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Extraction of Nb(v) by quaternary ammonium-based solvents: toward organic hexaniobate systems†

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Solvent extraction of Nb(v) from alkaline aqueous media using quaternary ammonium solutions, especially Aliquat® 336 diluted in an aliphatic diluent, was investigated. The hexaniobate ions ($\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$) were extracted into the organic phase with very high yields at room temperature and within a few minutes, affording easy access to organic solutions of hexaniobates. Several parameters were found to influence the extraction of $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ including the nature and concentration of alkali cations, confirming subtle effects previously described for polyoxoniobates such as ion-pairing with alkali ions. The extraction of $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ with Aliquat® 336 is also influenced if competing anions are present in the aqueous phase (NO_3^- , Cl^- , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} and CO_3^{2-}) and varies with the pH mainly due to the competitive extraction of hydroxide ions at high pH. The co-extraction of sodium ions with $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ was observed as well as the co-extraction of water molecules, suggesting a self-association of the extractant. The proposed liquid–liquid extraction generic system paves the way for innovative niobium (and potentially tantalum) hydrometallurgical processes and it may also afford more direct routes for exploring the chemistry of hexaniobates in organic solvents.

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Introduction

Solvent extraction of niobium (Nb; $Z = 41$) has been extensively studied in acidic media and, most frequently, in the presence of a large excess of strongly complexing agents like $\text{HF}_{(\text{aq})}$ or $\text{NH}_4\text{F}_{(\text{aq})}$.¹ Indeed, Nb is mainly studied in concentrated fluoride-based media because the group V elements are highly soluble in such systems. Another advantage of the fluoride-containing aqueous solutions is that Nb(v) forms distinct complexes that can be separated from other metallic impurities (usually Ta, Ti and Fe) by solvent extraction using methylisobutyl ketone or octanol derivatives.^{2–4} As a consequence, the industrial processes that are currently used to purify Nb by solvent extraction are all operated in the presence of fluoride reagents.^{5–7} However, environmental concerns inherent to fluorides pushed industrial companies and researchers to develop cleaner solutions.

One of the rare alternatives to fluorinated systems to solubilize and process Nb is alkaline media. Niobium, which only exhibits the +v oxidation state in aqueous solutions, is also soluble at a basic pH due to the formation of polyoxometalates. While various polyoxoniobates can be isolated in the solid state or at a near-neutral pH,^{8,9} the aqueous chemistry of Nb(v) in basic media (at $\text{pH} \geq 9$) is dominated by the Lindqvist ions, *i.e.*, $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ ($0 \leq x \leq 3$). A similar assertion can be made for tantalum, which forms $\text{H}_x\text{Ta}_6\text{O}_{19}^{x-8}$ ions and whose chemistry is almost identical to that of niobium.^{10,11} These hexametallate entities are readily stable in aqueous systems and are even formed during the lixiviation of natural ores under harsh alkaline conditions.^{12–14} We also recently showed that niobium oxide ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) is naturally transformed into hydrated sodium hexaniobate ($\text{Na}_7\text{HNB}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$) when equilibrated with $\text{NaOH}_{(\text{aq})}$ under mild conditions ($\text{pH} = 10\text{--}12$).¹⁵ Although alkaline solutions of $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ (at $\text{pH} \geq 9$) have been investigated since the 1960s,^{16,17} studies have been limited to $\text{NaOH}_{(\text{aq})}$ and $\text{KOH}_{(\text{aq})}$ solutions until recently. It was only in the 2000s that the aqueous chemistry of $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ and $\text{H}_x\text{Ta}_6\text{O}_{19}^{x-8}$ ions was extended to lithium-, rubidium- and cesium-based alkaline media owing to the synthesis of their corresponding water-soluble salts: $\text{A}_{8-x}\text{H}_x\text{M}_6\text{O}_{19} \cdot n\text{H}_2\text{O}$ ($\text{A} = \text{Li}, \text{Rb}$ or Cs ; $0 \leq x \leq 2$).^{18–20} The basic conditions required to stabilize $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ in aqueous systems (*i.e.*, $\text{pH} \geq 9$) severely limit the list of cations that can be used when dealing with these highly negatively charged

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Table 1 Organic hexaniobate and hexatantalate salts reported in the literature

Compound	Synthetic method	Ref.
TMA ₈ [Nb ₆ O ₁₉]·15H ₂ O	Nb ₂ O ₅ · <i>n</i> H ₂ O reacted with TMAOH·5H ₂ O in ethanol at 120 °C for 18 h. Product precipitated with acetone.	26
TMA ₅ [H ₃ Nb ₆ O ₁₉]·20H ₂ O	Nb ₂ O ₅ · <i>n</i> H ₂ O dissolved in 2.8 M TMAOH at 90 °C. Product precipitated and washed with isopropanol.	27
TBA ₄ [H ₄ Nb ₆ O ₁₉]·7H ₂ O	K ₇ HNB ₆ O ₁₉ ·13H ₂ O solution acidified with HCl. Precipitate recovered, dried and reacted with 0.4 M TBAOH at 80 °C for 24 h. Recrystallized in THF–ethanol.	28
TMA ₆ [H ₂ Ta ₆ O ₁₉]·21H ₂ O	(NH ₄) ₃ Ta(O ₂) ₄ reacted with 1.4 M TMAOH (reflux, 5 h). Product extracted and washed with isopropanol	27
TBA ₆ [H ₂ Ta ₆ O ₁₉]·10H ₂ O	K ₈ Ta ₆ O ₁₉ ·17H ₂ O solution acidified with HCl. Precipitate recovered and reacted with 10% TBAOH at 85 °C for 43 h. Recrystallized in toluene–ethanol.	29
TBA _{3.5} [H _{4.5} (Ta ₆ O ₁₉)]·2THF·5.5H ₂ O	K ₈ Ta ₆ O ₁₉ ·17H ₂ O solution acidified with HCl. Precipitate recovered and reacted with 10% TBAOH at 90 °C for 72 h then evaporated to dryness under vacuum. Solid dried and reacted with toluene (85 °C, 16 h). Recrystallized in THF–ethanol.	30

species. For example, alkaline earth ions, although non-hydrolyzed at a basic pH, form very insoluble precipitates with hexaniobate and hexatantalate ions.²¹ Few aqueous hexatantalate and hexaniobate complexes with ruthenium have also been recently reported.^{22,23} The unusually high alkalinity required to form and stabilize the hexaniobate and hexatantalate ions also prevent their interaction in aqueous solutions with other polyoxometalates, like those of tungsten and molybdenum, which only exist in acidic media.²⁴ This has limited the studies on hexaniobate (and hexatantalate) chemistry to a narrow pH-range and mainly to their interactions with alkali cations.

Surprisingly, the chemistry of polyoxoniobates in organic solvents is still largely unexplored. Whereas the hexaniobate ions are unable to interact with the simplest ammonium ion, *i.e.*, NH₄⁺, in aqueous solutions due to a pH mismatch, few quaternary ammonium salts of hexaniobate (and their hexatantalate analogues) have been isolated during the past decades (Table 1). The synthesis procedures to obtain such organic–inorganic polyoxometalate salts are rather long, necessitate several steps and are not quantitative. Nonetheless, the synthesis of tetramethylammonium (TMA⁺) and tetrabutylammonium (TBA⁺) salts of hexaniobate ions seems to be a privileged route to obtain organic systems containing H_xM₆O₁₉^{x–8} (M = Nb, Ta) ions to date. In 2000, Zhou and Tokuda²⁵ also investigated the liquid–liquid extraction of Nb(v) from KOH/KCl alkaline solutions (6.6 < pH < 13.6) with methyltrioctylammonium chloride diluted in toluene. Although highly speculative and rather qualitative, the report from Zhou and Tokuda offered a glimpse into another option for stabilizing polyoxoniobates in organic solvents.

In fact, the liquid–liquid extraction of Nb(v) from basic media has been overlooked since the emergence of polyoxoniobate chemistry and the work from Zhou and Tokuda has been the only study on this topic so far. Based on the recent report of the short-chain quaternary ammonium salts of H_xNb₆O₁₉^{x–8} (Table 1) and inspired by the pioneer work from Zhou and Tokuda, we developed a fast and efficient liquid–liquid extraction system containing long-chain quaternary ammonium salts, which is able to extract and stabilize hexaniobate ions in organic solvents. More specifically, the physico-chemistry of the extraction of hexaniobate ions by the commercial extractant

Aliquat® 336 was investigated and put in perspective with recent studies on Nb speciation in alkaline media. The influence of several parameters on the extraction of niobates, including the pH, the extractant concentration in the organic phase and the presence of cations (Li⁺, Na⁺, K⁺ and Cs⁺) and anions (NO₃[–], Cl[–], C₂O₄^{2–}, SO₄^{2–} and CO₃^{2–}) in the aqueous phase was also studied. The proposed system affords straightforward access to hexaniobate organic solutions and paves the way for innovative hydrometallurgical processes for niobium and possibly new reaction schemes using polyoxoniobates in organic solvents.

Experimental section

Materials

All aqueous stock solutions were prepared with deionized water (*R* > 18.2 Mohm). Nb₂O₅ (99.9%, Sigma Aldrich), NbCl₅ (99%, Alfa Aesar), LiCl (>99%, Fluka), NaCl (>99.5%, Prolabo Normapur), KCl (>99.5%, Prolabo Normapur), CsCl (>99%, Sigma Aldrich), LiOH·H₂O (>98%, Sigma Aldrich), NaNO₃ (>99%, Sigma Aldrich), Na₂C₂O₄ (>99.5%, Sigma Aldrich), Na₂CO₃ (>99.5%, Sigma Aldrich) and Na₂SO₄ (>99.5%, Sigma Aldrich) were used without further purification. NaOH solutions (Prolabo Normadose) and KOH solutions (Alfa Aesar, Selectipur®) were prepared from standardized solutions. An AgNO₃ standard solution (VWR, Titrimorm®) was used for chloride titrations. Na₇HNB₆O₁₉·15H₂O, K₈Nb₆O₁₉·16H₂O and Na₈Ta₆O₁₉·24.5H₂O were synthesized starting from Nb₂O₅ and NbCl₅, respectively, as previously reported.^{15,31} Li₈Nb₆O₁₉·15.5H₂O and Cs₈Nb₆O₁₉·14H₂O were synthesized from literature methods.^{19,20} Stock solutions of Nb and Ta were prepared by direct dissolution of their hexametallate salts in Milli-Q water (final pH ~ 11–12). Aliquots of the stocks were taken to prepare the aqueous samples in the studied media (10.5 ≤ pH ≤ 13.0). Methyltrioctylammonium bromide (≥97%) was purchased from VWR. Methyltrioctylammonium chloride (≥97%) and Aliquat® 336 were purchased from Sigma Aldrich. Aliquat® 336 is a mixture of methyltrioctylammonium, methylodioctyldecylammonium, methyloctyldidecylammonium and methyltridecylammonium chloride, the major component

being methyltrioctylammonium chloride.^{32,33} Elixore 205 (Total Special Fluids) modified with 1% (v/v) isotridecanol (BASF) was used as a diluent in all liquid–liquid extraction experiments.

Elixore 205 is a 100% aliphatic diluent with a flash point and boiling point equal to 75 °C and 201–234 °C, respectively.

Methods

Nb and Ta concentrations were determined by ICP-OES using an iCAP 6000 series spectrometer (Thermo Scientific). The samples were diluted in 2% HNO₃ containing 0.7% H₂O₂. Quantitative analyses of Nb and Ta were performed at the 309.418 nm and 240.063 nm spectral emission lines, respectively. Nb concentrations were also confirmed by UV-vis spectroscopy using a recently reported method.¹⁰ All UV spectra were measured on a Cary 100-Scan spectrophotometer in double beam mode. pH measurements were performed with an 827 pH-lab (Metrohm) pH-meter and a low alkaline error combined electrode (Unitrode, Metrohm). The pH-meter was calibrated with standards at pH 4.01, 7.00 and 12.00 (Mettler Toledo). Water contents in the organic phase were determined using a Mettler Toledo V20 volumetric Karl–Fisher titration device filled with the Hydranal®-Composite 5 reagent. Water titrations were performed in anhydrous methanol. Chloride ions released in the aqueous phase by Aliquat® 336 were titrated by the classical argentometric method. Solution-state ²³Na NMR spectra were acquired on a Bruker Advance 400 MHz spectrometer. ²³Na NMR spectra were referenced to a 1.0 M NaCl aqueous solution.

Solvent extraction procedures

All organic phases containing the long-chain quaternary ammonium salts were prepared by direct dissolution of the ammonium salt in Elixore 205 modified with 1% (v/v) isotridecanol. Due to the high viscosity of the ammonium salts, the solvents were stirred for at least 30 min to ensure complete dissolution prior to the extraction tests. The concentrations of ammonium ions were calculated using the mass introduced (accuracy of 0.1 mg) in the system, the density, the molecular weight (442 g mol⁻¹) and purity provided by the manufacturers. In order to facilitate the phase separation after liquid–liquid extraction, 1% (v/v) of isotridecanol was added in the initial organic phases. Tests with and without isotridecanol showed that it has no effect on the extraction yield of Nb. Tests in the presence of isotridecanol and without ammonium salt also showed that isotridecanol does not extract Nb. Typically, 5 mL of an aqueous phase containing the polyoxometalate ions, the background electrolyte and a given volume of the organic phase (ammonium salt in diluent) were placed in a 15 mL polypropylene tube (BD Falcon™). The biphasic samples were then shaken for 30 min at 25 (±0.5) °C in a thermostated shaker (VTO 500, Gerhardt). Preliminary tests showed that the metal extractions reach a steady state in less than 10 min. Phase separations were accomplished in a separating funnel. Fast phase separation was obtained and no precipitation was observed.

Metal extraction yields were calculated as follows:

$$\% \text{Ext}(\text{M}) = \frac{[\overline{\text{M}}]_{\text{eq}} \times V_{\text{org}}}{[\text{M}]_{\text{ini}} \times V_{\text{aq}}} \times 100 \quad (1)$$

$$\% \text{Ext}(\text{M}) = \frac{[\text{M}]_{\text{ini}} - [\text{M}]_{\text{eq}}}{[\text{M}]_{\text{ini}}} \times 100 \quad (2)$$

[M]_{ini} and [M]_{eq} denote the concentration of M in the initial aqueous phase and in the aqueous phase at equilibrium, respectively. $\overline{[\text{M}]_{\text{eq}}}$ denotes the concentration of M in the organic phase at equilibrium. V_{aq} and V_{org} are the volumes of the aqueous phase and the organic phase, respectively.

The distribution coefficients of metals are defined as follows:

$$D_{\text{M}} = \frac{\overline{[\text{M}]_{\text{eq}}}}{[\text{M}]_{\text{eq}}} \quad (3)$$

Results and discussion

The extraction of hexaniobate ions from alkaline solution was first tested using Aliquat® 336 as the extractant. This commercially available compound is a mixture of methyltrioctylammonium, methyldioctyldecylammonium, methyl-octyldidecylammonium and methyltridecylammonium chloride, the major component being methyltrioctylammonium chloride.^{32,33}

Fig. 1 gives the Nb extraction yield for aqueous solutions of Na₇HNb₆O₁₉·15H₂O containing different concentrations of NaCl. At pH 12, which is the natural pH for a hexaniobate ion solution, gram-scale quantities of Nb(v) can be extracted into the organic phase which was composed of Aliquat® 336

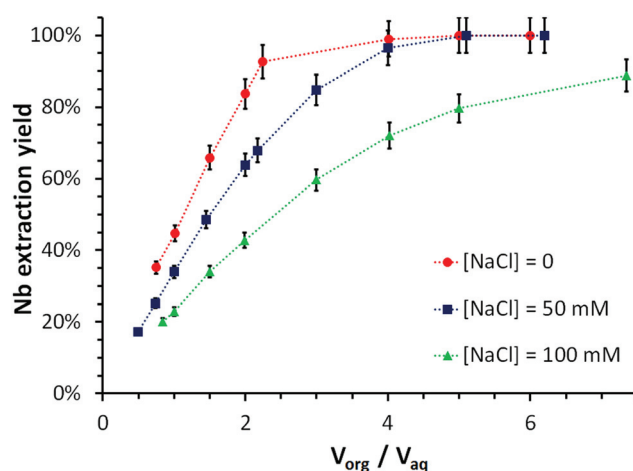


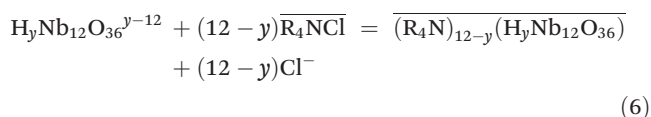
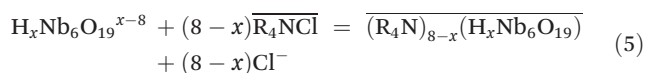
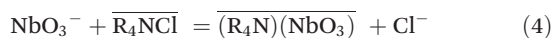
Fig. 1 Extraction yields measured for Nb as a function of the volume phase ratio. Organic phase: 8.84 mM Aliquat® 336 diluted in Elixore 205 + 1% (v/v) isotridecanol. Initial aqueous phase: 3 mM Na₇HNb₆O₁₉·15H₂O. Background electrolyte: 10 mM NaOH + 0 (circles), 50 (squares) or 100 mM (triangles) NaCl. Extraction: 1 contact, *t* = 30 min, *T* = 25 °C, pH_{eq} = 11.9 ± 0.1. Error bars: ± 5%.

diluted in an aliphatic diluent (Elixore 205). Preliminary tests with an aromatic diluent (toluene) showed that hexaniobates can also be quantitatively extracted in such diluents. As expected, similar results were obtained when replacing Aliquat® 336 with pure methyltrioctylammonium chloride (Table S1†). Extraction experiments realized with methyltrioctylammonium bromide or sulfate, carbonate and hydroxide derivatives of Aliquat® 336 showed very high extraction yields for niobium (Table S1†). Likewise, very high extraction yields were also obtained for corresponding hexatantalate ions using Aliquat® 336 (Fig. S1†). Consequently, with only one contact of a few minutes at room temperature between the two phases, polyoxoniobate (or polyoxotantalate) ions can be transferred into an organic solvent. The reaction is also quantitative, depending on the volume ratio between the organic and aqueous layers, and it mainly depends on the concentration of the extractant used in the system as detailed below. The liquid–liquid extraction of hexaniobate ions using quaternary ammonium extractants therefore affords simple and direct access to organic solutions of polyoxoniobates.

Moreover, the extraction of Nb (and Ta) from alkaline media represents a cleaner alternative when compared to traditional extraction processes that require fluoride-based aqueous solutions and a pure methylisobutyl ketone as the extractant.^{1–4} The metal concentration range used in the present study is also relevant with the hydrometallurgical processes operated in sodium-based alkaline media which are currently developed by the Nb and Ta industry.³⁴ Higher metal concentrations in the organic phase can also be obtained by increasing the extractant concentration and using a more soluble salt in the aqueous phase such as potassium, rubidium or cesium hexaniobate.¹⁹

The extraction yield of $H_xNb_6O_{19}^{x-8}$ ions decreases when the concentration of chloride ions in the initial aqueous phase increases as expected for an ion exchange mechanism (Fig. 1). Furthermore, the anion exchange mechanism was confirmed by analyzing the chloride ions released into the aqueous phase by the quaternary ammonium salt upon extraction of niobium (Fig. S2†).

As mentioned above, Zhou and Tokuda²⁵ investigated the extraction of Nb(v) from alkaline solutions (KCl/KOH from pH 6.6 to 13.6 and an ionic strength of 50 to 200 mM) using methyltrioctylammonium chloride diluted in toluene. In order to explain their extraction data, Zhou and Tokuda used the slope analysis method and proposed the following three extraction equilibria assuming an anion-exchange mechanism:



Overbars refer to species in the organic phase and the absence of an overbar denotes aqueous species. R_4NCl stands for a quaternary ammonium chloride salt, here methyltrioctylammonium chloride.

However, reactions (4) and (6) are highly speculative as far as the extraction of Nb(v) from alkaline media is concerned because it is now well established that the speciation of Nb(v) in alkaline media is dominated by $H_xNb_6O_{19}^{x-8}$ ions.^{16,19,35–37} The species NbO_3^- is a hypothetical species which was mentioned in few solubility studies^{38,39} in order to model the solubility curves of Nb_2O_5 or $Nb_2O_5 \cdot nH_2O$, but this species has never been characterized experimentally and is not likely to exist in the concentration range typically encountered in liquid–liquid extraction experiments. The existence of the dodecameric ions, $H_yNb_{12}O_{36}^{y-12}$ ($2 \leq x \leq 6$), have been reported in pioneer studies but under peculiar conditions, such as after the very slow acidification of hexaniobate solutions to a pH lower than 8.^{40–42}

Conversely, as mentioned above, several studies confirmed the predominance of $H_xNb_6O_{19}^{x-8}$ in alkaline solutions. Equilibria involving hexaniobates and other minor species which would be more extractible cannot be excluded, but given the current knowledge on polyoxoniobate chemistry, the extraction of hexaniobates seems the most likely mechanism at a pH higher than ~ 10 . Therefore, reaction (5) can be considered to be a rational basis to describe the extraction of Nb(v) with methyltrioctylammonium chloride from alkaline media. Furthermore, reaction (5) is supported by a series of previous studies that describe the synthesis and isolation of tetramethylammonium (TMA^+) and tetrabutylammonium (TBA^+) salts of hexaniobates and hexatantalates (Table 1).

Considering reaction (5), its associated equilibrium constant K_{ext} expressed in terms of concentrations (eqn (7)) and assuming that $H_xNb_6O_{19}^{x-8}$ ions are predominant in the range of working pH and concentration, the logarithm of the distribution ratio of Nb(v), $\log D_{Nb}$, should be given by eqn (8):

$$K_{ext} = \frac{[\overline{(R_4N)_{8-x}(H_xNb_6O_{19})}] \times [Cl^-]^{8-x}}{[H_xNb_6O_{19}^{x-8}] \times [R_4NCl]^{8-x}} \quad (7)$$

$$\log D_{Nb} = \log K_{ext} - (8-x)\log[Cl^-] + (8-x)\log[\overline{R_4NCl}] \quad (8)$$

R_4NCl denotes the extractant, *i.e.*, a quaternary ammonium chloride (for example Aliquat® 336) and D_{Nb} is given by the following equation:

$$D_{Nb} = \frac{[\overline{Nb}]}{[Nb]} = \frac{[\overline{(R_4N)_{8-x}(H_xNb_6O_{19})}]}{[H_xNb_6O_{19}^{x-8}]} \quad (9)$$

In the present work, the influence of several parameters on the distribution ratio of Nb(v) has been investigated using Aliquat® 336 as the extractant. Fig. 2 gives the variation of the decimal logarithm of D_{Nb} versus one of the concentrations of the free extractant at equilibrium, under various conditions of the ionic strength and initial concentration of Nb. As shown in

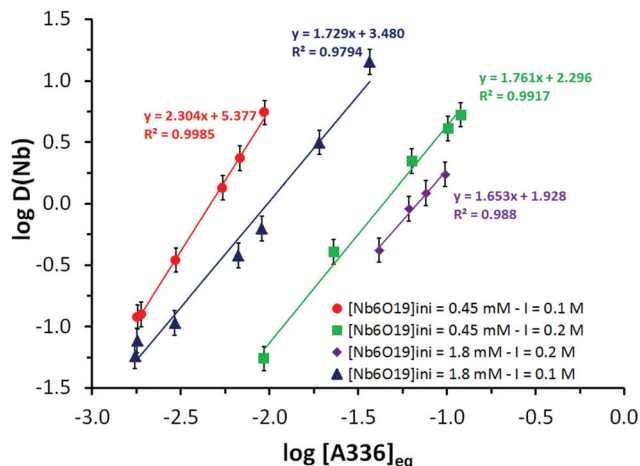


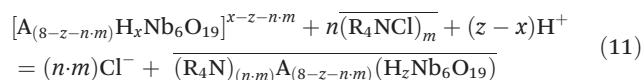
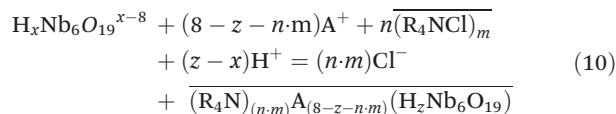
Fig. 2 Variation of $\log D_{\text{Nb}}$ versus $\log [\overline{\text{R}_4\text{NCl}}]_{\text{eq}}$. $[\overline{\text{R}_4\text{NCl}}]$ denotes the Aliquat® 336 concentration at the equilibrium, i.e., $[\overline{\text{R}_4\text{NCl}}] = [\text{R}_4\text{NCl}]_{\text{ini}} - \text{slope} \times [\text{Nb}_6\text{O}_{19}]_{\text{eq}}$. Initial conditions in the aqueous phase: 0.45 mM $\text{Na}_7\text{HNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$, 10 mM NaOH, 90 mM NaCl (circles); 1.80 mM $\text{Na}_7\text{HNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$, 10 mM NaOH, 90 mM NaCl (triangles); 0.45 mM $\text{Na}_7\text{HNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$, 10 mM NaOH, 190 mM NaCl (squares); 1.80 mM $\text{Na}_7\text{HNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$, 10 mM NaOH, 190 mM NaCl (diamonds). Solvent: Aliquat® 336 diluted in Elixore 205 + isotridecanol 1% (v/v). Extraction: 1 contact, $t = 30$ min, $T = 25$ °C, phase volume ratio O/A, $\text{pH}_{\text{eq}} = 11.9 \pm 0.1$. Error bars: $\pm 5\%$.

Fig. 2, $\log D_{\text{Nb}}$ is proportional to $\log [\overline{\text{R}_4\text{NCl}}]_{\text{eq}}$, with slopes ranging from 1.6 to 2.3. Taking into account the reported pK_a 's of $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ (9.37 ± 0.03 , 10.6 ± 0.5 and 13.6 ± 0.2 for $x = 3$, 2 and 1, respectively³¹) and the pH used for the extraction experiments ($\text{pH} = 12$), the mono-protonated species $\text{HNb}_6\text{O}_{19}^{7-}$ is expected to be the major species in the aqueous solutions. Therefore, the slope derived from eqn (8), suggested by Zhou and Tokuda,²⁵ should be close to 7.0, which is in clear disagreement with the results obtained and suggests a different equilibrium for the extraction of $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ with the quaternary ammonium extractants.

The physico-chemistry of the present extraction system is much more complex than that represented by the sole reaction (5), even if the latter is of interest in describing the mechanism of anion exchange which is at the origin of the extraction of Nb(v). Among the phenomena which may take place in parallel with the aforementioned anion exchange reaction, one can identify: (i) the formation of ion pairs between hexaniobate anions and alkali cations (Li^+ , Na^+ , K^+ , Cs^+) in the aqueous phase^{31,37,43,44} with possible co-extraction of such alkali cations; (ii) a possible change of the degree of protonation of $\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$ during the extraction process; (iii) the self-association of the extractant in the organic phase; (iv) the possible extraction of the hydroxide ions with R_4NCl in the higher range of the investigated pH and subsequent competition with the extraction of the hexaniobate ions; and (v) the possible co-extraction of water molecules.

By taking into account the first three phenomena above, reaction (5) can be replaced by a series of generalized reactions such as reaction (10) (without alkali-hexaniobate ion-pairing)

and reaction (11) (with ion-pairing), given here for the sake of illustration:



With $0 \leq x \leq 3$, $0 \leq z \leq 7$, $1 \leq n\cdot m \leq 8$. A^+ denotes an alkali ion.

Examination of reactions (10) or (11) shows that up to 36 different species could be formed in the organic phase when considering that the Nb extracted species can contain between 0 and 7 protons, 0 and 7 Na^+ , and 1 and 8 extractant molecules. The high number of possible extracted species is a consequence of the exceptionally high negative charge of the hexaniobate ions (up to 8-), which gives a high degree of freedom to the system compared to those classically encountered in liquid-liquid extraction of metal ions. This can also be put in perspective with the numerous hexaniobate salts that can be isolated in the solid-state.⁹ The reactions mentioned above underline the complexity of the extraction of polyoxoniobate ions, even if only some extracted species may dominate the mass transfer process. Some features of the above phenomena are discussed in more detail hereafter.

Self-association of Aliquat® 336

Hydrophobic tetraalkylammonium salts R_4NX , including Aliquat® 336, exhibit strong surface active properties which can lead to the formation of micelles. Such a system has been extensively investigated for the solubilization/extraction of enzymes, proteins, *etc.* For instance, it has been shown that Aliquat® 336 decreases the interfacial tension when its concentration exceeds 10^{-5} M in bi-phasic systems containing isopropylmyristate and a 50 mM aqueous solution of phosphate-borax buffer at pH 9, and its critical micellar concentration (CMC) was found to be equal to 2.5×10^{-3} M.⁴⁵ In another liquid-liquid system containing 4.0×10^{-2} M Aliquat® 336 in isooctane modified with isotridecanol (between 0.4 and 5%) and 25 mM aqueous borax buffer, it was found that a significant amount of water was extracted in the organic phase, which is an indication of the formation of reverse micelles, and the amount of water decreased from 7.9 to 2.8 g L^{-1} when the concentration of isotridecanol was increased from 0.4 to 5% (v/v). The formation of reversed micelles was also observed and their hydrodynamic radius was determined to be 2.2 nm with a water core of about 1.7 nm.⁴⁵ In an isooctane diluent containing 1% (v/v) of isotridecanol, the concentration of water extracted with Aliquat® 336 was found to equal 6.1 g L^{-1} , corresponding to a molar ratio of water to Aliquat® 336 in the organic phase, w_o , of 8.5. From the data published by Jolival *et al.*,⁴⁵ it can be calculated that the reverse micelles formed by using Aliquat® 336 in isooctane modified with 1% (v/v) isotridecanol in equilibrium with 2.5 mM borax buffer ($\text{pH} = 9$)

contain about 25 molecules of the surfactant (*i.e.*, $m = 25$ in reactions (10) and (11)).

Fig. 3 displays the concentration of water co-extracted with Nb(v) in the organic phase for two different concentrations of Aliquat® 336. A linear relationship was found between the concentration of extracted hexaniobate and the water content of the organic phase, meaning that the Nb species in the organic phase contain water molecules. The slopes given in Fig. 3 give a molar ratio $\text{H}_2\text{O}/\text{Nb}_6\text{O}_{19}$ between 44 and 51. It is of interest that the concentration of water extracted in the organic phase extrapolated in the absence of niobium is equal to 2.1 mM and 22.0 mM, for 1.84 and 5.67 mM Aliquat® 336, respectively.

This corresponds to a global molar ratio w_o of water to Aliquat® 336 in the organic phase to be about 1 and 4, respectively. Compared to the values of w_o previously reported at a higher concentration of Aliquat® 336 (*e.g.*, $w_o = 8.5$ for 40 mM Aliquat® 336 in isoctane modified by 1% isotridecanol⁴⁵), the values of 1 and 4 found here for w_o suggest that the micellar structure is not yet fully developed under the conditions of Fig. 3. This is supported by the conclusions of Sawada *et al.*⁴⁶ that tetraalkylammonium salts (RX with $\text{R} = (\text{C}_n\text{H}_{2n+1})_4\text{N}^+$ and $n = 5-8$ or $(\text{C}_8\text{H}_{17})_3(\text{CH}_3)\text{N}^+$ and with $\text{X} = \text{Cl}^-$, Br^- , BF_4^- , ClO_4^- , NO_3^- or SCN^-) diluted in xylene and equilibrated with water form an ion-pair $[\text{R}^+, \text{X}^-]$ partially dimerized as $[\text{R}^+, \text{X}^-]_2$. The dimerization constant of methyltrioctylammonium chloride (the main component of Aliquat® 336) in xylene equilibrated with water was reported as equal to $4.6 \times 10^2 \text{ mol}^{-1} \text{ L}$. This physical model was also found to apply up to 10^{-2} M Aliquat® 336 under its chloride form, *i.e.*, for an extractant concentration range broader than the one investigated here.

From the above considerations, it clearly appears that Aliquat® 336 cannot be considered as monomeric in the organic phase as suggested by reaction (5). More likely,

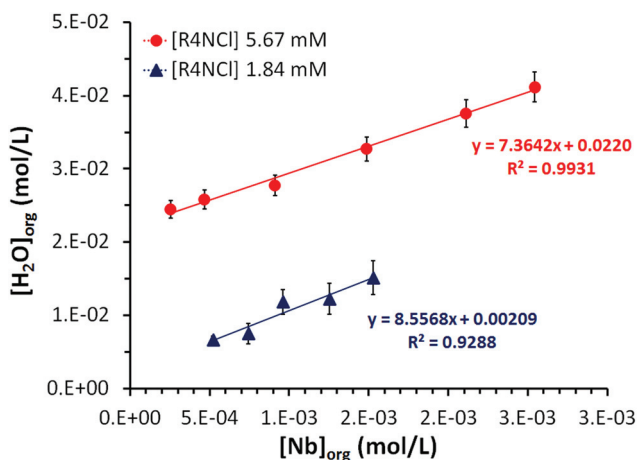
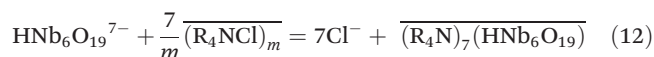


Fig. 3 H_2O concentration measured in the organic phase at equilibrium after bringing in contact with an aqueous solution initially containing 0.45 mM of $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ and 10 mM NaOH. Organic phase: 5.67 mM (circles) or 1.84 mM (triangles) Aliquat® 336 diluted in Elixore 205 + 1% (v/v) isotridecanol. Error bars correspond to the standard deviation obtained from triplicate measurements. Extraction conditions: 1 contact, $V_{\text{org}}/V_{\text{aq}} = 1$, $t = 30 \text{ min}$, $\text{pH}_{\text{eq}} = 11.9 \pm 0.1$, $T = 25 \text{ }^\circ\text{C}$.

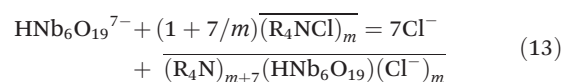
Aliquat® 336 aggregates progressively as its concentration increases, leading to a full micellar structure above a certain concentration which depends on various factors, including the nature of the diluent, the nature and concentration of the phase modifier, the presence and concentration of the electrolyte in the aqueous phase, *etc.* Thus, reactions (10) and (11) may describe in reality various situations, where $(\text{R}_4\text{NCl})_m$ represents small aggregates ($m = 2, 3 \dots$) for the lowest concentrations of the extractant investigated in Fig. 2 and much larger reverse micelles ($m = \text{about } 20 \text{ or higher}$) for the highest concentrations of the extractant. If reaction (10) is rewritten in its simplest form, ignoring temporarily phenomena (i), (ii), (iv) and (v) described above, one may obtain:

- At a low Aliquat® 336 concentration where the micellar structure is not yet developed:



With $m = 3$ on average to explain the slope 2.3 observed in Fig. 2.

- At a much higher Aliquat® 336 concentration where the micellar structure is fully developed:



where $m = \text{about } 12-15$ to explain the slope of 1.6 observed in Fig. 2.

Reaction (13) assumes that the extracted $\text{HNb}_6\text{O}_{19}^{7-}$ ion is located inside the micelles $(\text{R}_4\text{NCl})_m$ which may have a tendency to enlarge to host Nb(v) and the water molecules co-extracted with it (Fig. 3). This geometry seems likely due to the sphere-like shape of the hexaniobate ions³⁷ which could favor such organization. The formation of reverse micelles upon extraction of heteropolytungstate anions with tetraalkylammoniums in organic solvents has been previously suggested.⁴⁷ Obviously, the above considerations, regarding hexaniobates, need further evidence to be ascertained, although they are in agreement with the conclusions of Wionczyk and Apostoluk.⁴⁸ They also underline the importance of quaternary ammonium aggregation in the understanding of the niobium extraction mechanism from alkaline media, even if other phenomena, such as (i), (ii) and (iv) evocated above, deserve to be considered.

Influence of cations on the background electrolyte

The co-extraction of alkali ions with hexaniobates into the organic phase, as suggested by reactions (10) and (11), was probed by ^{23}Na NMR since this non-invasive method affords direct evidence of the presence of the targeted element in the sample.

The ^{23}Na NMR spectra given in Fig. 4 confirmed the presence of Na^+ ions in the organic phase after contacting it with an aqueous solution of $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$. Usually, the ^{23}Na chemical shift is very sensitive to the interactions between sodium ions and anions or solvent molecules (contact and

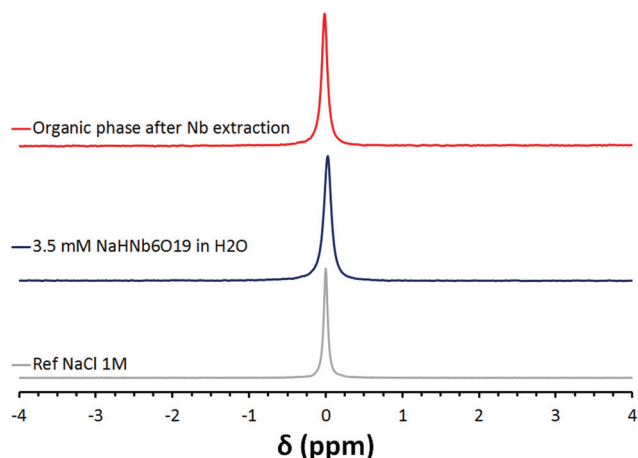


Fig. 4 ^{23}Na NMR spectra of the organic phase after bringing in contact with an aqueous solution of $\text{Na}_7\text{HNB}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (top). Organic phase: 36 mM Aliquat® 336 + isotridecanol 1% (v/v) + Elixore 205 (diluent); $[\text{Nb}_6\text{O}_{19}] = 1.7$ mM. For comparison purpose, the ^{23}Na NMR spectra of a 3.5 mM $\text{Na}_7\text{HNB}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ aqueous solution before extraction (middle) and that of an aqueous solution of 1 M NaCl (bottom) are also reported.

separated ion-pairs, solvation, *etc.*^{49,50}). In the case of the hexaniobate–Aliquat® 336 system, it was observed that the co-extracted Na^+ ions exhibit a ^{23}Na chemical shift identical to that of the aqueous solutions of $\text{Na}_7\text{HNB}_6\text{O}_{19}$ or NaCl (Fig. 4).

This suggests that the Na^+ ions are weakly coordinated to the hexaniobate ions in the organic phase. Such a conclusion is in accordance with the stability of the alkali–hexaniobate ion-pairs observed in the aqueous systems, which follows the following trend: $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.^{31,37,43} The influence of alkali ions on the extraction of hexaniobate ions was further investigated in lithium-, potassium- and cesium-based media, taking the sodium hexaniobate system as a reference.

Fig. 5 shows that the nature of the cations in the aqueous phase also strongly influences the distribution ratio of Nb. For a given chloride ion concentration, an increase of the K^+/Na^+ or Cs^+/Na^+ ratio is responsible for a decrease in the distribution ratio of Nb between the organic and aqueous phases. The effect is also higher in the case of Cs^+ ions than that in K^+ ions. Extraction experiments with $\text{Li}_8\text{Nb}_6\text{O}_{19}\cdot 15.5\text{H}_2\text{O}$, $\text{Na}_7\text{HNB}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ and $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ dissolved in LiOH/LiCl, NaOH/NaCl and KOH/KCl aqueous solutions, respectively, have also been performed. By bringing these mono-alkali solutions in contact with 4 mM Aliquat® 336 diluted in Elixore 205 modified with 1% (v/v) isotridecanol yielded Nb extraction efficiencies of 94.4%, 90.7% and 89.5% in the presence of Li^+ , Na^+ and K^+ , respectively (Table S2†), thus confirming the trend given in Fig. 5. Consequently, the best extraction yields for hexaniobates are obtained in Li-based media even if the other alkali-based systems exhibit high extraction efficiencies.

The effect of the nature of the alkali ions on the distribution ratio of Nb can be explained by two intrinsically linked phenomena. On the one hand, the results given in Fig. 5 suggest that the formation of the ion-pairs in the aqueous

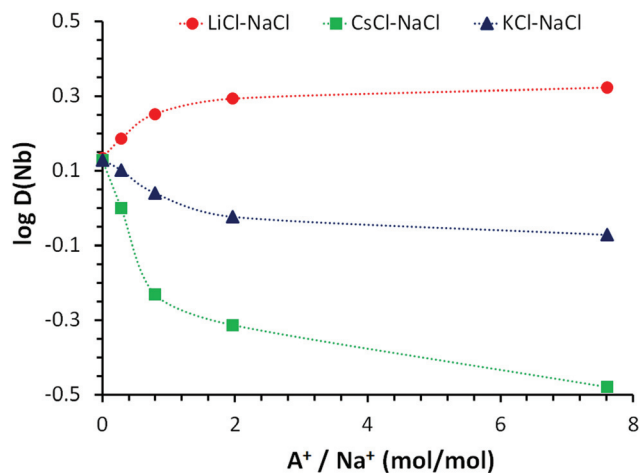


Fig. 5 Influence of the nature of the alkali cation on the extraction of Nb. Organic phase: 5.4 mM Aliquat® 336 diluted in Elixore 205 + 1% (v/v) isotridecanol. Initial aqueous phase: 0.45 mM $\text{Na}_7\text{HNB}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$, 10 mM NaOH + LiCl/NaCl (circles) or KCl/NaCl (triangles) or CsCl/NaCl (squares). $[\text{Cl}]_{\text{total}} = 100$ mM. Extraction: 1 contact, $V_{\text{org}}/V_{\text{aq}} = 1$, $\text{pH}_{\text{eq}} = 11.9 \pm 0.1$, $t = 30$ min, $T = 25$ °C.

phase ($[\text{Cs}_y\text{H}_x\text{Nb}_6\text{O}_{19}]^{x+y-8}$ and $[\text{K}_y\text{H}_x\text{Nb}_6\text{O}_{19}]^{x+y-8}$) competes with the extraction of the ion-pairs or of the bare cluster ($\text{H}_x\text{Nb}_6\text{O}_{19}^{x-8}$) into the organic layer. Conversely, the extraction of hexaniobates is exalted in the presence of Li^+ ions, and since the association lithium–hexaniobate is known to be weak,^{37,43} this suggests that the extraction of the bare cluster is predominant over the extraction of the ion-pairs itself. Extraction experiments performed until the solvent was saturated in sodium hexaniobates (Fig. S3†) yielded a molar ratio Aliquat® 336/ Nb_6O_{19} in the organic phase of 6.74 (± 0.34). Taking into account that the hexaniobate is mono-protonated at pH 12,^{10,17} these results correspond, in average, to the extraction of 0.3 sodium ion per cluster. Even if the results were obtained at solvent saturation, they indicate that the extracted species have, in average, a low alkali/cluster ratio. Therefore, the important effect of the nature of the alkali ions on the extraction yield of Nb (Fig. 5) seems primarily due the alkali–hexaniobate association in the aqueous phase which competes with the extraction of species exhibiting a low alkali/hexaniobate ratio.

On the other hand, the strength of the interactions between the alkali ions and hexaniobates can potentially modify the protonation state of the cluster. Indeed, the strong association with Cs^+ or K^+ ^{8,19,27,37} is susceptible to remove the last proton of $\text{HNB}_6\text{O}_{19}^{7-}$ (major species at the studied pH in Na^+ media) yielding a cluster of a higher charge and more difficult to extract. Modification of the pK_a of $\text{HNB}_6\text{O}_{19}^{7-}$ in K^+ media compared to Na^+ media has also been reported elsewhere.¹⁰ Hence, the extraction of hexaniobate ions may be considered as a balance between (i) association with alkali ions in aqueous solution, (ii) extraction of the ion-pairs and (iii) extraction of the bare cluster. These phenomena are summarized in eqn (10) and (11).

Influence of anions in the background electrolyte

The influence of the anions present in the aqueous phase in the extraction of Nb by using Aliquat® 336 has also been investigated. Indeed, Aliquat® 336 is an anionic exchanger and the anions present in the system may compete against the extraction of polyoxoanions $H_xNb_6O_{19}^{x-8}$.

Fig. 6 gives the influence of the carbonate, sulfate, oxalate, chloride and nitrate concentrations in the aqueous phase on the extraction efficiency of hexaniobates. The nitrate ions have the most negative effect on the extraction of Nb with an extraction yield dropping to 0 in the presence of 0.05 M $NaNO_3$. For a given concentration, the influence of the anions in the aqueous phase follows the order $NO_3^- > Cl^- \gg C_2O_4^{2-} \sim SO_4^{2-} > CO_3^{2-}$. Such a trend is due to the affinity of the extractant for these anions, as already noted in the case of the extraction of Cr(vi) from acidic solutions with organic solutions of Aliquat® 336.⁵¹ The results depicted in Fig. 6 also highlight the high affinity of Aliquat® 336 for the hexaniobate ions compared to the other anions since, in these experiments, the concentration ratio of anions/hexaniobates was really high (up to 330 equivalents).

The competitive extraction between hexaniobate ions and other common anions can be of interest for designing hydrometallurgical processes where Nb has to be back extracted in an aqueous media. Extraction and back-extraction procedures could also be implemented for exchanging the alkali ions surrounding the hexaniobates. For example, it is known that sodium and potassium hexaniobate salts are easier and cheaper to synthesize than the other alkali or quaternary ammonium salts.^{9,18,19} Using the liquid-liquid extraction system described in this study, a sodium or potassium hexaniobate solution could be extracted and then back-extracted with high yields in alkali nitrate- or chloride-based media.

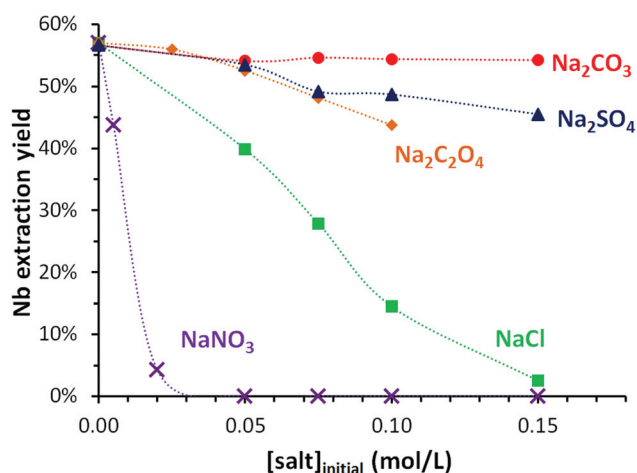


Fig. 6 Influence of the background electrolyte of the aqueous phase on the extraction of Nb. Organic phase: 1.8 mM Aliquat® 336 diluted in Elixore 205 + 1% (v/v) isotridecanol. Initial aqueous phase: 0.45 mM $Na_7H_9Nb_6O_{19} \cdot 15H_2O$, 10 mM NaOH + $NaNO_3$ (crosses), NaCl (squares), $Na_2C_2O_4$ (diamonds), Na_2SO_4 (triangles) or Na_2CO_3 (circles). Extraction: 1 contact, $V_{org}/V_{aq} = 1$, $pH_{eq} = 11.9 \pm 0.1$, $t = 30$ min, $T = 25$ °C.

Moreover, the back extraction step could be performed at high pH, as discussed below.

Influence of pH

The pH of the aqueous phase was also found to influence the extraction of hexaniobates by using quaternary ammonium salts as illustrated in Fig. 7.

The extraction of $H_xNb_6O_{19}^{x-8}$ decreased from 80% to 58% when the pH was increased from 10.8 to 12.9 at a constant concentration of sodium and chloride ions. The highest extraction yields for Nb are therefore obtained at lower pH values, although, for processes requiring a high pH, increasing the extractant concentration may compensate for the decrease in the extraction yield at high alkalinity. The decrease in extraction efficiency with the increasing pH was also observed in the case of the extraction of Cr(III) from alkaline media (*i.e.*, 0.1 to 0.5 M NaOH) with Aliquat® 336.⁴⁸

The authors interpreted such an effect as a result of an increase in the ionic strength due to the change of the $NaOH_{(aq)}$ concentration from 0.1 to 0.5 M, but have not considered the possible competitive extraction of hydroxides against Cr(III) anions. Variations in Nb extraction with a varying pH was observed by Zhou and Tokuda²⁵ when using methyltriocetylammmonium chloride as an extractant but the experiments were not performed at constant alkali and chloride concentrations, so the variations observed may have been a result of multiple parallel phenomena (ion-pairing, competition with Cl^- and HO^-). In our case, the competitive extraction of HO^- against $H_xNb_6O_{19}^{x-8}$ may explain the decrease in the yield of extraction of Nb (Fig. 7) since both Na^+ and Cl^- concentrations were held constant. Moreover, since Nb(v) is mainly present as $HNb_6O_{19}^{7-}$ in aqueous solutions at a pH between 11 and 13,¹⁰ the change in protonation of

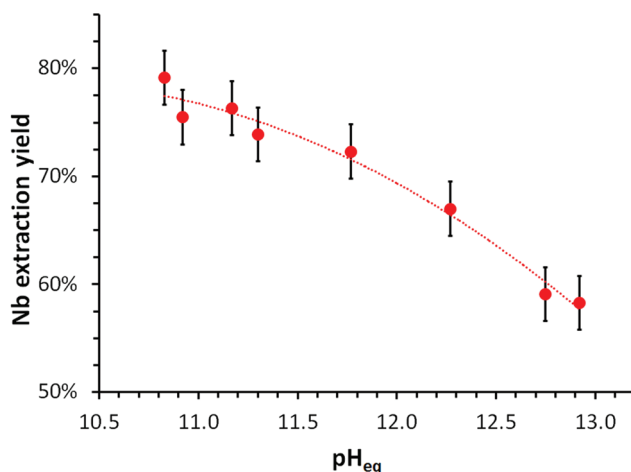


Fig. 7 Extraction yields measured for Nb as a function of aqueous pH at equilibrium. Organic phase: 5.4 mM Aliquat® 336 diluted in Elixore 205 + 1% (v/v) isotridecanol. Initial aqueous phase: 0.45 mM $Na_7H_9Nb_6O_{19} \cdot 15H_2O$ + 50 mM NaCl + $Na_2CO_3/NaOH$, $[Na^+]_{total} = 250$ mM. Extraction: 1 contact, $V_{org}/V_{aq} = 1$, $t = 30$ min, $T = 25$ °C.

$H_xNb_6O_{19}^{x-8}$ in this pH range cannot be considered as strongly contributing to the decrease of the extraction yield of Nb(v) displayed in Fig. 7. Finally, one may consider that the degree of protonation of $HNb_6O_{19}^{7-}$ may change during the extraction process leading, for instance, to the presence of $H_xNb_6O_{19}^{x-8}$ ($x > 1$) in the extracted species. Even if the extraction of such species explains the decrease in extraction with the increasing pH, such a phenomenon remains speculative and further studies of the speciation of hexaniobate ions in organic solvents are needed. Nonetheless, it should be noted that quaternary ammonium hexaniobate salts containing up to 4.5 protons, such as $TBA_4H_4Nb_6O_{19} \cdot 7H_2O$ and $TBA_{3.5}H_{4.5}Ta_6O_{19} \cdot 2THF \cdot 5.5H_2O$, have been recently isolated (Table 1). The decrease of the Nb extraction yield with the increasing hydroxide concentration in the aqueous phase could also be used to recover hexaniobate ions after their extraction with organic solutions of quaternary ammonium salts. This could be of interest for future hydrometallurgical processes using highly alkaline niobium solutions or for new synthetic procedures involving hexaniobate ions.

Conclusions

Organic solutions of quaternary ammonium salts, like Aliquat® 336 diluted in an aliphatic or aromatic diluent, can extract with high efficiency Nb(v) and Ta(v) from alkaline media at room temperature. The extraction is based on an anion exchange mechanism between the chloride anions of the quaternary ammonium and the hexaniobate ions ($H_xNb_6O_{19}^{x-8}$) present in the solutions of Nb at a pH higher than ~10, and more especially $HNb_6O_{19}^{7-}$ between pH 11 and 13. In spite of the apparent simplicity of the anion exchange mechanism, the extraction of Nb by Aliquat® 336 involves a series of subtle phenomena. In particular, the interaction of $H_xNb_6O_{19}^{x-8}$ with alkali ions and the potential alkali-induced deprotonation of the cluster in the aqueous phase reduce the Nb extraction in the following order: $Cs^+ > K^+ > Na^+ > Li^+$. The presence of competing anionic species also depresses the efficiency of the Nb extraction, in accordance with the affinity of the quaternary ammonium for these anions ($NO_3^- > Cl^- \gg C_2O_4^{2-} \sim SO_4^{2-} > CO_3^{2-}$). Between pH 10 and 13, the pH of the aqueous phase was also found to influence the extraction of $HNb_6O_{19}^{7-}$, with the highest extraction yields observed at the lower pH values. This effect may be a result of multiple phenomena, but the competitive extraction of hydroxides against hexaniobates may significantly contribute to the observed trend. The results obtained also underline the importance of the aggregation properties of quaternary ammoniums in understanding the extraction of Nb(v) from basic media. Finally, the extraction of hexaniobate and hexatantalate ions in organic solvents using quaternary ammonium salts affords straightforward access to polyoxometalate organic solutions and opens opportunities for the design of innovative hydrometallurgical processes for niobium and tantalum.

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