Solvent and Reversed Phase Extraction Chromatographic Separation of Molybdenum and Tungsten with Quaternary Ammonium Salt Reagent, Aliquat 336

Nitya Ranjan DAS* and Putul CHATTOPADHYAY
Nuclear Chemistry Division, Saha Institute of Nuclear Physics,
Sector-1, Block-'AF', Bidhannagar, Calcutta-700064, India

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A quaternary ammonium salt reagent, Aliquat 336 has effectively been used for radioanalytical separations of molybdenum and tungsten through the techniques of solvent extraction and reversed phase extraction chromatography (RPEC). Studies on solvent extraction revealed that quantitative separations of the elements in a mixture can be achieved by extracting tungsten with ca. 10^{-4} mol dm^{-3} solution of Aliquat 336 in cyclohexane from an aqueous solution of 1 mol dm^{-3} H_3PO_4. The efficiency of separation of the elements which form varieties of metal salts of poly- and heteropolyanion species in aqueous solution is very much dependent on the types of acids as well as on the reagent concentration. In RPEC system, both the elements were found to be quantitatively extracted by an Aliquat 336 impregnated column of Kieselguhr from an alkaline solution containing a hydroxy compound like tartaric acid. The extracted species were subsequently separated by eluting molybdenum and tungsten respectively with HCl solutions of 0.05 mol dm^{-3} and 0.1 mol dm^{-3} concentrations. The purity of the separated species at various stages of their separations was verified by means of gamma-ray spectrometry.

The elements, molybdenum and tungsten, due to lanthanoid contraction, form a critical pair of elements having very close chemical properties. In respect of occurrence, metallurgy and properties of metals, the elements are markedly similar. They exist in varieties of oxidation states and their aqueous chemistry is very complex amongst the transitional elements. Since the formations of varieties of metal complexes, especially poly- and heteropolyanion species are most important feature of the chemistry of both molybdenum and tungsten, it was expected that the high molecular weight amines or the quaternary ammonium salts which are very selective for different elements[1—10)] under specific experimental conditions would be very effective in anion-exchange separation of the elements from each other. In this respect, a quaternary ammonium salt reagent, Aliquat 336 ($R_3R'NCl$), has been shown to be a versatile extractant in both solvent and reversed-phase extraction chromatographic (RPEC) separations of metals that are capable of existing as complex anionic species in aqueous solutions.[11—20)] Several workers[21)] have effectively used the extractant in studying the extraction behaviors of both molybdenum and tungsten in different experimental conditions. Recently, Shabana et al.[22)] reported the extraction separation of tungsten in radiochemical purity with Aliquat 336 from rhenium in different acid media. Studies on the extraction chromatographic separation of small quantities of Cr(IV), W(VI), and Mo(VI) in Aliquat 336–HCl system was also reported by Stro'nski.[23)] Although Aliquat 336 has been used for extraction separation of molybdenum and tungsten in various systems, no systematic studies on their mutual separation through solvent extraction and RPEC have yet been attempted. The present investigation deals with the development of suitable radioanalytical procedures involving both the extraction techniques for clean separation of molybdenum and tungsten in a mixture using Aliquat 336 as liquid anion exchanger.

Experimental

Reagent. Chemical reagents used were of analytical grade. The extractant, Aliquat 336 (trialkylammonium chloride) of molecular wt. 404.17 was supplied by Aldrich Chemical Co., Inc. USA. The radiotracers, ^{99}Mo(67h), ^{185}W (73d), and ^{187}W (24h), were procured from BARC, Trombay, as sodium molybdate and sodium tungstate respectively in sodium hydroxide solution having high specific activity which were diluted as per requirements.

For gamma-spectrometric study, an ND65 8K channel analyzer connected with a High Purity Germanium detector of 30 cm^3 active volume and with resolution of 2.06 keV at 1.33 MeV was used.

Solvent Extraction Procedure. In solvent extraction separation, 20 ml of aqueous feed containing the tracers ^{99}Mo and ^{185}W or ^{187}W ($<10^{-7}$ mol dm^{-3}) in different acid media was equilibrated with equal volume of Aliquat 336 of desired concentration in different diluents together with 3% (v/v) 1-octanol for a certain period. After disengagement of the liquid phases, radioactivities present in both the phases were rediometrically measured and identified whereby tungsten was found to be preferentially or completely extracted by the organic extractant depending upon the experimental conditions.

Reversed-Phase Extraction Chromatographic Procedure (RPEC). The column material, Kieselguhr, used for reversed-phase extraction chromatographic separation was first hydrophobised with dimethyldichlorosilane and then impregnated with Aliquat 336 following the procedure developed earlier.[24)] A packed column (3 cm×0.3 cm) of impregnated Kieselguhr was prepared in a stoppered glass tube. A syringe was inserted through a rubber cork fitted at the top of the glass tube. The flow rate of the eluent percolated in the column through this syringe was regulated throughout the experiment with a peristaltic pump (LKB 2132 Micro Perpex). Before loading of the radiotracer on the column, it was preconditioned by passing a 8 mol dm^{-3} LiNO$_3$-0.01 mol cm^{-3} HNO$_3$ solution which made the column more effective in the separation of the elements pair.

In RPEC separation system, small amount of tartaric acid was added to the tracer mixture containing molybdenum and tungsten in alkaline medium and was allowed to extract by the impregnated reagent in the column. After complete extraction, the elements were separated by eluting molybdenum first with a 0.05 mol dm^{-3} HCl solution and then tungsten by a 0.1 mol dm^{-3} HCl solution. A flow rate of 10—12 drops per minute was maintained throughout the experiment. Activities present in different fractions of the effluents were verified and measured by GM counters.

Initially, both solvent extraction and RPEC procedures were tried with individual radiotracers, ^{99}Mo and ^{185}W or ^{187}W, under similar experimental conditions. The purity and extent of separation of the radiotracers at different stages of separation procedures were verified radiometrically.

Discussion

Studies on the solvent extraction behavior of molybdenum and tungsten at tracer scales, in various acid media, namely, HCl, HNO$_3$, H$_2$SO$_4$, and H$_3$PO$_4$, with Aliquat 336 as extractant revealed that the extractability of tungsten, in general, is always higher than that of molybdenum whatever be the acidity of the media (Table 1). For both the elements, the extents of extractions follow a decreasing trend with increasing acidity of the aqueous solution but interestingly, it has been found that the differences in the distribution ratio values for the elements at different acidities are very much pronounced in case of orthophosphoric acid.

Extraction studies of molybdenum and tungsten with Aliquat 336 in cyclohexane from phosphoric acid solutions at different acidities, as shown in the Fig. 1, indicate that complete extraction of tungsten free from molybdenum can be achieved at ca. 1 mol dm^{-3} H$_3$PO$_4$ concentration below of which partial extraction of molybdenum along with tungsten always takes place. However, at phosphoric acid concentration>1 mol dm^{-3}, although the extraction of molybdenum is very insignificant, extraction of tungsten also follows a decreasing trend. Thus the optimal conditions for extraction of tungsten free from molybdenum is to extract tungsten with a reagent solution of 10^{-4} mol dm^{-3} concentration in cyclohexane from an aqueous phosphoric acid solution of ca. 1 mol dm^{-3} concentration.

The extraction of tungsten from orthophosphoric acid medium at different concentration follows almost similarly with that of molybdenum but with higher degree of extraction (Fig. 1). The insignificant extractibility of molybdenum at higher acidity beyond 1 mol dm^{-3} is attributed to the fact that in this region, it exists mostly in the cationic forms, such as

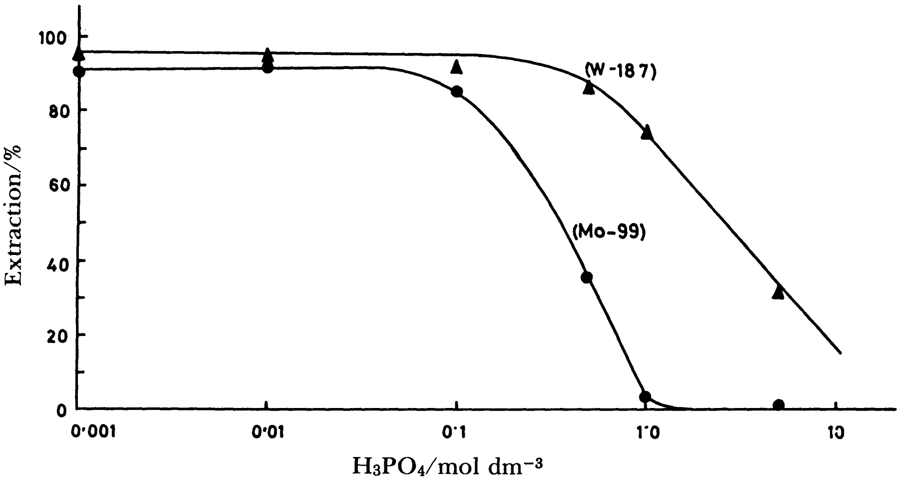

Fig. 1. Extractions of ^{99}Mo and ^{187}W with Aliquat 336 (ca. 10^{-4} mol dm^{-3}) at different concentrations of H$_3$PO$_4$.

Table 1. Extraction of Molybdenum and Tungstn from Different Acids at Different Concentrations with 10^{-4} mol dm^{-3} Aliquat 336 in Cyclohexan

Acid concentration/mol dm^{-3}	HCl		HNO$_3$		H$_2$SO$_4$		H$_3$PO$_4$	
	Mo/%	W/%	Mo/%	W/%	Mo/%	W/%	Mo/%	W/%
0.01	21.7	33.8	1.1	15.7	4.4	22.7	92.2	94.5
0.10	18.5	31.6	0.4	12.5	2.5	21.8	85.4	90.0
1.00	7.4	9.2	0.3	10.4	0.7	13.5	2.8	75.7
5.00	1.9	2.1	0.1	7.5	0.5	11.5	0.5	35.4

$[MoO_2]^{2+}$, $[MoO(OH)_2]^{2+}$, or $Mo_2O(OH)_8\cdot 2H_2O^{2+}$ [25] and in very strong acid it is present mainly as $[MoO_2]^{2+}$ [26,27] which are not extractable by the anionic extractant, Aliquat 336. But at comparatively lower acidity, the possibility of formation of heteropoly species like $H_3PMo_{12}O_{40}$[25] increases resulting in higher extraction of molybdenum by the reagent. Higher extraction of molybdenum with a quaternary ammonium salt at lower acidity as observed by us also corroborates to the findings of Akaiwa et al.[28] who reported that at higher acidity the extracted species, $(R_3R'N)_3PMo_{12}O_{40}$ changes to $(R_3R'N)_2HPMo_{12}O_{40}$ resulting in the decrease of extraction of molybdenum by the reagent. Similarly in strong acid solution the extraction of tungsten is low, but with decreasing acidity, the efficiency of extraction increases appreciably probably due to gradual formation of the heteropoly species like $H_3PW_{12}O_{40}\cdot xH_2O$ and ultimately the existence of varieties of polytungstate anions helps in complete extraction of tungsten by the reagent. The large variation in the distribution ratio values for molybdenum and tungsten which form almost similar types of complex species is perhaps due to the fact that the heteropoly anions of tungsten are in general more stable than those of molybdenum[25] and the existence of varieties of paratungsten anions in solution as well.

Studies on the effect of concentration of Aliquat 336 on the extraction of the elements concerned, as shown in Fig. 2, indicate that the distribution ratio values for molybdenum increase with increasing concentration of the extractant starting from ca. 10^{-4} mol dm^{-3} whereas almost complete extraction of tungsten is possible with the reagent at this concentration other parameters remaining same. Thus to avoid the possibility of contamination due to molybdenum, extraction of tungsten with the reagent of higher concentration is not favored.

The effect of diluents on the extraction behavior of the extractant in extracting the elements was studied with different diluents. Diluents like heptane, cyclohexane, carbon tetrachloride, benzene, and toluene having very close dielectric constant values (1.9—2.38)[29] behave similarly as there is no significant change in D values with change of diluents in the extraction systems. But in case of chloroform which has comparatively a higher dielectric constant value of 5.05, some variations in the D values were observed. It has been reported that the dielectric properties of the diluents effects the extraction efficiency of the extractant and the change in the D values as observed in the study was due to different dielectric constant value of chloroform.

In RPEC system, the extractions of both molybdenum and tungsten by the Aliquat 336 impregnated column in simple sodium hydroxide medium were found to be partial. However, presence of small amount of tartaric acid in alkaline medium containing the tracers, helps in complete extraction of the elements by the reagent in the column. The extracted elements are later separated by eluting molybdenum first and then tungsten with hydrochloric acid solution of 0.05 mol dm^{-3} and 0.1 mol dm^{-3} concentrations respectively (Fig. 3).

In alkaline medium, the oxoanions, MoO_4^{2-} and WO_4^{2-}, with hydroxy compound like tartaric acid form anionic complexes which are found to be totally extracted by the impregnated reagent. Under the experimental conditions, the anionic complexes[30,31]

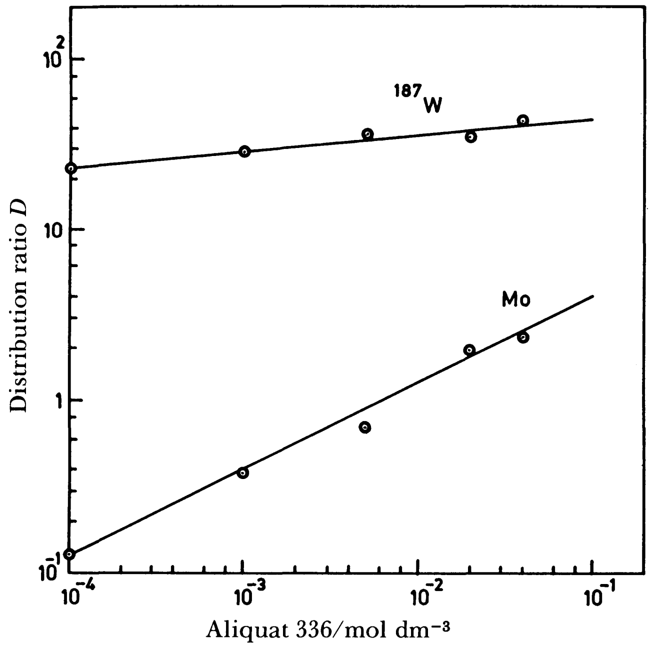

Fig. 2. Extractions of ^{99}Mo and ^{187}W from 1 mol dm^{-3} H_3PO_4 solution with Aliquat 336 solutions of different concentrations.

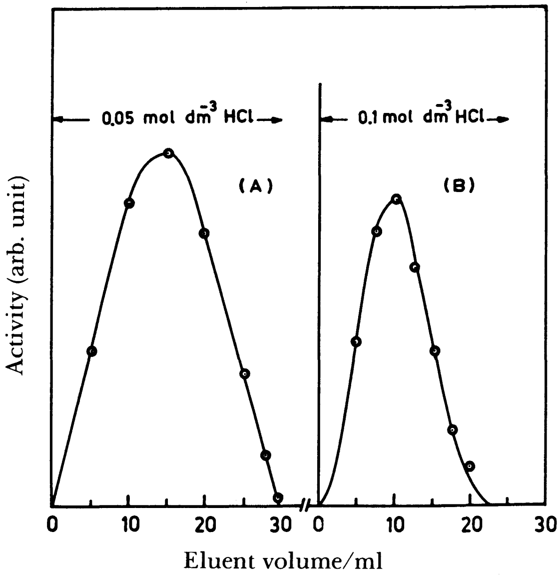

Fig. 3. Elution curves for ^{99}Mo and ^{187}W in RPEC: (A) elution of ^{99}Mo by 0.5 mol dm^{-3} HCl and (B) elution of ^{187}W by 0.1 mol dm^{-3} HCl.

formed by tungsten are comparatively more stable than those of molybdenum and it is expected that tungsten would be bonded more firmly to the reagent than that of molybdenum. Although the nature of anionic species are yet to be ascertained, but the experimental results corroborate the assumptions. For elution of tungsten species which are bonded strongly with the reagent, a solution comparatively of higher acid concentration is required.

Since both the elements in question form varieties of metal anion complexes, more or less of similar types, in different aqueous media, the general reaction responsible for extractions of the elements by the reagent in analogy of our previous investigations,[24,32] may be depicted as:

$$q\mathrm{R_3R'N^+Cl^-_{org}} + \mathrm{MX^{q-}_{aq}} \rightarrow (\mathrm{R_3R'N})_q\mathrm{MX_{org}} + q\mathrm{Cl^-_{aq}}$$

where MX^{q-} is the metal anionic species, $R_3R'N^+Cl^-$ is the quaternary salt having R="capryl" (C_8—C_{10} alkyl) group and R'=methyl group.

For both the techniques, the preliminary measurements of the radioactivities due to the respective isotopes, ^{99}Mo, ^{185}W, or ^{187}W, in different separated media were made by a GM counter. The purity of the separated elements were verified by taking recourse to gamma-ray spectrometry. The presence of molybdenum and tungsten in different phases were characterized by the photopeaks corresponding to the gamma energies of 140.5, 180.9, and 740.0 keV due to ^{99}Mo and of 72.3, 134.3, 479.3, 551.4, 618.1, 685.7, and 772.9 keV due to ^{187}W respectively. Typical gamma spectra of a mixture of the radiotracers, ^{99}Mo and ^{187}W and the isotopes in separated phases, as shown in Fig. 4, indicate complete separation of the elements through solvent extraction.

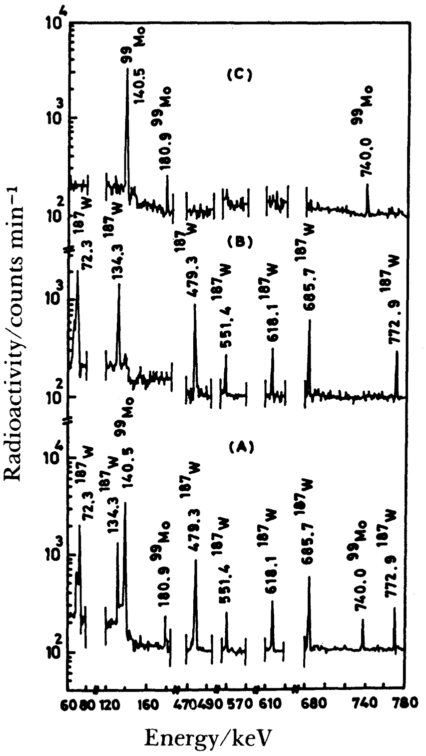

Fig. 4. Gamma-spectra of ^{99}Mo and ^{187}W in solvent extraction system: (A) a mixture of the radiotracers, ^{99}Mo and ^{187}W, (B), organic extractant (ca. 10^{-4} mol dm^{-3} Aliquat 336), and (C) aqueous phase left after extraction of ^{187}W.

As regards column meterial in RPEC system, Kieselguhr which has been used as inert solid support for the extractant has got the favorable properties of considerable chemical stability, higher absorbing capacity for the extractant and also the resistivity towards any nuclear radiation which is essential in any radiochemical studies.

The extraction profile of the elements under the experimental conditions shows that the methods of solvent extraction and RPEC are almost complementary to each other. The developed procedures are simple and effective in mutual separation of the elements in tracer concentrations. The methods are of considerable importance especially in the field of nuclear technology where the purity of the element is of prime importance.

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