Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article El-Sweify, F. H. , Fattah, A. A. Abdel and Ali, S. M.(2009) 'Comparative Studies on the Extraction of Protactinium Using Different Kinds of Organic Extractants', Separation Science and Technology, 44: 3, 753 — 772
To link to this Article: DOI: 10.1080/01496390802437016
URL: http://dx.doi.org/10.1080/01496390802437016

Separation Science and Technology, 44: 753–772, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802437016

Comparative Studies on the Extraction of Protactinium Using Different Kinds of Organic Extractants

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Abstract: The extraction behavior of Pa(V) from various aqueous solutions was studied using different extractants, namely Amberlite-LA-2 (Amb-LA2), diethylhexyl phosphoric acid (HDEHP), tributylphosphate (TBP) and Tricaprylylmethyl ammonium chloride (TCMA) in toluene. The extraction was carried out from slightly acidic as well as strong acidic solutions of HCl, HBr, and HI, at various temperatures. The extracted species in every case were postulated. Extraction chromatography behavior of Pa(V), its homologue Nb(V), and the chemically similar elements Zr(IV) and Hf(IV) were also studied in the case of TCMA. Radioactive isotopes were used for tracing the corresponding elements. Some separation alternatives were achieved.

Keywords: HBr, HCl, HI, organic extractants, protactinium

INTRODUCTION

Protactinium is the third member of the actinide series. In its highest valence state (V) it resembles the group (Vb) elements rather than exhibiting characteristics similar to those of the lanthanides. The radioactive isotope ^{233}Pa is highly available in radiochemical analysis and has reasonable half-life time (27.0 d). The determination of ^{233}Pa in neutron

Received 13 October 2007; accepted 2 July 2008.

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irradiated natural ^{232}Th was achieved via its β or γ activity (1). The behavior of protactinium ions in solution is very complex because of the tendency of the element to hydrolyze and polymerize and large number of ionic species being formed. The simultaneous presence of Pa ions with different charges, polymerization etc. interfere with the choice of a suitable method for the determination of Pa and its separation from other elements (2). Solvent extraction is a very suitable method for the separation of Pa in many cases (3). The isotope Pa-233 is artificially produced during the thorex process, where good separation of Th(IV), Pa(V), and Zr(IV) is possible only at low aqueous feed acidity (4). In addition, for an analysis of natural ores and environmental samples containing lanthanides and thorium, chemical separation has to be carried out to avoid interferences in the characteristic gamma lines of ^{233}Pa and some irradiation-induced radioisotopes of some lanthanides. Consequently, it is important to separate ^{233}Pa from the irradiated samples to enable its determination, and consequently determination of Th as well as the lanthanides. It is also important to separate Pa from its homologue Nb and the chemically similar Zr and Hf. Besides, natural radioactive tracers of Pa are used for estimation of age, geochemical studies, and investigation of environmental changes (5–9).

A study of the extraction of mixed fluoride, chloride, and bromide complexes, of Nb, Pa, Ta, and the element 105 into aliphatic amines has been carried out in order to perform a systematic study of halide complexation of the group five elements in concentrated acid solutions (10).

Recovery of Pa from various kinds of aqueous solutions have been carried out. The distribution behavior of Pa has been studied in the presence of varying amounts of Th (up to 250 g/L) and U (20 g/L) from aqueous nitric acid solutions (1–6 M) employing a 1 M solution of di-2-ethylhexyl-isobutylamide (D2EHTBA) in n-dodecane (11). Different extractants such as TLA, TBP, and IBMK were used for studying the extraction of Pa and Th from different acidic solutions containing inorganic and organic additives (low alcohols or acetone) (12). A rapid and efficient procedure for the separation of trace Pa from Th irradiated by 14 MeV neutrons was described using 1-phenyl-3-methyl-4-benzoyl pyrazolone-5 (PMBP) and tri-iso-octyl amine (TIOA) as extractants and HCl-HF acid solution as back extractant (13).

A study has been performed for the separation of ^{232}U from irradiated ^{231}Pa containing Zr, Nb, Ti, and Si impurities using solvent extraction with 30% tributyl phosphate (TBP) in carbon tetrachloride (14). Solvent extraction using thenoyl tri fluoro acetone (TTA) has been used to study the hydrolysis of Pa at the tracer scale (2). A simple and fast radiochemical procedure was used for the separation of protactinium from uranium and a variety of reaction products using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and tri-iso-octyl amine as extractants (15). Partitioning in Purex process for high level waste including Zr and Nb as fission products using HDEHP and TBP extractants have been described (4,16).

The aim of the present work is to study the extraction behavior of Pa by different organic extractants from slightly and strong acidic solutions of HCl, HBr, and HI for speciation and in order to find the optimum conditions for separating Pa from some waste solutions at low as well as high aqueous acidities using dilute extractants, and for the purpose of carrying out radiochemical neutron activation analysis (RNAA) for samples containing thorium together with lanthanides to avoid gamma-ray interferences. In addition, studying the extraction chromatographic behavior of Pa, its homologue Nb, and the chemically similar elements Zr and Hf aiming at their separation from each other, is another target of this study.

EXPERIMENTAL

Chemicals and Reagents

All used chemicals were of analytical grade quality. HCl, HBr, HNO_3, $ZrOCl_2 \cdot 8H_2O$, and tri-caprylyl methyl ammonium chloride (Aliquat-336, TCMA) were Merck products. Aliquat-336 is $C_{26}H_{17}Cl$, taking the formula $CH_3N[(CH_2)_7CH_3]_3$, which is a mixture of $C_8 - C_{10}$ chains and C_8 dominating. KI, toluene, xylene, TBP, tri-n-octyl amine, and TTA were B. D. H. products. Amberlite-LA-2, M.W. 353–395, a secondary amine (RR′NH), where $R = CH_3(CH_2)_{11}$- and $R' = CH_3C(CH_3)_2(CH_2C(CH_3)_2)_2$- known as N-lauryl tri alkyl methyl amine, was a product of Rhom and Haas. Di-(2-ethyl hexyl) phosphoric acid (HDEHP) was a product of Fluka and Buchs. Thorium nitrate was a Fisher product. All solvents were used without further purification.

Instrumentation

A pH meter of the type HANNA-HI-9812 (Italy), having a combined glass electrode with a temperature sensor, was used for all pH measurements. A shaker thermostat of HAAKE-SWB-20 (Germany) type, was used for equilibrating aqueous and organic phases at the desired temperature. An analytical balance of the Mettler type with a sensitivity of 1×10^{-5} g was used for weighing the chemical samples. All the elements were assayed radiometrically using suitable radioactive isotopes as tracers. The radioactivities of the corresponding radionuclides were assayed by γ-measurements using a multi-channel analyzer, a Geni-2000 with 8192 channels connected to a hyper pure Ge-detector (Canberra-USA). A single channel analyzer, model 550 scaler and 2010 Amplifier, Nucleus, USA was used for some radiometric measurements of ^{233}Pa.

Preparation of Radioactive Tracers

The studied elements, zirconium, niobium, hafnium, and protactinium were traced using the corresponding radioactive isotopes, ^{95}Zr, ^{95}Nb, ^{181}Hf, and ^{233}Pa, respectively.

^{95}Zr was selected as a tracer for measurements of Zr(IV) in the extraction studies. It was obtained by irradiating accurately weighed samples of $ZrOCl_2 \cdot 8H_2O$ target in the Egyptian reactor ET-RR-II at Inshas. The sample was then dissolved in 6 M HCl solution of known volume. Zirconium was purified from its daughter ^{95}Nb by extraction into 0.5 M TTA in xylene as reported elsewhere (17). Solution of Zr traced with ^{95}Zr was prepared and was used as 10^{-4} M in different aqueous media.

^{95}Nb was obtained as a decay product of ^{95}Zr. A mixture of the two isotopes is obtained at equilibrium. This mixture was used without separation. ^{95}Zr and ^{95}Nb radioactivities were measured without interference from each other at γ-energies 724 and 766 KeV, respectively.

^{181}Hf isotope was obtained in a mixture of ^{95}Zr and ^{95}Nb by irradiating samples of $ZrOCl_2 \cdot 8H_2O$ target containing 0.1% Hf at the Egyptian reactor ET-RR-II at Inshas. The irradiated samples were then dissolved in 6 M HCl solution of known volumes. ^{181}Hf was assayed radiometrically at γ-energy of 482 keV.

^{233}Pa was produced from thorium by irradiation in the nuclear reactor ET-RR-II through the following nuclear reaction:

$$^{232}\text{Th} \xrightarrow{\text{n},\gamma} {}^{233}\text{Th} \xrightarrow[\text{T}_{1/2}=22.3\text{m}]{\beta^-,\gamma} {}^{233}\text{Pa} \xrightarrow[\text{T}_{1/2}=27\text{d}]{\beta,\gamma} \underset{(\text{T}_{1/2}=1.59\times10^5\ \text{y})}{{}^{233}\text{U}} \tag{1}$$

The irradiated sample was then dissolved in a suitable volume of 6 M HCl and ^{233}Pa was separated from ^{232}Th and ^{233}U by selective extraction using 0.3 M tri-n-octyl amine in toluene as described elsewhere (12,18). The solution of the separated Pa (trace concentration) was adjusted to 6 M HCl.

All the prepared radioactive stock solutions were stored in polyethylene bottles till needed, to avoid adsorption on glass.

Extraction Procedure

Mineral acids solutions were used as the aqueous media for the extraction processes. Different concentrations or pH's of these aqueous phases containing the studied elements were prepared. All experiments were carried out at three different temperatures, namely 10, 25, and $40 \pm 1°C$. Equal volumes of both organic and aqueous phases were pre-equilibrated where 2 ml of organic and aqueous phases, were brought in contact in stoppered glass tubes together with the accurately added radioactive isotope. The tubes were firmly closed and put in the shaker thermostat to be vigorously shaken at the desired temperature. Preliminary experiments showed that 30 minutes were sufficient for equilibrium attainment. The adsorption of Pa on the glass tube walls during this short shaking time was found to be negligable (not exceed 5%) which was observed from comparing the original added radioactivity with the sum of the radioactivities in both organic and aqueous phases. This was found also in previous work on Pa (19,20). The distribution ratio, D, was determined by dividing the counts/minute of the used radioactive isotope in the organic phase by those in the aqueous phase according to the following equation:

$$D = A_o/A_{aq} \tag{2}$$

where A_o and A_{aq} are the radioactivities of the studied isotope in organic and aqueous phases at equilibrium, respectively.

Extraction Chromatographic Technique

For preparing the stationary phase, 10 g of Bio-Glass-2500 as dry supporting material was impregnated with 20 ml of 0.2 M Aliquat-336 in toluene and dried in the drying oven at 40°C for 8 hours. The column was prepared by packing compactly 0.7 g of the prepared stationary phase in a clean glass column of internal diameter 0.5 cm fitted with a tap for flow rate regulation. The bed height was 12 cm and the flow rate was 0.3 ml/ min. Solution mixture of ^{233}Pa, ^{95}Zr, ^{95}Nb, and ^{181}Hf radioactive isotopes, were loaded on the top of various columns. The sorbed elements were eluted by 6 M HCl then by 0.5 M HCl after adjusting the flow rate of the column to 0.3 ml/min. The eluate was collected as fractions of 1 ml in test tubes until complete elution attainment. The gamma counts of each isotope in each tube was measured using the multi-channel analyzer and the elution curves were plotted as γ-counts/min vs eluate volume in ml.

Aliquat-336 was chosen for the extraction chromatography for its advantage over the other extractants since it is very stable against radiation and hydrolysis; consequently it may be used several times for separation from highly radioactive solutions, without intermediate purification.

RESULTS AND DISCUSSION

Extraction Behavior of Pa(V):

The extraction behavior of ^{233}Pa was studied from aqueous solutions of HCl, HBr, and HI acid solutions under different conditions using different types of extractants, namely solutions of Amberlite LA-2, TBP, HDEHP, and Aliquat 336 (TCMA) in toluene at various concentrations.

Toluene as an aromatic diluent has been used in this work because aromatic diluents have a role in the reduction of aggregation formation in the case of amine extraction. The aggregation number increases also with the increase of concentration, so the employed extractants have been used as dilute solutions. However, this problem has been extensively studied elsewhere (21).

Extraction of Pa(V) from Slightly Acidic Solutions

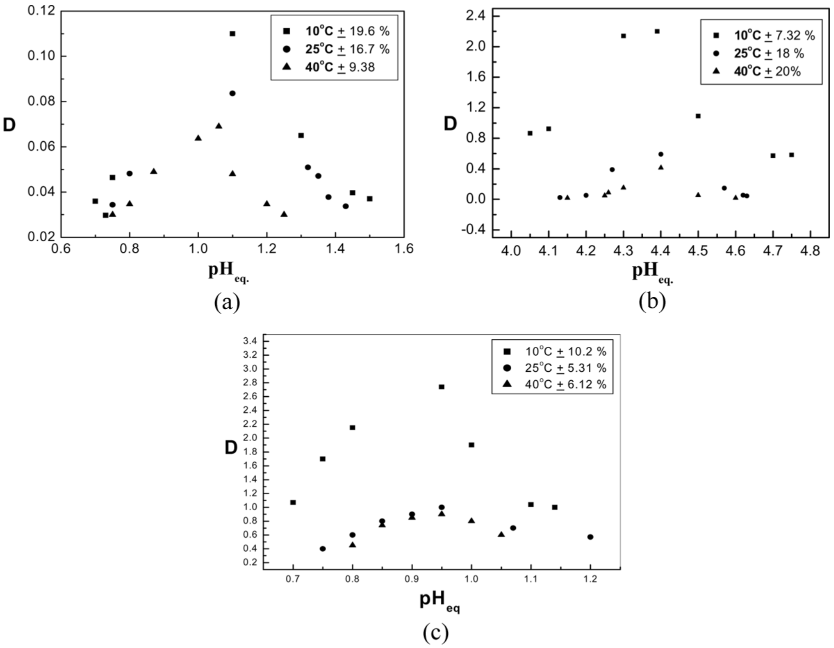
Figure (1a,b,c) shows the effect of pH on the D-values for the extraction of Pa(V) from slightly acidic HCl solutions by 10 v/v% TBP, 10 v/v% Amberlite LA-2 and 0.01 M HDEHP in toluene at 10, 25, and 40 ± 1°C.

As can be seen from this figure the extraction behavior is similar in all cases. The relation between D_{pa} and pH is represented by a curve which has a maximum at a definite pH, in all cases. Besides, it can be seen from these figures that the change in the temperature has a marked effect on the D-values, in the investigated systems, where $D_{10} > D_{25} > D_{40C}$.

Figures (2a,b,c) and (3a,b,c) show the extraction behavior of Pa(V) from slightly acidic solutions of HBr and HI, respectively. As can be seen from these figures the extraction behavior is very similar to that in the case of HCl solution.

Generally, it is found that the kind of halide ion has a very slight effect on the values of D_{Pa} for the extraction by the three used extractants.

Although the D-values are generally low, in all cases the extraction of Pa is relatively higher at low temperature (10°C) at definite pH values; in the case of HDEHP (pH = 0.9–1.3) and Amberlite LA-2 (pH ~4.5) D-values of 1.7–2.75 and 1.7–2.1, are obtained respectively. In the case of TBP, however, the D-values do not exceed 0.11.

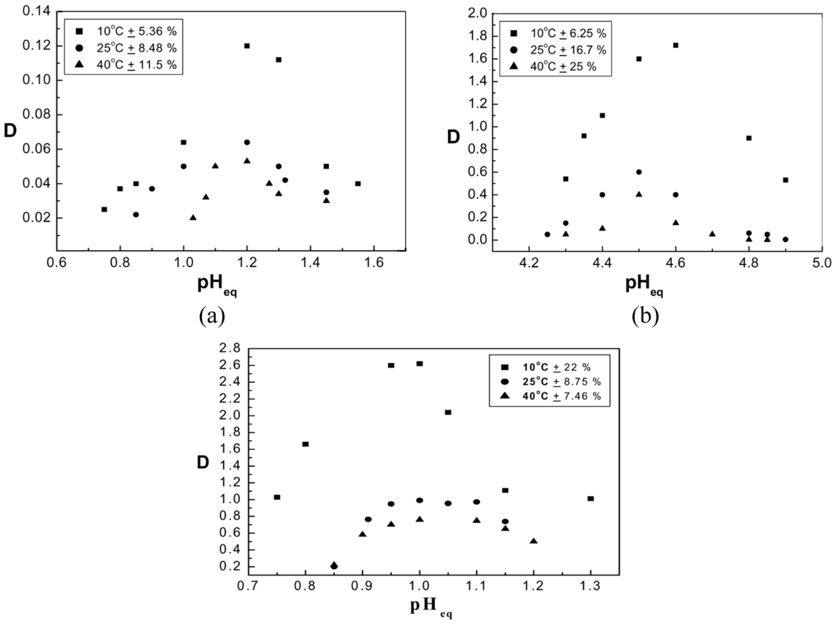


(a) (b) (c)

Figure 1. Effect of pH_{eq} on extraction of Pa(V) from slightly acidic solutions of HCl at 10, 25, and 40 ± 1°C, by (a) 10 v/v% TBP in toluene. (b) 10 v/v% Amberlite LA-2 in toluene. (c) 0.01 M HDEHP in toluene.

The stable valency of protactinium in aqueous solutions is Pa^{5+}, but this ion does not occur in significant amounts due to the extreme tendency of Pa to hydrolyse. Consequently it is difficult to predict the behavior of Pa(V) in solution (1).

It was found in another study that in the absence of polymeric forms of Pa in acidic solutions equilibrium is usually established fairly rapidly in solutions and the extraction is independent on the temperature between 1 and 40°C (22). However, in slightly acidic solutions Pa tends to hydrolyse very strongly. In solution, Pa(V) forms no discrete PaO_2^+ ions (in contrast to other pentavalent actinides) but occurs, even in concentrated acids only in the form of partially hydrolyzed species such as $PaO(OH)_2^+$and $PaO(OH)^{2+}$. Dimeric and polymeric ionic species are to be observed in concentrated Pa(V) solutions ($>10^{-6}$ M). The degree of condensation and hence the chemical behavior of Pa(V) are strongly dependent on the concentration of Pa(V) in aqueous solutions, which makes the chemistry of Pa(V) in aqueous solutions difficult and shows close similarities to niobium and tantalum (23). Consequently, the



(a) (b)

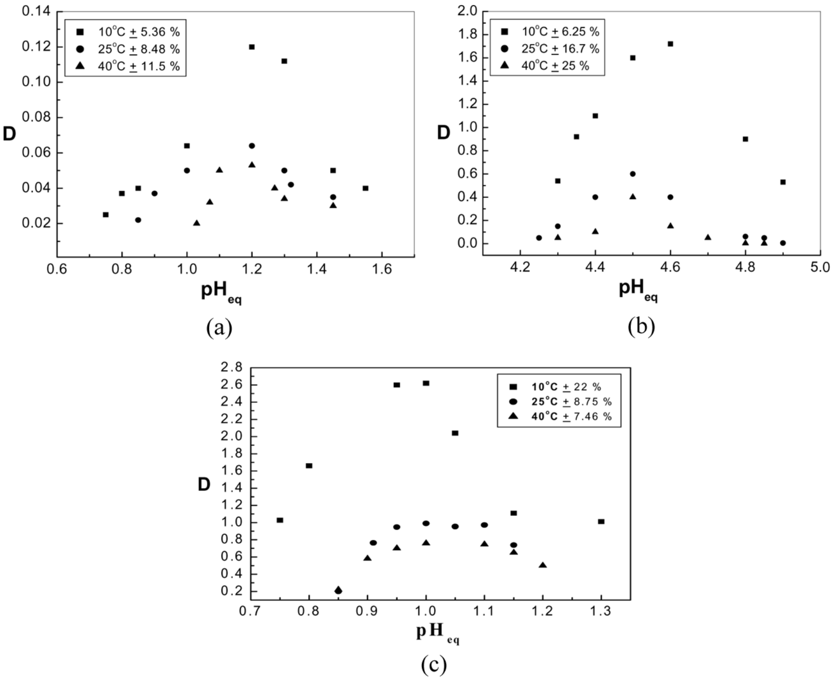
(c)

Figure 2. Effect of pH_{eq} on extraction of Pa(V) from slightly acidic solutions of HBr at 10, 25, and 40 ± 1°C, by (a) 10 v/v% TBP in toluene. (b) 10 v/v% Amberlite LA-2 in toluene. (c) 0.01 M HDEHP in toluene.

obtained results may be discussed in the light of the Pa(V) hydrolysis. This process is extremely complicated and has by no means been fully cleared up. The stability of Pa(V) solutions depends not only on their concentration but also on their "age."

Since the Pa=O group has been shown to be relatively stable, the partially hydrolyzed products are propably present as oxohydroxo complexes and not as pure hydroxyl complexes (12). The proportion of the relevant ionic species is a function of the solution pH and composed of the following species: $[Pa(OH)_5]$, $[PaO(OH)_2]^+$ and $[PaO(OH)]^{2+}$ (24).

As a consequence of the hydrolysis of Pa in slightly acidic solutions, it is expected that the extraction will be low. This explains the obtained results in the present study for the extraction by TBP, HDEHP, and Amberlite LA-2. Besides, the extracted species of Pa(V) in the case of HDEHP at the observed pH_{max}. should be a mixture of $[PaO(OH)_2]^+$ and $[PaO(OH)]^{2+}$. On the other hand, the extracted species in the case of Amberlite LA-2 may be a mixture of $[PaO(OH)_2X_2]^-$ and $[Pa(OH)_5X]^-$ where $X = Cl^-$, Br^- or I^- since amines and ammonium



(a) (b)

(c)

Figure 3. Effect of pH_{eq} on extraction of Pa(V) from slightly acidic solutions of HI at 10, 25, and 40 ± 1°C, by (a) 10 v/v% TBP in toluene. (b) 10 v/v% Amberlite LA-2 in toluene. (c) 0.01 M HDEHP in toluene.

salts extract metals in the form of their anionic complexes. As can be observed from Figs. 1–3 the proportion of the extracted species is very sensitive to the variation of the solution pH. The hydrolysis is the predominated factor compared to the reaction with Cl^-, Br^-, or I^-.

From the obtained results it is obvious that Pa(V) can be extracted to a relatively reasonable extent from slightly acidic solutions of HCl, HBr, and HI as metal salts either by Amberlite-LA-2 (amine) in the form of anionic complexes or by HDEHP in the form of cationic species. This may be important for isolation of Pa(V) from solutions which have these properties, as for example in the treatment of some radioactive waste solutions. The advantage of the extraction from slightly acidic solutions is that the highly corrosive concentrated halide solutions are no longer necessary, consequently, the used extractors and process lines may be made of stainless steel instead of the expensive tantalum or zircaloy. However, in the course of extraction measurements, it was found that the proportion of Pa(V) that can be extracted diminishes while the proportion of Pa(V) colloids increases with time (ageing). This condensation is reversible in its initial steps, but the more highly condensed types of ions can no longer be depolymerized by acid treatment or at least only to a very limited extent (23). Gobel et al., indicated through their extraction of ^{233}Pa from HBr or HI solutions that bromide and iodide complexes are less stable than the chloride complexes (25).

The different ionic forms of Protactinium formed in hydrochloric acid solutions are extensively provided. It is stated that Protactinium is present in HCl solutions as hydroxy chloride, oxychlorode, and chloride complex ions. No literature data are available on the state of Pa ions in HBr and HI solutions. The stability of the formed Pa–halide complexes decreases in the order $Cl^- > Br^- > I^-$ which is the order of increasing ionic radius of X^- (2).

Several scientists determined the stability constants (formation constants) of chloride complexes of Protactinium. Guillaumont found for the extraction of Pa(V) by 0.1 M TTA in benzene at 25°C in the system $HCLO_4$-HCl at acidities between 1–3 M, $Cl^- = 1$ M, the complex formed has the formula $[Pa(OH)_3Cl]^+$, its formation constant is 1.2 (2).

Davydov et al., studied the sorption of Pa(V) on silica gel from HNO_3-HCl solutions and concluded that at $[H^+] = 6$ M and $[Cl^-] =$ 1–4 M, two complexes 1:1 and 1:2, of the general formula $[Pa(OH)_x(NO_3)_yCl_j]^{5-x-y-j}$ with respective stability constants 0.025 and 0.069 are formed (2).

Scherff and Hermann calculated the formation constants of the ions $[Pa(OH)_3Cl]^+$, $[Pa(OH)Cl_6]^{2-}$ and $[PaCl]^-$ as 1.0, 1.4×10^{-12} and 1.6×10^{-14}, respectively (2). Guillaumont suggested the following hydrolysis equilibrium for acidic solutions of Pa (2):

$$[Pa(OH)_3]^{2+} + H_2O \longleftrightarrow [Pa(OH)_4]^+ + H^+ \qquad (3)$$

the equilibrium constant being $K = 9 \times 10^{-2}$ at 25°C (2).

Extraction of Pa(V) from Highly Acidic Solutions

Extraction by Amberlite LA-2

Figure 4a,b, and c shows the relation between the distribution ratio and acid concentration for the extraction of Pa(V) from HCl, HBr, and HI, respectively at various temperatures. In these series of experiments it was found that equilibrium is attained fairly rapidly, which indicates the absence of polymeric formation of the element. The D-values decrease with the increase of temperature which means that the extraction

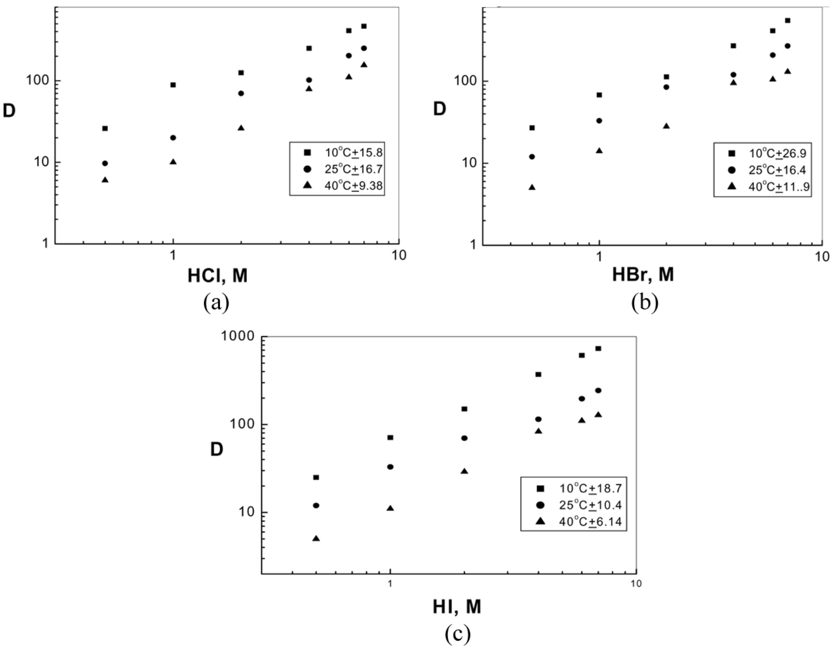


Figure 4. Effect of HX concentration on extraction of Pa(V) by 10 v/v% Amberlite LA-2 in toluene at 10, 25 and 40 ± 1°C. (a) HCl, (b) HBr, (c) HI.

reaction proceeds exothermically. The distribution ratio increases markedly with increasing acidity of the solutions of the three studied acids. As mentioned earlier, Amberlite LA-2 as one of the high-molecular weight amines extract mineral acids forming quaternary ammonium salts, consequently it acts as an effective extractant for acids and anionic complexes of Pa(V). The extraction process may be described by the following anion exchange mechanism (2,21).

$$[\mathrm{R_2NH}]_{\mathrm{org}} + \mathrm{H^+_{aq}} + \mathrm{X^-_{aq}} \longleftrightarrow \{[\mathrm{R_2NH_2}^+\ \mathrm{X}^-]\}_{\mathrm{org}} \tag{4}$$

$$\{[\mathrm{R_2NH_2^+X^-}]\}_{\mathrm{org.}} + [\mathrm{Pa\ Cl_6}]^-_{\mathrm{aq}} \longleftrightarrow [\mathrm{R_2NH_2}^+\ (\mathrm{PaCl_6})^-]_{\mathrm{org.}} + \mathrm{X}^- \tag{5}$$

where R_2NH represents Amberlite LA-2 and X^- represents Cl^-, Br^-, or I^-.

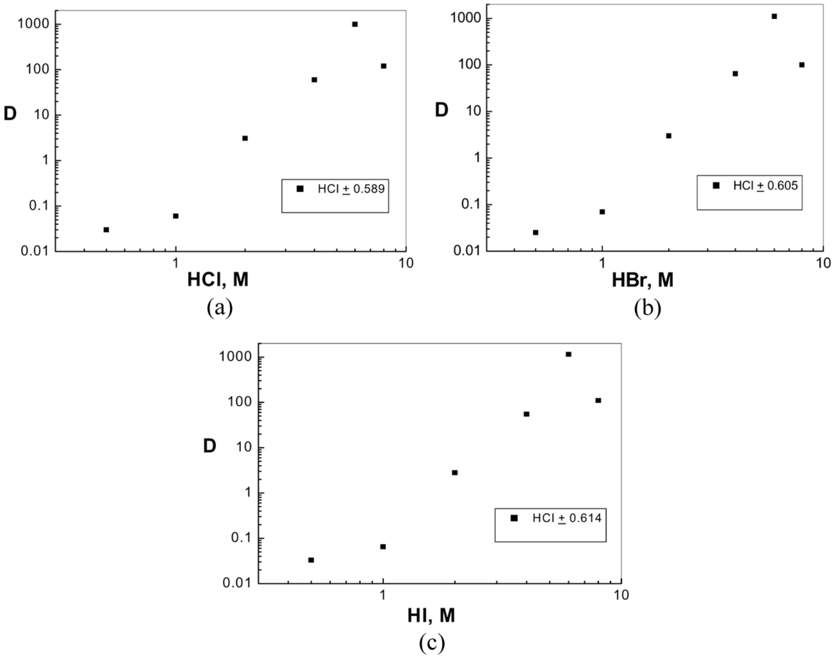
However, the relation between D and [HX] in this figure indicates that only one halide ion participates in the formation of the extracted species, under the studied conditions, which proves that Pa(V) is extracted in the form of hydrolyzed species using Amberlite-LA-2 solutions.

According to Pal'shin et al. (2), the extracted anionic-complexes may be singly charged or doubly charged. Accordingly, complexes of the type [Pa $(OH)_{6-y}.X_y]^-$ and [Pa $(OH)_{7-y}.X_y]^{2-}$, may be proposed for the extracted species. According to Keller, other hydrolysed oxy-hydroxy species of Pa(V) are also possible in solution (23).

Comparing the results in Fig. 4 it is clear that D-values of Pa(V) vary very slightly with the variation of the halide kind. Accordingly, the distribution coefficient of Pa, like that of many other elements depends to a large extent on the structure of the amine which may be attributed to steric and electronic effects (2). The degree of the extraction depends also on the charge on the extracted complex anion, the size of the cation formed by the amine and the polarity of the solvent.

Extraction by TCMA

The extraction of Pa(V) from solutions of HCl, HBr and HI with 0.2 M Aliquat-336 in toluene studied at 25°C is discussed in this part. Figure 5a,b,c represents the relation between the distribution ratio and



(a) (b) (c)

Figure 5. Effect of HX concentration on the extraction of Pa(V) by 0.2 M Aliquat-336 in toluene at 25 ± 1°C. (a) HCl, (b) HBr, (c) HI.

the acid concentration on a log–log scale. As can be seen from this figure, D increases sharply as the acid concentration increases from 1 M to 6 M, then a decrease in the D-values is observed. Pa(V) has the same extraction behavior from the three acid solutions HCl, HBr, and HI. The slope analysis of the straight part of Fig. 5 indicates that the extracted species are $[\mathrm{Pa\,X_6}]^-$ where X^- is Cl^-, Br^-, or I^-. This means that the extracted species in the case of TCMA are non-hydrolysed species, in contrast to the extraction by Amberlite LA-2. The extraction process can be represented as follows:

$$[R_4N^+Cl^-]_{org} + \mathrm{Pa\ Cl}^-_{6\ aq} \longleftrightarrow [R_4N^+(\mathrm{PaCl_6})^-]_{org} + Cl^- \qquad (6)$$

where R_4N^+ refers to TCMA cation. It is also an anion exchange mechanism.

The contact between the organic phase, i.e. TCMA solutions and the aqueous phase of Pa(V) may cause a shift in the equilibrium between the formed species of Pa(V) in the aqueous phase and enhance the formation of $[\mathrm{Pa\ Cl_6}]^-$. This finding may be attributed to the nature and kind of the amine.

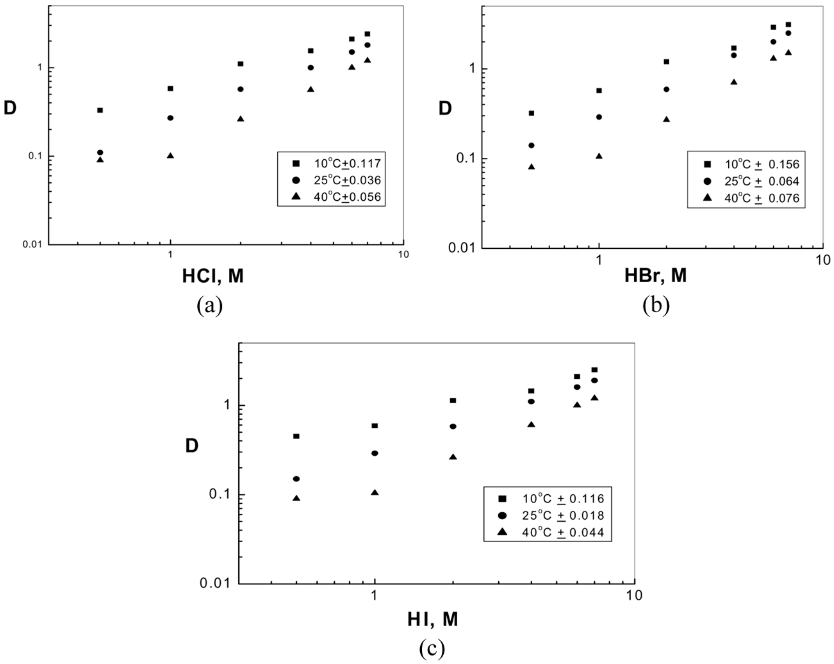
Comparing D-values in the case of the extraction using TCMA with that using Amberlite LA-2, it can be seen that the D-values are slightly higher in the case of the secondary amine than in the case of the quaternary ammonium salt at lower acid concentration up to 5 M.

Extraction by TBP

TBP is mostly employed as extractant in the case of extracting Pa(V) in the form of molecular compounds. In the present study solutions of 10 v/v% TBP in toluene are used. The extraction investigation was carried out from solutions of HCl, HBr, and HI, at 10, 25 and 40 ± 1°C. Fig. 6a,b,c represents the extraction-acid dependence in the case of HCl, HBr, and HI, respectively. In all cases D increases with acid concentration. On the other hand, D decreases with increasing temperature indicating once more that the extraction reaction is an exothermic one. It has been confirmed in most of the cases that the extracted Pa(V) complexes include two TBP molecules (2).

As can be predicted from Fig. (6) the kind of the halo-acid has nearly no effect on the value of D. These results are more or less in a good agreement with those published on the extraction of Pa(V) from HCl solutions using 10 v/v% TBP (3). The probable mechanism can be expressed as:

$$[\mathrm{Pa(OH)_xCl_y}] + \mathrm{n\ TBP} \longleftrightarrow [\mathrm{Pa(OH)_xCl_y}]\,.\,\mathrm{n\ TBP} \qquad (7)$$



(a) (b)

(c)

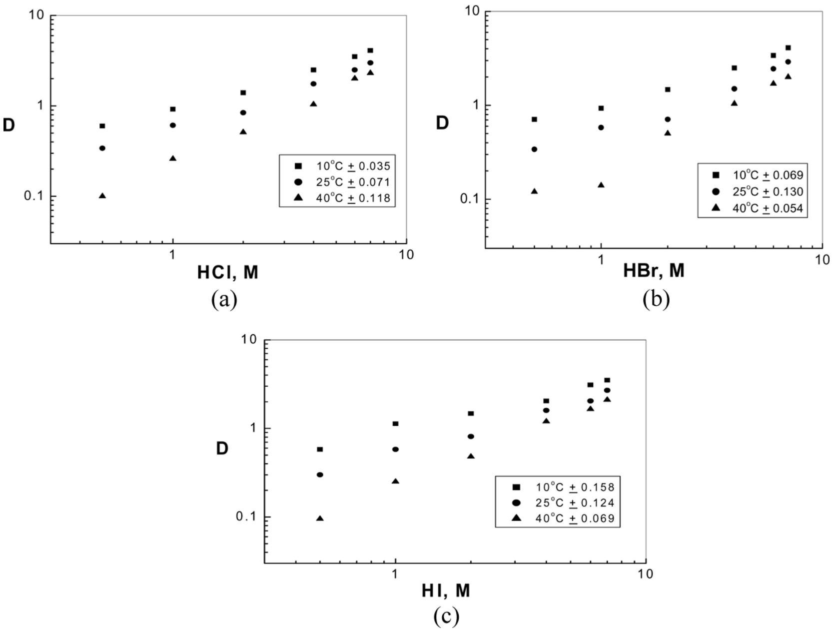
Figure 6. Effect of HX concentration on extraction of Pa(V) by 10 v/v% TBP in toluene at 10, 25 and 40 ± 1°C. (a) HCl, (b) HBr, (c) HI.

which is an adduct formation mechanism there are several neutral species of Pa in HCl solutions may be extracted by TBP from HCl and other hydrohalic acid solutions (2).

Extraction by HDEHP

The extraction of Pa(V) from HCl, HBr, and HI aqueous solutions by 0.01 M HDEHP in toluene is studied at 10, 25, and 40 ± 1°C. The relation between D and acid concentration for HCl, HBr, and HI is shown in Fig. 7a,b,c. As can be seen from this figure the D-values decrease with increasing temperature indicating that the extraction reaction is an exothermic one.

It is, however, noticeable from Fig. (7) that the D-values increase with acid concentration this may be explained by the effect of increasing acidity on decreasing the hydrolysis extent, especially when the extraction is carried out using dilute extractant solutions. Under these conditions the extractant has a slight effect on the equilibrium displacement between



(a) (b)

(c)

Figure 7. Effect of HX concentration on extraction of Pa(V) by 0.01 M HDEHP in toluene at 10, 25 and 40 ± 1°C. (a) HCl, (b) HBr, (c) HI.

various Pa-species in the aqueous phase. Consequently the percentage of the extractable species is not so high.

Extraction of Pa(V) by HDEHP is expected to proceed mainly by a cation exchange mechanism of the cationic protactinum species in the investigated halide media as given by the following equation:

$$\{[\mathrm{Pa(OH)_3Cl}]^+\}_{\mathrm{aq}} + \{[\mathrm{HDEHP}]_2\}_{\mathrm{org}} \longleftrightarrow \{\mathrm{Pa(OH)_3Cl\ H(DEHP)_2}\}_{\mathrm{org}} + \mathrm{H}^+_{\mathrm{aq}} \qquad (8)$$

where HDEHP present as a dimer in the organic phase (21). Other extractable cationic species of Pa may be present in HCl as reported (2).

Extraction experiments have been carried out at different temperatures to investigate the type of the extraction reaction whether exothermic or endothermic. As can be concluded from the present data, the different extraction processes experimented are exothermic. This means negative enthalpy changes (negative $\Delta H°$) will be obtained in these extraction systems. In general, the distribution ratio of a neutral metal complex increases with increasing temperature for complexes with significant hydrophilic character. However, for systems in which the solvation in the organic phase is significant or hydration in the aqueous phase is minor, which may be the case for Pa species, the temperature effect may, in fact, be reversed (26). According to this work, carrying out a Pa extraction at low temperatures may enhance the separation of Pa from some other elements when present in a mixture. The decrease in D_{Pa} at high temperatures may be due to the decrease of the extractable species of Pa by the hydrolytic reactions or by the decomposition of the extractable species (27).

EXTRACTION CHROMATOGRAPHY STUDIES

In this part the obtained data on the application of extraction chromatography using the quaternary ammonium chloride, Aliquat-336 for separation investigations are discussed. Different columns are prepared as described in the experimental part for studying the loading and elution behaviors of Pa(V) in addition to Nb(V), Zr(IV), and Hf(IV). The latter three elements are chosen because of their similarity in chemical behavior with Pa(V). The use of radioactive isotopes ^{233}Pa, ^{95}Nb, ^{95}Zr, and ^{181}Hf for tracing the corresponding elements facilitates these studies. Figure (8) represents the elution curves for a mixture of the aforementioned metal species loaded on the column from 6 M HCl solution. Elution of this mixture was carried out using 6 M HCl for Nb(V), Zr(IV), and Hf(IV) and 0.5 M HCl for partial elution of Pa(V). The curves in this figure show a maximum at 1.8 ml for Hf(IV) and at 3.3 mL for Zr(IV). With respect

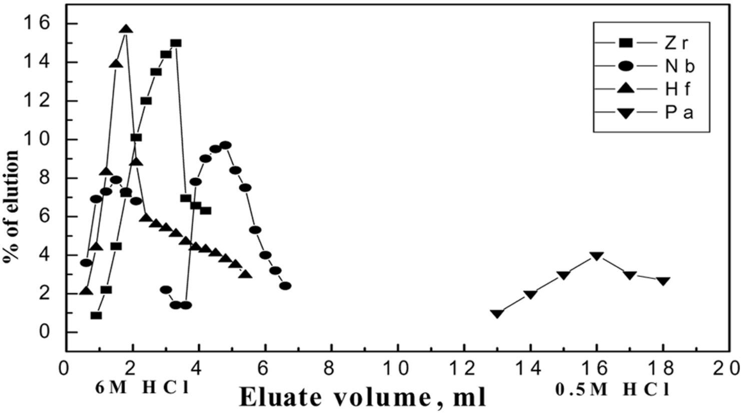


Figure 8. Elution curves of Zr(IV), Hf(IV), Nb(V) and Pa(V) at room temperature. Eluent 6 M HCl and 0.5 M HCl stationary phase Bio-glass 2500 loaded with Aliquat-336 in toluene; ϕ = 0.5 cm, bed height = 12 cm, flow rate = 0.3 ml/min.

to Nb(V) two broad maxima appeared at 1.5 mL and at 4.5 mL. On the other side Pa(V) is partially eluted using 0.5 M HCl with a maximum at 16 mL. With respect to Nb(V) it seems that it is eluted in the form of two different chemical species, where one of these species is less adsorbed on the column and is eluted first at 1.5 mL and the other is eluted at 4.5 mL. Nb(V) is present in HCl in the form of $NbOCl_4^-$ and $NbOCl_5^{2-}$ (28). The elution behaviors of Zr(IV) and Hf(IV) is similar to that for the elution from the anion exchanger Dowex-2 employing 9 M HCl (29). As can be concluded from this study, good separation of Pa(V) from the other metal species is possible. However, the other three elements are partially separated from each other. These results are similar to those obtained by using hollow fibers membrane chromatography (30) and hollow fibers supported liquid membranes (31).

Complete elution of Pa(V) from the column is difficult using HCl solutions at the studied concentrations. It was reported that a mixture of HCl and HF could be used for elution of Pa(V) from anion exchanger column (2).

CONCLUSION

It can be concluded from this study that:

1. From slightly acidic solutions of HCl, HBr, and HI, Pa(V) can be extracted to a relatively considerable extent. D_{Pa} has relatively low values. This is attributed to the hydrolysis of Pa(V). The proportion of the extracted ionic species is very sensitive to the variation of the solution pH. The extracted Pa species in the case of HDEHP may be a mixture of the cationic species $[PaO(OH)_2]^+$ and $[PaO(OH)]^{2+}$ whereas in case of Amberlite LA-2 it may be a mixture of $[PaO(OH)_2X_2]^-$ and $[Pa(OH)_5X]^-$ where $X = Cl^-$, Br^-, or I^-. Weaker extraction has been obtained on using TBP and this may be due to the lack of extractable neutral species of Pa at such low acid concentrations. The hydrolysis is the predominated factor compared to the complexing ability with Cl^-, Br^-, or I^-.

   The change in temperature has a marked effect on D-values in all cases where the sequence:

   $$D_{10} > D_{25} > D_{40}{}^\circ C.$$

   is obtained, indicating exothermic extraction systems, i.e., negative ΔH° values are obtained.

   Extraction from slightly acidic solutions may have the advantage of avoiding high corrosion in concentrated halide solutions.

2. On extraction from strong acidic solutions equilibrium is attained fairly rapidly. D-values increase markedly with increasing acidity of solution and decrease with the increase of temperature. D-values vary very slightly with the variation of acid kind in the case of extraction by Amberlite LA-2 and the extracted species are hydrolyzed complexes of the type $[Pa(OH)_{6-y}X_y]^-$ and $[Pa(OH)_{7-y}X_y]^{2-}$.
   In the case of quaternary ammonium salt, Aliquat-336 (TCMA), D_{Pa} has slightly lower values than in the case of Amberlite LA-2 up to 5 M, then increases sharply with the acid concentration up to 6 M. The kind of the acid has nearly no affect on D-values. The extracted species in the case of TCMA are non-hydrolyzed species of the type $[Pa\ X_6]^-$.
   In the case of extraction by Amberlite LA-2, TBP and HDEHP from strong acidic solutions D_{Pa} has moderate values, however:

$$D_{AmbLA2} > D_{HDEHP} > D_{TBP}$$

   Again, D_{Pa} decreases with temperature increase from highly acidic solutions as obtained from slightly acidic solutions.
   Good separation of Pa(V) is achieved from the similar metal species Nb(V), Zr(IV), and Hf(IV) using extraction chromatography with stationary phase composed of 0.25 M Aliquat-336 in toluene loaded on Bio-Glass-2500. Partial separation of Nb(V), Zr(IV), and Hf(IV) from each other is also achievable.

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