribution ratio values for Nb and Ta, respectively. For establishing the extraction profiles, the aqueous phase acidity was varied from 0.01 M to 4 M HNO₃ at 300 K keeping other experimental parameters constant as mentioned above. The ligand concentration was kept at ca. 100 mM for all distribution studies. For understanding the kinetics of mass transfer, liquid–liquid extraction studies were performed from 2 M HNO₃ as the aqueous phase using 100 mM of FIL in ionic liquid at 300 K, while the time of equilibration was varied from 5 to 180 min keeping all other experimental parameters unchanged. For understanding the effect of temperature on the metal ion extraction, similar distribution experiments were performed at different temperatures in the range of 27–60 °C. For understanding the metal–ligand stoichiometry, the ligand concentration in the ionic liquid phase was varied in the range of 60–500 mM, keeping all other parameters unchanged. Similarly, to evaluate the participation of nitrate ion, C₄mim⁺, C₈mim⁺, NTf₂⁻, and F⁻, concentrations of NH₄NO₃, C₄mim·Br, C₈mim·Br, LiNTf₂, and NH₄HF₂ were varied in the range 1.5–10 M, 0.1–10 mM, 0.1–10 mM, 1–10 mM, and 1–6 mM, respectively.

Usually, ionizing radiation degrades the solvent system, thereby affecting the metal ion extraction ability of the solvent. The radiation-induced performance deterioration experiments were performed by putting the solvent systems inside the ⁶⁰Co chamber, GB5000, from the Food Technology Division (FTD), BARC for the requisite time to have the predecided

gamma ray exposure. Using these irradiated solvent systems, extraction experiments were performed, and the *D_{Nb}* and *D_{Ta}* values were determined and compared. From the point of view of sustainability, one needs to reuse the solvent and this requires an efficient stripping solution for the back extraction of the metal ions. In the case of back extraction experiments, two steps were followed. The first step was the extraction of Nb and Ta from 2 M HNO₃ using 100 mM FIL in ionic liquid for 3 h equilibration at 300 K with an aqueous/organic phase ratio of 1 followed by 5 min centrifugation for phase separation as mentioned above. In the second step, the loaded ionic liquid phase was allowed to be equilibrated with the stripping solutions as mentioned for 15 min at 300 K with the phase ratio of 1:1, followed by 5 min of centrifugation. Then, the % back extraction was calculated from the amount of metal loaded in the first step and the amount of the same back extracted in the second step. In the case of multiple contacts, after the first back extraction, the loaded organic phase was again allowed to be equilibrated with a fresh lot of stripping solution and the same experiment was repeated. All the back-extracted solutions were collected to calculate the cumulative (%) back extraction.

RESULTS AND DISCUSSION

Effect of Equilibration Time. Figure 2 shows the variation in *D* values of Nb and Ta from 2 M HNO₃ using 100 mM FIL

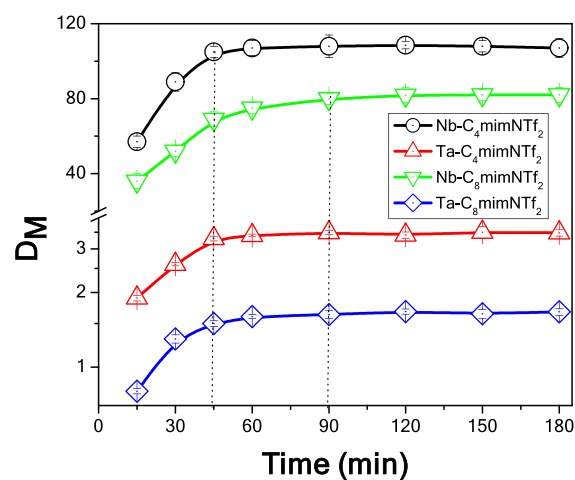


Figure 2. Variation in *D* values for Nb and Ta as a function of different times of equilibration between two phases from 2 M HNO₃ with phase ratio 1 at 300 K.

in C₄mim·NTf₂ and C₈mim·NTf₂ at varying times of equilibration. This exercise is very important in order to understand how much time is required to reach equilibrium *D* values. *D_{Nb}*^{C₄mim·NTf₂} and *D_{Ta}*^{C₄mim·NTf₂} values were found to enhance with an increase in the time of equilibration between the aqueous phase and the ionic liquid phase for the initial 45 min followed by a plateau. Similarly, the continuous increase in the *D_{Nb}*^{C₈mim·NTf₂} and *D_{Ta}*^{C₈mim·NTf₂} values with time was observed until 90 min followed by a plateau. These observations implied that at least 45 and 90 min were required for getting the equilibrium *D* values for the C₄mim·NTf₂- and C₈mim·NTf₂-based solvent systems. The slower extraction kinetics in the ionic liquid compared to that in the case of the molecular diluent was also reported earlier and was attributed to the higher viscosity coefficient of the ionic liquid. Higher

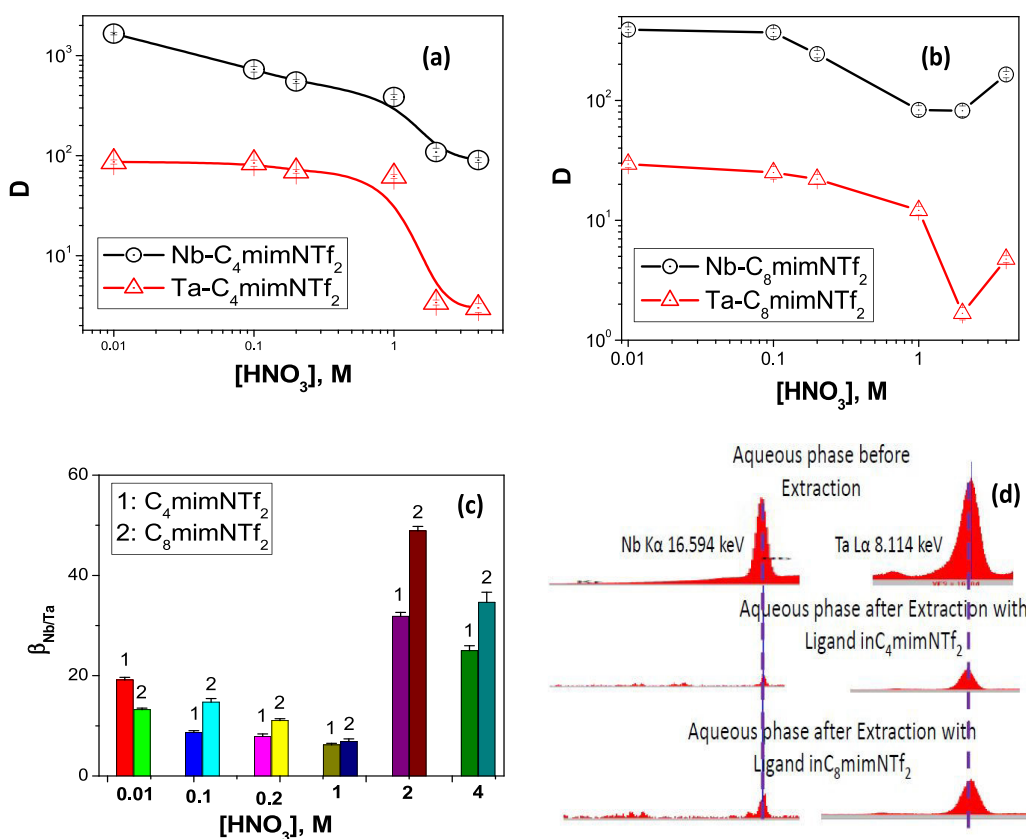


Figure 3. Variation in D values as a function of nitric acid concentration in aqueous phase (time of equilibration 120 min, phase ratio 1, at 300 K) in (a) $C_4mim\cdot NTf_2$; (b) $C_8mim\cdot NTf_2$; (c) the separation factor ($\beta_{Nb/Ta}$) of Nb over Ta at different acidity for both the ionic liquids; and (d) EDXRF spectra for Nb and Ta in aqueous phase before and after extraction (2 M HNO_3 , 300 K, phase ratio 1).

viscosity of the ionic liquid resulted in poor dispersion of the two phases with each other and hence, poor mass transfer. The viscosity coefficient for $C_8mim\cdot NTf_2$ was higher than that of $C_4mim\cdot NTf_2$, thereby leading to the slower mass transfer for the former.^{46,47}

Extraction Profile. Figure 3 gives the experimentally obtained D values for Nb and Ta from different nitric acid concentrations in the aqueous phase ranging from 0.01 M to 4 M HNO_3 using 0.1 M of FIL diluted in $C_4mim\cdot NTf_2$ and $C_8mim\cdot NTf_2$. For $C_4mim\cdot NTf_2$ as the diluent, the D_{Nb} and D_{Ta} values were found to be a maximum at 0.01 M HNO_3 ($D_{Nb} \sim 1900$ and $D_{Ta} \sim 90$), resulting in a separation factor ($\beta_{Nb/Ta}$) value of ~ 20 . The D values for Nb and Ta in $C_4mim\cdot NTf_2$ and $C_8mim\cdot NTf_2$ from 0.01 M HNO_3 in the absence of FIL are as follows: $D_{Nb}^{C_4mim\cdot NTf_2} \sim 0.03$, $D_{Ta}^{C_4mim\cdot NTf_2} \sim 0.022$; $D_{Nb}^{C_8mim\cdot NTf_2} \sim 0.018$; and $D_{Ta}^{C_8mim\cdot NTf_2} \sim 0.016$. The D values for both Nb and Ta were found to decrease moderately with increasing nitric acid concentration in the aqueous phase up to 1 M HNO_3 beyond which a drastic reduction in the D values was noticed. This kind of extraction profile is just the reverse of the trend seen for neutral extractants dissolved in molecular diluents which is also termed as the “solvation” mechanism.^{24,29} Unlike the “solvation” mechanism involving neutral metal–ligand complexed species; in lower alkyl chain bearing ionic liquid, such as $C_4mim\cdot NTf_2$, this trend is quite common and has been reported for several solvent systems.^{48–50} This trend has been attributed to the formation of a cation exchange mechanism involving cationic metal–ligand complexed species. The separation factor of Nb over Ta showed an interesting trend: it was also found to decrease with

an increase in the nitric acid concentration in the aqueous phase, followed by a peak at 2 M HNO_3 with the $\beta_{Nb/Ta} \sim 32$ followed by a sudden reduction (Figure 3c). A similar trend in the D values was also found in the case of $C_8mim\cdot NTf_2$ with a maximum at $\beta_{Nb/Ta} \sim 48$. The enhancement of D values for Nb and Ta in $C_8mim\cdot NTf_2$ was also reported during the extraction of Am^{3+} using a tripodal DGA in ionic liquid.⁵¹ This can be attributed to the prevalence of the “cation exchange” mechanism for Nb and Ta at lower nitric acid concentrations, i.e., up to ~ 1.5 M HNO_3 , while beyond that the solvation mechanism involving neutral species was found to be operative. It is also required to be emphasized that the extraction profiles are indicative only of the particular extraction mechanism. However, a detailed speciation study was required to further confirm the same. In $C_8mim\cdot NTf_2$ -based solvent system, the $\beta_{Nb/Ta}$ values were found to vary in the narrow range of 6–14 for the aqueous phase containing 0.01 M–1 M HNO_3 . Beyond this acid concentration range, there was an increase; the maximum $\beta_{Nb/Ta}$ at 2 M HNO_3 had a value of ~ 49 , while at 3 M HNO_3 it was ~ 35 . In the acidity range of 0.01 M–1 M HNO_3 , where the cation exchange mechanism was predominantly operative for all the systems, the D_{Nb} and D_{Ta} values were found to be higher in $C_4mim\cdot NTf_2$ compared to $C_8mim\cdot NTf_2$. This can be explained based on the dissolution characteristics of the methyl imidazolium ion. During the cation exchange mechanism, since the metal–ligand complex species is cationic in nature, charge neutrality after mass transfer is being maintained by an exchange of equivalent amount of the methylimidazolium ion from the ionic liquid phase to the aqueous phase. Due to the presence of

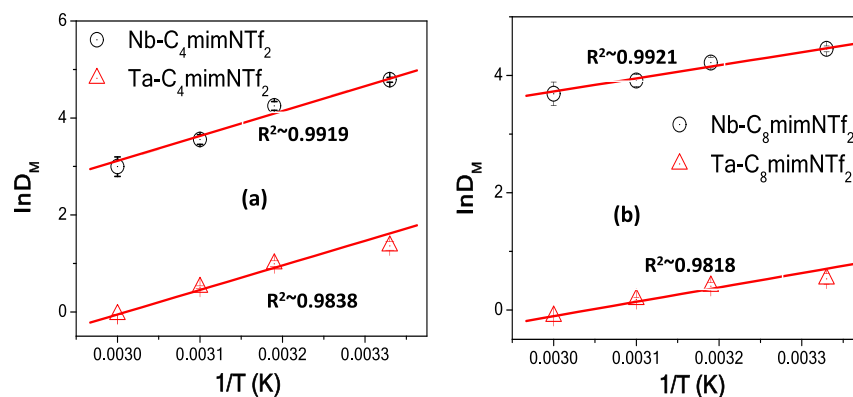


Figure 4. Variation in $\ln D$ values as a function of the reciprocal of absolute temperature for Nb and Ta extraction in (a) $C_4\text{mim}\cdot\text{NTf}_2$ and (b) $C_8\text{mim}\cdot\text{NTf}_2$

the longer *n*-octyl chain as compared to the *n*-butyl group, the aqueous solubility of the $C_8\text{mim}^+$ ion is considered to be lower as compared to that of the $C_4\text{mim}^+$ ion which can explain the observed behavior.⁵²

Figure 3d shows the typical EDXRF spectra of the aqueous phase prior and after the extraction of Nb and Ta using 100 mM of the FIL in $C_4\text{mim}\cdot\text{NTf}_2$ and $C_8\text{mim}\cdot\text{NTf}_2$. The Nb amount was monitored using the K_α ray at 16.594 keV, whereas, for Ta, the L_α line at 8.114 keV was chosen.^{53,54} From the spectra, it was clear that the leftover Nb or Ta present in the aqueous phase after their extraction roughly followed the trend: $C_{\text{Nb}}^{C_4\text{mim}\cdot\text{NTf}_2} < C_{\text{Nb}}^{C_8\text{mim}\cdot\text{NTf}_2} < C_{\text{Ta}}^{C_4\text{mim}\cdot\text{NTf}_2} < C_{\text{Ta}}^{C_8\text{mim}\cdot\text{NTf}_2}$.

Effect of Temperature. Figure 4 shows the variation in the $\ln D$ values as a function of reciprocal absolute temperature ($1/T$). The D values were found to decrease with increase in the temperature, suggesting that the metal ion extraction is exothermic in nature. According to Vant Hoff equation^{55,56}

$$\ln K_{\text{ex}} = -\frac{\Delta H}{RT} + A \quad (3)$$

where K_{ex} is the extraction constant, R is the universal gas constant, and A is the integration constant. The K_{ex} is directly proportional to the change in the enthalpy of the extraction process (ΔH) and inversely to the absolute temperature (T). The linear regression coefficients, obtained for the Vant Hoff plots are: $\chi_{\text{Nb}}^2_{C_4\text{mim}\cdot\text{NTf}_2} \sim 0.9919$, $\chi_{\text{Ta}}^2_{C_4\text{mim}\cdot\text{NTf}_2} \sim 0.9838$, $\chi_{\text{Nb}}^2_{C_8\text{mim}\cdot\text{NTf}_2} \sim 0.9924$ and $\chi_{\text{Ta}}^2_{C_8\text{mim}\cdot\text{NTf}_2} \sim 0.9818$. The change in the enthalpy values was calculated from the slope of the Vant Hoff plots and followed the trend: $\Delta H_{\text{Nb}}^{C_4\text{mim}\cdot\text{NTf}_2} (-33.09 \text{ kJ mol}^{-1}) > \Delta H_{\text{Ta}}^{C_4\text{mim}\cdot\text{NTf}_2} (-25.93 \text{ kJ mol}^{-1}) > \Delta H_{\text{Nb}}^{C_8\text{mim}\cdot\text{NTf}_2} (-14.22 \text{ kJ mol}^{-1}) > \Delta H_{\text{Ta}}^{C_8\text{mim}\cdot\text{NTf}_2} (11.45 \text{ kJ mol}^{-1})$ (Table 1). The change in the Gibbs free energy (ΔG) due to the biphasic extraction was estimated from the

Table 1. Thermodynamic Parameters for the Extractive Mass Transfer of Nb and Ta using 100 mM FIL in $C_4\text{mim}\cdot\text{NTf}_2$ and $C_8\text{mim}\cdot\text{NTf}_2$

system	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
Nb- $C_4\text{mim}\cdot\text{NTf}_2$	-11.94	-33.09	-70.5
Ta- $C_4\text{mim}\cdot\text{NTf}_2$	-3.39	-25.93	-75.1
Nb- $C_8\text{mim}\cdot\text{NTf}_2$	-11.11	-14.22	-10.4
Ta- $C_8\text{mim}\cdot\text{NTf}_2$	-1.32	-11.45	-33.8

extraction constant at a particular temperature (T) using the following equation:

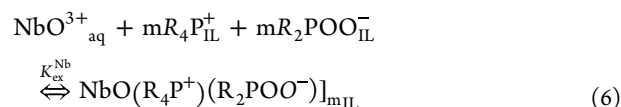
$$\Delta G = -RT \ln K_{\text{ex}} \quad (4)$$

The ΔG values calculated in the present case were found to be negative revealing the spontaneous nature of the solvent extraction processes. The ΔG values, obtained from eq 4, followed the same trend as observed for the D values, i.e., $\Delta G_{\text{Nb}}^{C_4\text{mim}\cdot\text{NTf}_2} (-11.94 \text{ kJ mol}^{-1}) > \Delta G_{\text{Nb}}^{C_8\text{mim}\cdot\text{NTf}_2} (-11.11 \text{ kJ mol}^{-1}) > \Delta G_{\text{Ta}}^{C_4\text{mim}\cdot\text{NTf}_2} (-3.39 \text{ kJ mol}^{-1}) > \Delta G_{\text{Ta}}^{C_8\text{mim}\cdot\text{NTf}_2} (-1.32 \text{ kJ mol}^{-1})$. The change in the entropy (ΔS) was evaluated from the ΔG and ΔH values, as per the following equation.

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The overall entropy change was found to decrease during the extraction of the metal ions (Table 1). The reduction in entropy change for Ta extraction was found to be larger than that for Nb for both $C_4\text{mim}\cdot\text{NTf}_2$ - and $C_8\text{mim}\cdot\text{NTf}_2$ -based solvent systems. The negative entropy change might be due to the restriction in the conformation of the ligand functionality, which was not compensated by the release of the coordinated water molecules during the extractive mass transfer. The results also indicated that the extraction processes might be based on the formation of outer sphere complexes, leading to the decrease in the entropy as the possibility of the dehydration of metal ions or desolvation of the ligand molecules was very limited.

Extraction Mechanism and Speciation. As discussed above, a “cation exchange” mechanism was predominantly operative for the extraction of Nb and Ta from 2 M HNO_3 using $C_4\text{mim}\cdot\text{NTf}_2$ as the diluent, while for $C_8\text{mim}\cdot\text{NTf}_2$, a “solvation” mechanism might be predominating. In the present case, the FIL consists of a phosphonium cation (R_4P^+) and phosphinate ($R_2\text{POO}^-$) anion. The anion is the coordinating site for the metal ions existing as NbO^{3+} or TaO^{3+} . The solvation mechanism involved neutral metal–ligand species and can be expressed as follows:



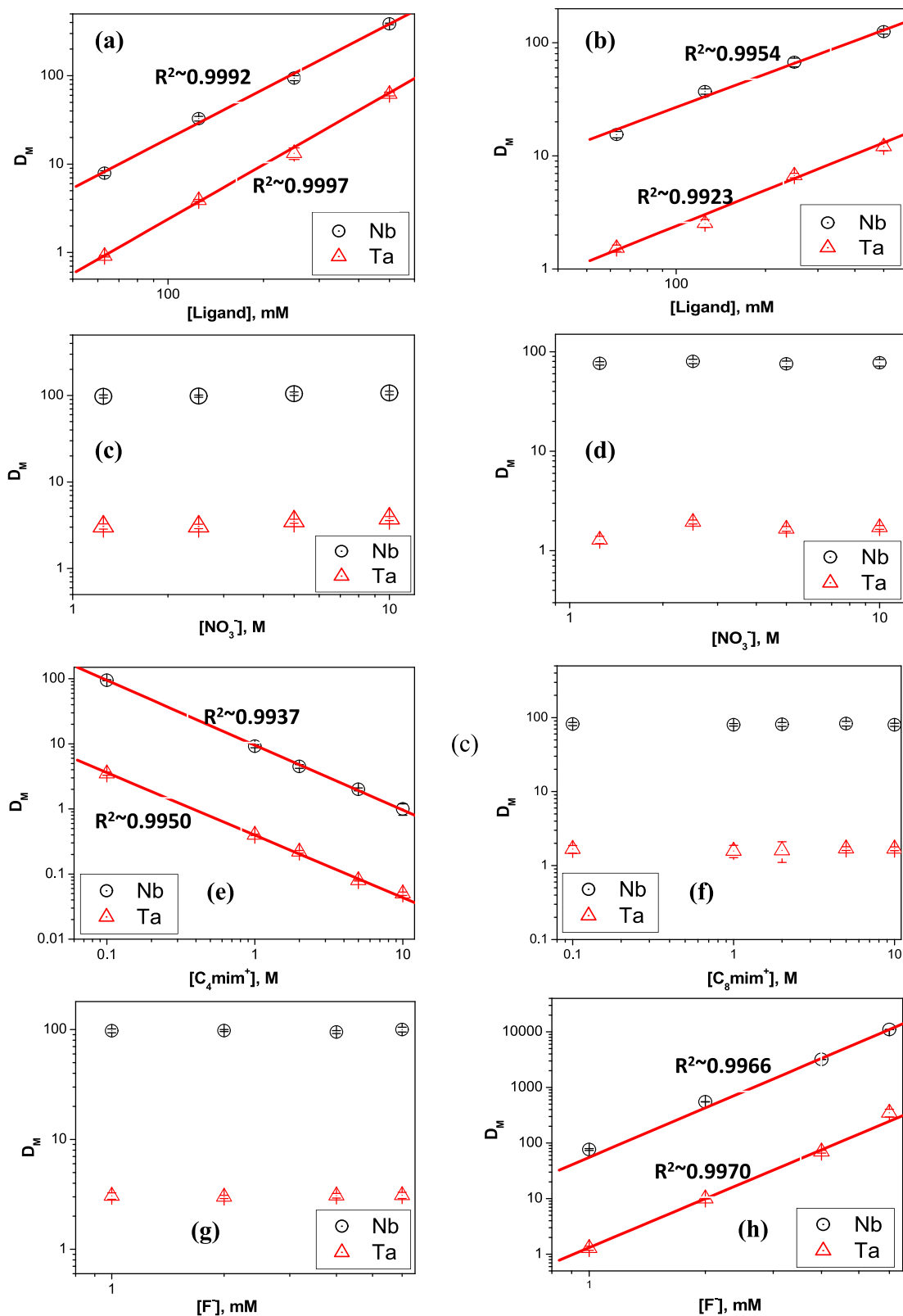
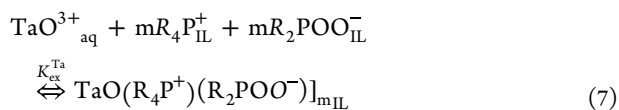


Figure 5. Variation in D_{Nb} and D_{Ta} with concentration of FIL in (a) $\text{C}_4\text{mim}\cdot\text{NTF}_2$ or (b) $\text{C}_8\text{mim}\cdot\text{NTF}_2$ from 2 M HNO_3 ; concentration of nitrate anion in aqueous phase for FIL in (c) $\text{C}_4\text{mim}\cdot\text{NTF}_2$ or (d) $\text{C}_8\text{mim}\cdot\text{NTF}_2$; concentration of C_4mim^+ or C_8mim^+ in aqueous phase for FIL in (e) $\text{C}_4\text{mim}\cdot\text{NTF}_2$ or (f) $\text{C}_8\text{mim}\cdot\text{NTF}_2$ and concentration of fluoride anion in aqueous phase FIL in (g) $\text{C}_4\text{mim}\cdot\text{NTF}_2$ or (h) $\text{C}_8\text{mim}\cdot\text{NTF}_2$.



where m is the number of FIL coordinated to the metal ions, and $K_{\text{ex}}^{\text{Nb}}$ and $K_{\text{ex}}^{\text{Ta}}$ are the extraction constants for Nb and Ta, respectively. Though the anionic part of the FIL is actually coordinated to the metal ion, it was also associated with the

cations of the FIL. The extraction constant for the above-mentioned extraction reactions can be expressed as follows:

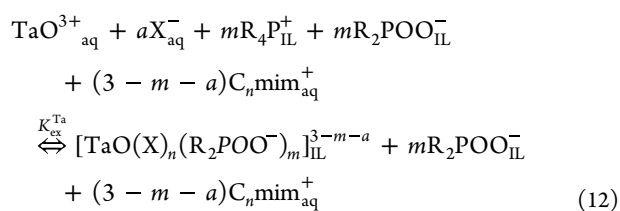
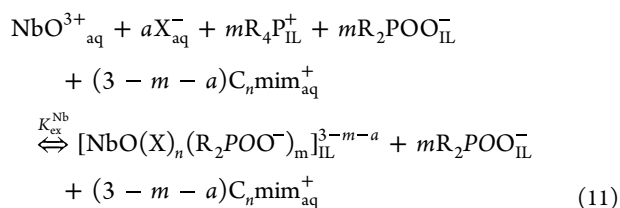
$$K_{\text{ex}}^{\text{Nb}} = \frac{[\text{NbO}(\text{R}_4\text{P}^+)(\text{R}_2\text{POO}^-)]_{\text{mIL}}}{[\text{NbO}^{3+}_{\text{aq}}][\text{FIL}^+][\text{FIL}^-]_{\text{IL}}^m} \quad (8)$$

$$K_{\text{ex}}^{\text{Nb}} = \frac{D_{\text{Nb}}}{([\text{R}_4\text{P}^+][\text{R}_2\text{POO}^-]_{\text{IL}})^m} \quad (9)$$

Taking the logarithm on both sides, one gets the following equation:

$$\ln D_{\text{Nb}} = \ln K_{\text{ex}}^{\text{Nb}} + m \cdot \ln [(\text{R}_4\text{P}^+)(\text{R}_2\text{POO}^-)] \quad (10)$$

The above equation is equivalent to the linear expression for the plot $\ln D_{\text{Nb}}$ vs $\ln [(\text{R}_4\text{P}^+)(\text{R}_2\text{POO}^-)]$. The slope of the above straight-line equation would indicate the number of the FIL ligand molecules associated with each Nb. A similar expression can also be made for Tb for the 'solvation' mechanism. However, the cation exchange mechanism indicated the formation of cationic species and charge neutrality between the two phases being maintained by the exchange of the ionic liquid cation from the ionic liquid phase to the aqueous phase in an equivalent amount. For Nb and Ta, the most probable cation exchange reaction can be expressed as follows:



where m is the number of FIL moieties attached to either Nb or Ta, ' a ' is the number of anions (either F^- or NO_3^-) attached to the metal–ligand complexed species. The extraction constant can be expressed as

$$K_{\text{ex}}^{\text{Nb}} = \frac{[[\text{NbO}(\text{X})_n(\text{R}_2\text{POO}^-)]_{\text{mIL}}]^{3-m-a} [\text{R}_2\text{POO}_{\text{IL}}^-]^m [\text{C}_n\text{mim}_{\text{aq}}^+]^{(3-m-a)}}{[\text{NbO}^{3+}_{\text{aq}}][\text{X}_{\text{aq}}^-]^a [\text{R}_4\text{P}_{\text{IL}}^+]^m [\text{R}_2\text{POO}_{\text{IL}}^-]^m [\text{C}_n\text{mim}_{\text{IL}}^+]^{(3-m-a)}} \quad (13)$$

After mathematical treatment, it becomes,

$$K_{\text{ex}}^{\text{Nb}} = \frac{D_{\text{Nb}}[\text{C}_n\text{mim}_{\text{aq}}^+]^{(3-m-a)}}{[\text{X}_{\text{aq}}^-]^a [\text{R}_2\text{POO}_{\text{IL}}^-]^m [\text{C}_n\text{mim}_{\text{IL}}^+]^{(3-m-a)}} \quad (14)$$

At a particular temperature and fixed experimental conditions, the ratio of the concentration of the C_nmim^+ cation in the aqueous phase and that in the ionic liquid phase is considered constant and is termed the partition coefficient of the species. Incorporating all the constants together with the conditional extraction constant ($K_{\text{ex}}^{\text{Nb}}$), the D can be expressed as follows:

$$\ln D_{\text{Nb}} = \ln K_{\text{ex}}^{\text{Nb}} + m \ln [\text{R}_2\text{POO}_{\text{IL}}^-] + a \ln [\text{X}_{\text{aq}}^-] \quad (15)$$

The expression was found to be similar to that of the "solvation" mechanism and followed a linear relationship. The same expression holds true for the Ta extraction by the "cation exchange" mechanism.

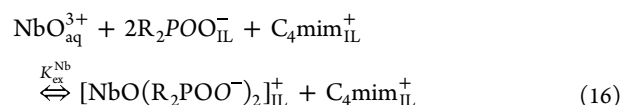
Figure 5 depicts the variation in the D values of Nb and Ta as a function of the FIL concentration in $\text{C}_4\text{mim}\cdot\text{NTf}_2$ as well as $\text{C}_8\text{mim}\cdot\text{NTf}_2$ as the diluent medium. The linear relationship holds good for all the cases as observed from their respective regression coefficient values (Supplementary Table S1). The slope values implied that, in $\text{C}_4\text{mim}\cdot\text{NTf}_2$, there was the formation of the ML_2 complex for both Nb and Ta, while in $\text{C}_8\text{mim}\cdot\text{NTf}_2$, both the metals formed ML_1 complexes. Figure 5c,d gives the variation in the D values of Nb and Ta as a function of NO_3^- ion concentration in the aqueous phase for $\text{C}_4\text{mim}\cdot\text{NTf}_2$ and $\text{C}_8\text{mim}\cdot\text{NTf}_2$. The D values are found to be insensitive to the nitrate ion concentration in the aqueous phase suggesting that the nitrate ion did not directly participate in the metal–ligand bearing extracted species.

Figure 5 depicts the variation in the D values of Nb and Ta as a function of the C_4mim^+ and C_8mim^+ ion concentrations in the aqueous phase. This concentration variation was performed by using the respective bromide salts ($\text{C}_4\text{mim}\cdot\text{Br}$ and $\text{C}_8\text{mim}\cdot\text{Br}$) in the aqueous phase. In the $\text{C}_8\text{mim}\cdot\text{NTf}_2$ based solvent system, the D_{Nb} and D_{Ta} values were found to be insensitive to the variation in the C_8mim^+ ion concentration in the aqueous phase, indicating the predominance of the neutral Nb and Ta complexes during the metal ion extraction.

However, for $\text{C}_4\text{mim}\cdot\text{NTf}_2$, the D values for Nb and Ta were found to decrease with an increase in the C_4mim^+ ion concentration in the aqueous phase, and the obtained slope values of the best-fit straight lines were 0.93 and 0.88, respectively. It revealed that the presence of C_4mim^+ ion in the aqueous phase would impart a negative impact on the Nb and Ta extraction, and one C_4mim^+ got exchanged from the ionic liquid phase to the aqueous phase during the mass transfer of each of the Nb or Ta atom. This also revealed the formation of monocationic metal (Nb and Ta)-ligand complexes with the extraction agent associated with the "cation exchange" mechanism.

Figure 5g,h presents the variation in the D values as a function of the F^- ion concentration in the aqueous phase. This experiment was performed in view of the fact that the F^- ion was invariably present in the aqueous phase due to the use of the fluoride-based Nb and Ta salts. The linear regression analyses revealed that for $\text{C}_4\text{mim}\cdot\text{NTf}_2$ as the diluent medium, F^- ions did not participate in the complexation of Nb and Ta. However, for the $\text{C}_8\text{mim}\cdot\text{NTf}_2$ based solvent systems, three F^- ions were associated with each of the Nb or Ta atoms during the complexation reaction. Based on these results, the following conclusions can be made: in the $\text{C}_4\text{mim}\cdot\text{NTf}_2$ based system, the extracted species to be $[\text{NbO}(\text{R}_2\text{POO}^-)]_2^+$ and $[\text{TaO}(\text{R}_2\text{POO}^-)]_2^+$, respectively, whereas in $\text{C}_8\text{mim}\cdot\text{NTf}_2$, the species were $\text{NbOF}_3(\text{R}_4\text{P}^+)(\text{R}_2\text{POO}^-)$ and $\text{TaOF}_3(\text{R}_4\text{P}^+)$, where R_4P^+ and R_2POO^- are the cation and anion part of the FIL. The proposed extraction mechanism can be given as follows:

in $\text{C}_4\text{mim}\cdot\text{NTf}_2$



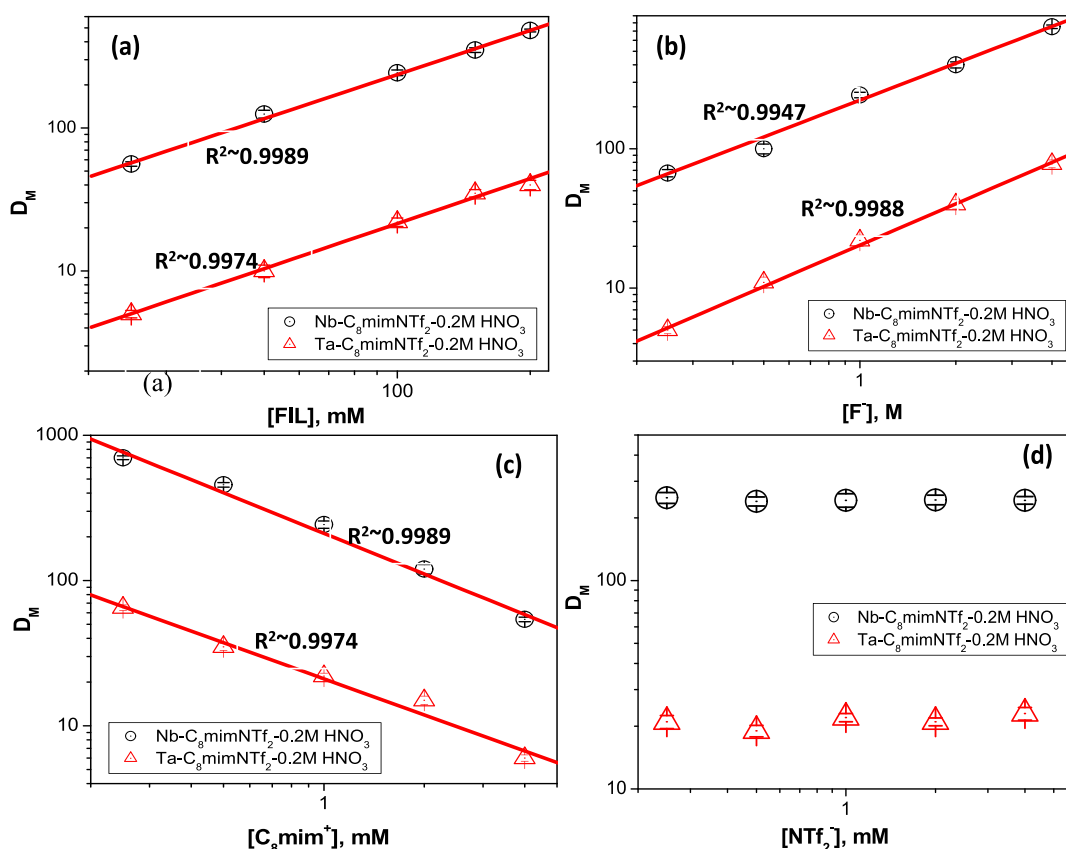
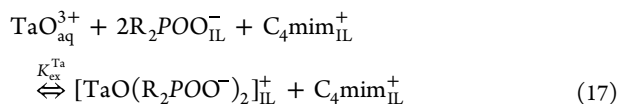


Figure 6. Variation in D_{Nb} and D_{Ta} with (a) concentration of FIL in $C_8mim\cdot NTf_2$ from 0.2 M HNO_3 ; (b) concentration of fluoride anion in aqueous phase; (c) concentration of C_8mim^+ in aqueous phase; and (d) concentration of NTf_2^- ion in the aqueous phase.



while in $C_8mim\cdot NTf_2$

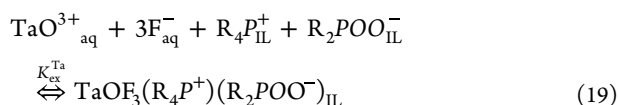
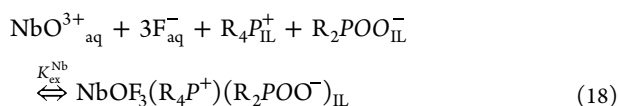


Figure S1 (ESI) shows the variation of D values for Nb and Ta as a function of the $LiNTf_2$ concentration in the aqueous phase. The D values were found to be insensitive to the NTf_2^- ion concentration for all four solvent systems. This exercise revealed that the anion exchange mechanism is not operative for the present case.

In summary, the extraction in $C_4mim\cdot NTf_2$ proceeded via a "cation exchange" mechanism involving the species $[NbO(R_2POO^-)_2]^+$ and $[TaO(R_2POO^-)_2]^+$, respectively. To maintain overall electrical neutrality, an equivalent amount of C_4mim^+ will be exchanged from the ionic liquid phase to the aqueous phase. Hence, the presence of C_4mim^+ in the aqueous phase did not favor the mass transfer resulting in the reduction in the D values of Nb and Ta. However, since there was no involvement of NTf_2^- ion during the mass transfer, the presence of NTf_2^- in the aqueous phase did not modify the D values for Nb and Ta. Since NO_3^- ions were not involved in

Nb/Ta complexes and subsequent mass transfer, the presence of different concentrations of nitrate ions in the aqueous phase exhibited insensitivity in modifying the D values for Nb and Ta. The reduction in the D values with increase in the nitric acid concentration was a typical signature of the 'cation exchange' mechanism as reported frequently in the literature.^{47–52} In $C_8mim\cdot NTf_2$, the extraction proceeded by 'solvation mechanism' involving the species: $NbOF_3(R_4P^+)(R_2POO^-)$ and $TaOF_3(R_4P^+)(R_2POO^-)$. Since, NO_3^- , C_8mim^+ , and NTf_2^- were not involved in the extraction, the presence of additives like NO_3^- , C_8mim^+ , and NTf_2^- in the aqueous phase did not show any effect on the D_{Nb} or D_{Ta} values. The effect of an additive like F^- ion in the aqueous phase exhibited insensitivity in D values for $C_4mim\cdot NTf_2$ -based extraction. However, it favored the extraction of Nb and Ta for $C_8mim\cdot NTf_2$ -based solvent systems.

Figure 6 gives the FIL dependency on the obtained D values when the metal ion extraction was performed from 0.2 M HNO_3 in $C_8mim\cdot NTf_2$. It suggested the formation of ML_1 species for Nb as well as Ta. There was also one F^- ion participation per Nb/Ta atom in the complex, as indicated by Figure 6b. Figure 6c clearly indicates that one C_8mim^+ was exchanged from the ionic liquid phase to the aqueous phase for the transfer of the extracted Nb/Ta complex. The extraction has predominantly proceeded via the cation exchange mechanism involving mono-positive metal–ligand species. The insensitivity in the D values as a function of the NTf_2^- ion concentration variation in the aqueous phase revealed that the anion exchange mechanism was not operative (Figure 6d). The overall speciation obtained in 0.2 M HNO_3 as the aqueous

feed was $[\text{NbOF}(\text{R}_2\text{POO}^-)]^+$ and $[\text{TaOF}(\text{R}_2\text{POO}^-)]^+$, respectively. Supplementary Table S2 summarizes the analytical results obtained from the linear regression of the above-mentioned experiments performed in 0.2 M HNO_3 feed.

Back Extraction and Reusability. Figure 7a depicts the % of back extraction of Nb and Ta from $\text{C}_4\text{mim}\cdot\text{NTf}_2$ - and

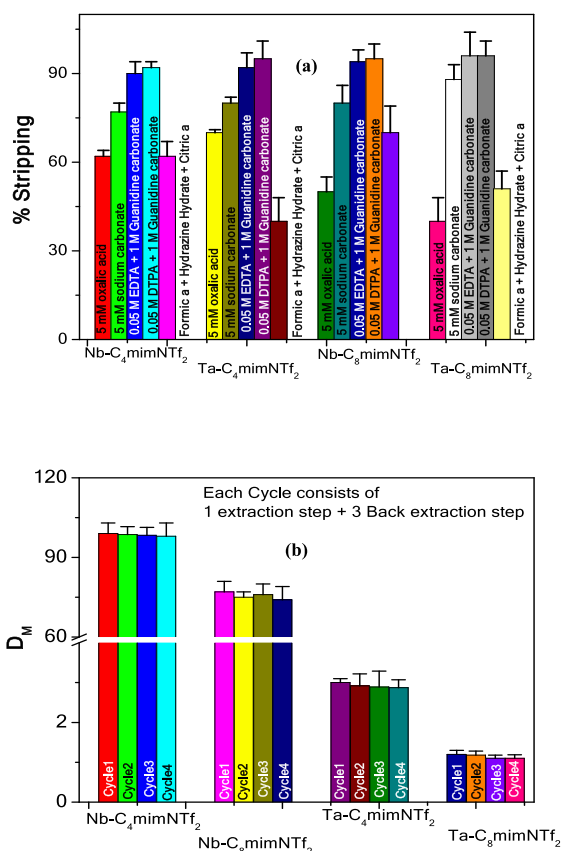


Figure 7. (a) % of back extraction of Nb and Ta from loaded extraction agent using single contact of the aqueous phase soluble complexing agents; and (b) recyclability of the ionic liquid phase after multiple cycles each consisting of extraction and three consecutive back extraction steps.

$\text{C}_8\text{mim}\cdot\text{NTf}_2$ -based solvent systems using several aqueous complexing agents, viz., 5 mM oxalic acid, 5 mM sodium carbonate, 0.05 M EDTA or DTPA in 1M guanidine carbonate and a mixture of 0.4 M formic acid + 0.4 M hydrazine hydrate + 0.2 M citric acid.^{57,58} 5 mM oxalic acid and 5 mM sodium carbonate were successful only for partial back extraction

(maximum up to ~70 and 88%, respectively) of the locked up Nb and Ta. Similarly, a mixture of formic acid, hydrazine hydrate, and citric acid was able to back-extract 40–70% of the locked-up Nb or Ta from the FIL complex in an ionic liquid. Mixtures of EDTA-guanidine carbonate or DTPA-guanidine carbonate were found to be the most effective stripping solution for the back extraction of Nb and Ta from the ionic liquid phase (maximum up to ~96% in a single contact). This exercise also revealed that a single contact of these solutions would not be successful in quantitative back extraction of either Nb or Ta from their FIL complex in an ionic liquid. The role of EDTA and DTPA in the stripping agent is to form a stable chelate complex with the metal ions, i.e., NbO^{3+} and TaO^{3+} , utilizing four coordinating carboxylic acid groups by EDTA and five carboxylic acid groups by DTPA. However, the effective chelation is favored by the formation of carboxylate ions by deprotonation of the carboxylic acid groups. This implied that the pH of the medium played a crucial role in chelation and subsequent back extraction. Guanidine carbonate has been used as a buffer to adjust the pH of the medium in the range of 10–12.5. Several reports are available in the literature on the application of a mixture of EDTA-guanidine carbonate and DTPA-guanidine carbonate for the back extraction of metal ions from their complexes in the ionic liquid phase.^{57,58}

Figure S2 (ESI) depicts the EDXRF spectra of the aqueous phase prior to extraction monitoring the K_{α} line of Nb at 16.594 keV and the L_{α} line of Ta at 8.114 keV. After extraction with 100 mM FIL in $\text{C}_4\text{mim}\cdot\text{NTf}_2$ and $\text{C}_8\text{mim}\cdot\text{NTf}_2$, the ionic liquid phase was subjected to the stripping solution mentioned above. Then, the aqueous EDXRF spectra were recorded for Nb and Ta in the aqueous phase containing the stripping solution after a single contact. The spectra typically indicated the effective stripping by EDTA-guanidine carbonate and DTPA-guanidine carbonate, while partial stripping of Nb and Ta using other stripping solutions.

Table 2 shows the cumulative % back extraction of Nb and Ta from their complexes in the ionic liquid after each contact of EDTA-guanidine carbonate or DTPA-guanidine carbonate. It was observed that after the second contact, >99% of the loaded Nb and Ta could be stripped back into the ionic liquid phase, while for quantitative back extraction, i.e., for more than 99.99% back extraction, three contacts were necessary.

Figure 7b gives the results of the recyclability studies. The solvent systems were subjected to Nb and Ta extraction from 2 M HNO_3 to obtain the D values for the first cycle. Subsequently, the loaded ionic liquid phase was subjected to three consecutive stripping steps using the DTPA-guanidine

Table 2. Cumulative Back Extraction of Nb and Ta from Loaded Extraction Agent Using EDTA/DTPA + Guanidine Carbonate

metal	ionic liquid	number of back extractions	1	2	3
		stripping agent			
Nb	$\text{C}_4\text{mim}\cdot\text{NTf}_2$	EDTA + guanidine carbonate	90.00	99.00	99.99
Nb		DTPA + guanidine carbonate	92.20	99.36	>99.99
Ta		EDTA + guanidine carbonate	92.60	99.36	>99.99
Ta		DTPA + guanidine carbonate	95.11	99.75	>99.99
Nb	$\text{C}_8\text{mim}\cdot\text{NTf}_2$	EDTA + guanidine carbonate	94.00	99.64	>99.99
Nb		DTPA + guanidine carbonate	95.00	99.75	>99.99
Ta		EDTA + guanidine carbonate	96.00	99.84	>99.99
Ta		DTPA + guanidine carbonate	96.00	99.84	>99.99

carbonate solution mixture. After that, the regenerated ionic liquid phase was subjected to another extraction step by equilibrating with a fresh lot of the aqueous phase containing Nb and Ta in 2 M HNO₃ to obtain the D values for the second cycle. In a similar manner, third and fourth cycles were also performed to obtain the corresponding D values. After four such cycles, there was $\sim 1\%$ reduction of D_{Nb} in C₄mim·NTf₂, while for D_{Ta} , $\sim 4\%$ reduction was noticed in the same solvent system. However, the extent of reduction was slightly higher for the C₈mim·NTf₂-based solvent systems. Almost 4.5% reduction in the D_{Nb} value was observed after four consecutive extraction–stripping cycles, whereas $\sim 7.6\%$ of reduction in the D_{Ta} was evidenced in the solvent containing C₈mim·NTf₂. These results indicate improved separation of the metal ions with the increasing number of recycling stages with a maximum separation factor of ~ 68 (Supplementary Table S3).

Radiolytic Stability. Radiolytic degradation of the solvent systems was studied by exposing those to a known dose of γ rays using a ⁶⁰Co based irradiator. The degradation of the solvent, if any, can lead to changes in the metal ion extraction. Figure 8 depicts the D values of Nb and Ta using the irradiated

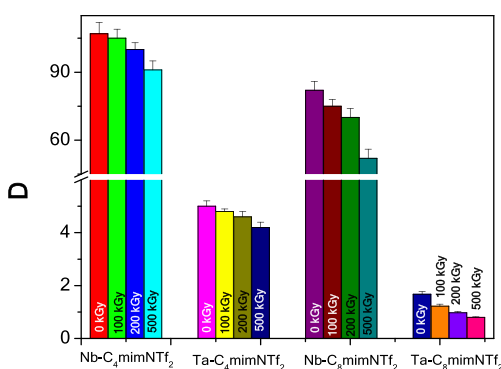


Figure 8. D values for Nb and Ta using C₄mim·NTf₂- and C₈mim·NTf₂-based solvent systems exposed toward various gamma dose.

solvents containing the FIL. The solvents were exposed to γ rays in a ⁶⁰Co gamma chamber at various absorbed dose values ranging from 100 to 500 kGy. With 100 kGy absorbed dose, the D_{Nb} values became 98 and 91% of the values obtained with the pristine solvents in C₄mim·NTf₂ and C₈mim·NTf₂, respectively, whereas for Ta there was somewhat larger decrease in the D values at 96 and 73%, respectively. The reduction in the D values for Nb and Ta was found to increase with increasing absorbed dose from 100 to 200 to 500 kGy for all the solvent systems. After 500 kGy exposure, the D_{Nb} in C₄mim·NTf₂ became 85% of its original value (with the pristine solvent), while the decrease in the D_{Ta} in C₄mim·NTf₂ was almost comparable at 84%. In the case of the C₈mim⁺-based solvent systems, D_{Nb} and D_{Ta} became 63 and 48% of their original values. The C₄mim·NTf₂-based solvent systems were found to be radiolytically more stable as compared to those containing C₈mim·NTf₂. The lesser radiolytic stability in C₈mim·NTf₂ might be attributed to the formation of less stable aliphatic radicals by the cleavage of the C–C bonds on gamma-ray exposure.^{59,60}

Comparative Evaluation. A comparative evaluation was done to understand whether the $\beta_{\text{Nb/Ta}}$ values in the present case were better or poorer than those reported in the literature (Table 3). The literature reported $\beta_{\text{Nb/Ta}}$ values were segregated into three sections for the convenience of

discussion. In the first section, $\beta_{\text{Nb/Ta}}$ values obtained in this study ($\beta_{\text{Nb/Ta}}^{\text{C4mim-NTf2}} \sim 32$ and $\beta_{\text{Nb/Ta}}^{\text{C8mim-NTf2}} \sim 48$) were compared with those obtained from different dissolution methods reported in the literature. Microwave dissolution of Nb₂O₅ and Ta₂O₅ in H₂SO₄ and H₃PO₄ were reported to have $\beta_{\text{Nb/Ta}}$ as much as 10.2 and 12.3, which, however, were 4–5 times lower than those obtained in the present case.¹⁹ Leaching of Nb and Ta from their minerals using a mixture of H₂SO₄–HNO₃ with solid to liquid ratio of 1:3 resulted in the $\beta_{\text{Nb/Ta}} \sim 1.05$, i.e., only slightly better leachability of Nb.⁶¹ NaOH and KOH roasting of Nb₂O₅ and Ta₂O₅ did not exhibit any selectivity in the dissolution of either of the elements resulting in a $\beta_{\text{Nb/Ta}}$ of ~ 1 .^{62,63} By shifting the precursor to low-grade Nb–Ta alloy and modifying the KOH to the ore mass ratio from 2:1 to 7:1, not much selectivity was induced.^{64,65}

The second section summarizes a comparison of the data reported with liquid–liquid extraction systems, where F[−] has not been added as HF or NH₄HF₂ or any other F[−] containing compounds/salts. The solutions of tertiary amines such as tri *n*-octylamine (TOA), tri *n*-decylamine (TDA), and tri *n*-dodecylamine (TDDA) in carbon tetrachloride (CCl₄) were used as the organic phase, while the aqueous phase contained 0.2 M oxalic acid and 0.5 M H₂SO₄. The maximum $\beta_{\text{Nb/Ta}}$ achieved was 1.02.⁶⁶ In the presence of oxalic acid, the extraction by di-*n*-octylamino ethanol (DOAE) and di-*n*-octylamino propanol (DOAP) could not exhibit any selectivity as reported by Djordjevic et al.⁶⁷ Solvent extraction by Alamine 336/Aliquat 336 from HClO₄ (7 M), HNO₃ (7–10 M), and HCl (9M) media did not show much improvement in the $\beta_{\text{Nb/Ta}}$ values (1.31, 1.01, and 1, respectively). However, almost 10 times preferential extraction of Ta was reported over Nb from 8 M H₂SO₄ medium, resulting in a $\beta_{\text{Nb/Ta}}$ value of ~ 0.16 .⁶⁸ Extraction of Nb and Ta by TTA was reported to depend on the aqueous phase acidity. In 7 M HClO₄, the $\beta_{\text{Nb/Ta}}$ was ~ 1.14 , which it became 2.95, when the extraction was performed from 9 M HCl. Extraction by D2EHPA from 8 to 10 M H₂SO₄ brought selectivity in the extraction of Ta over Nb of ~ 10 times, resulting in a $\beta_{\text{Nb/Ta}}$ value of ~ 0.1 .⁶⁹ However, for the same solvent system when used against 7 M HClO₄ as the aqueous medium, no selectivity was observed.⁶⁹ Extraction from 10 M HNO₃ and 9 M HCl exhibited slight selectivity for Ta ($\beta_{\text{Nb/Ta}} \sim 0.83$) and Nb ($\beta_{\text{Nb/Ta}} \sim 1.15$), respectively. Vin and Khopkar reported no selectivity when the aqueous feed contained 1–2 M HCl in the presence of K₂S₂O₇ and ammonium oxalate.⁷⁰ Therefore, the present separation was found to be 16–25 times better than the literature methods based on solvent extraction.

The third section summarizes the $\beta_{\text{Nb/Ta}}$ data obtained in the present study and those reported in the literature based on solvent extraction in the presence of HF or NH₄HF₂ or F[−] ion generating materials. Extraction by Alamine 336 from 0.2 M HF and 0.5 M H₂SO₄ in the presence of H₂O₂ was reported to have a $\beta_{\text{Nb/Ta}}$ value of ~ 1.05 ,⁷¹ while the use of 0.3 M HF in analogous solvent system resulted in a near similar $\beta_{\text{Nb/Ta}}$ of ~ 1.04 .⁷² Extraction by Cyanex 923 from 4.6 N HF as the aqueous phase resulted in a modest $\beta_{\text{Nb/Ta}}$ of ~ 1.05 , whereas almost 2.5 to 3 times better extraction efficiency for Ta was reported for Cyanex 921 from 4.6 N HF, with $\beta_{\text{Nb/Ta}} \sim 0.38$.⁷³ Extraction by methyl iso-butyl ketone (MIBK) in the presence of 4.6 N HF led to 94.5% of Nb extraction, while Ta extraction was found to be ca. 21.3%, resulting in an improved $\beta_{\text{Nb/Ta}}$ value of ~ 4.4 .⁷³ However, El-Hussaini and El-Hakamhdy

Table 3. Comparison of the Separation Factor ($\beta_{\text{Nb/Ta}}$) for the Present Case with that of Other Systems Reported in the Literature

acid/alkali leaching			without addition of fluoride containing materials			addition of fluoride containing materials		
system	separation factor	ref	system	separation factor	ref	system	separation factor	ref
			FIL in $\text{C}_4\text{mim}\cdot\text{NTf}_2$	32	present investigation			
			FIL in $\text{C}_8\text{mim}\cdot\text{NTf}_2$	48	present investigation			
microwave dissolution of Nb_2O_5 and Ta_2O_5 in H_2SO_4	10.2	19	extraction by TOA, TDA, and TDDA in CCl_4 , aqueous phase: 0.2 M oxalic acid and 0.5 M H_2SO_4	1	66	extraction by Alamine 336 from HF - H_2SO_4 and H_2O_2	1.05	71
microwave dissolution of Nb_2O_5 and Ta_2O_5 in H_2SO_4 , H_3PO_4	12.35	19	extraction by DOAE and DOAP in the presence of oxalic acid	1	67	extraction by Aliquat 336 from HF	1.04	72
Nb and Ta from their minerals by H_2SO_4 - HNO_3	1.058	61	extraction by Alamine 336/Aliquat 336 from HClO_4	1.31	68	extraction by Cyanex 923 from HF	1.05	73
NaOH roasting of Nb_2O_5 and Ta_2O_5	1	62	extraction by Alamine 336/Aliquat 336 from HNO_3	1	68	extraction by Cyanex 921 from HF	0.38	73
KaOH roasting of Nb_2O_5 and Ta_2O_5	1	63	extraction by Alamine 336/Aliquat 336 from HCl	1	68	extraction by MIBK from HF	4.43	74
Nb-Ta alloy by KOH (mass ratio from 2:1) 7:1	1.03	64	extraction by Alamine 336/Aliquat 336 from H_2SO_4	0.16	68	extraction by MIBK from 4.3 HF - 5.7 H_2SO_4	32.1	74
Nb-Ta alloy by KOH (mass ratio 7:1)	1.01	65	extraction by TTA from HClO_4	1.15	69	extraction by MIBK from 0.6 N HF + 1.6 N H_2SO_4	0.54	75
			extraction by TTA from HCl	2.95	69	extraction by MIBK from NH_4HF in less than 8 M H_2SO_4	0.14	75
			extraction by D2EHPA from H_2SO_4	0.1	69	extraction by OCL from H_2SO_4 -HF	0.19	76
			extraction by D2EHPA from HClO_4	1	69	extraction by TBP from HF	0.98	77
			extraction by D2EHPA from HNO_3	0.83	69	extraction by TBP from H_2SO_4 + NH_4F -HF	0.82	78
			extraction by D2EHPA from HCl	1.15	69			
			extraction by D2EHPA from HCl in the presence of $\text{K}_2\text{S}_2\text{O}_7$ -ammonium oxalate	1	70			

reported ~96% Nb extraction and 3% Ta extraction, from a mixture of 4.3 N HF and 5.7 N H₂SO₄⁷⁴ resulting in a very impressive $\beta_{\text{Nb/Ta}}$ value of ~32.1 which is comparable with that reported in the present C₄mim·NTf₂-based solvent system. This was, however, lower than the value obtained by us in the C₈mim·NTf₂-based solvent system. The concentrations of HF and H₂SO₄ were also found to be very important in inducing the selectivity of Nb over Ta. Yang et al. reported a $\beta_{\text{Nb/Ta}}$ value of ~0.54 for extraction by MIBK when the aqueous phase was 0.6 N HF + 1.6 N H₂SO₄. The same solvent showed a reversal in the selectivity when the aqueous phase contained NH₄·HF in less than 8 M H₂SO₄, where the $\beta_{\text{Nb/Ta}}$ value achieved was ~0.14.⁷⁵ Mayorov and Nikolaev reported octanol (OCL)-based extraction from 2 M H₂SO₄ in the presence of up to 2.4 M HF resulting in a $\beta_{\text{Nb/Ta}}$ value of ~0.19, i.e., better extraction of Ta as compared to that of Nb.⁷⁶ In a separate report, a TBP- and OCL-based solvent when used against aqueous phases of 15.9 N HF and mixture of 6 N H₂SO₄ + NH₄F·HF resulted in $\beta_{\text{Nb/Ta}}$ values of ~0.98 and 0.82, respectively.^{77,78}

CONCLUSIONS

The solutions of a FIL (alkyl phosphonium cation and phosphinate anion) in imidazolium-based ionic liquids, viz., C₄mim·NTf₂ and C₈mim·NTf₂ exhibited preferential Nb extraction over Ta with separation factors of 48 and 32, respectively. The extraction profiles indicated that the cation exchange mechanism was operative in C₄mim·NTf₂ by the formation of ML₂ type of complex, where only phosphinate anions were involved in the complexation. However, in C₈mim·NTf₂, though initially a cation exchange mechanism was predominant, a solvation mechanism was operative at 2 M HNO₃, which involves the ML (1:1) complex formation. In the case of the neutral extracted species, both the phosphonium cation and the phosphinate anion were involved. In C₄mim·NTf₂ based solvent, the overall metal–ligand species were found to have a unit positive charge, and the charge compensation took place by exchange of the C₄mim⁺ ion from the ionic liquid phase toward the aqueous phase. The negative Gibb's energy change indicated that the extraction processes were thermodynamically favorable. This was evidenced by the release of enthalpy during the metal ion extraction with a reduction in entropy change values. Aqueous phase complexing agents like EDTA or DTPA in guanidine carbonate solutions were found to be effective in stripping back the locked-up Nb and Ta from their FIL complexes in the ionic liquid phase. However, multiple contacts were required for quantitative (99.99%) back extraction. The radiolytic stability of the ionic liquid-based solvent systems was found to be better as compared to the conventional molecular diluent-based solvent systems. Out of the studied solvent systems, the C₄mim·NTf₂-based systems were found to be better than the C₈mim·NTf₂-based systems. Slower kinetics in the extraction of the metal ions in C₈mim·NTf₂ compared to that in C₄mim·NTf₂ was attributed to the higher viscosity coefficient of the former ionic liquid and hence restricted the mass transfer. In summary, the present work gives a very encouraging method for the separation of Nb from Ta, which can find many applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c05487>.

The effect of NTf₂⁻ ion concentration in the aqueous phase on D_{Nb} and D_{Ta} values; EDXRF spectra of the aqueous phase for Nb and Ta before the extraction and after stripping with different aqueous complexing agents; the linear regression analysis results summarized for variation in D_{Nb} and D_{Ta} as a function of FIL concentration in ionic liquid and F⁻C_nmim⁺ concentration in aqueous phase; and how the separation factor as a function of different consecutive cycle varied have been summarized (PDF)

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Notes

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H. NGUYEN AND M. S. LEE digestion and octanol solvent extraction. *Hydrometallurgy* **2012**, 129–130, 151–155.