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NOTE

Solvent Extraction of Molybdenum and Technetium with Alamine 336 from Acid Solutions

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Abstract

The distribution of Mo(VI) and Tc(VII) as molybdate and pertechnetate between Alamine 336 in benzene and other diluents and aqueous solutions of sulfuric and nitric acids was studied as a function of the concentration of acids and anions. The effect of the nature of the diluents and the presence of Tc on the extraction of Mo was studied.

INTRODUCTION

Molybdenum and technetium as ^{99}Mo and ^{99m}Tc in reactor coolant water need to be determined frequently. Since solvent extraction could be one of the techniques for isolating these isotopes from reactor water, studies were therefore undertaken to understand the solvent extraction chemistry of Mo(VI) and Tc(VII). In an earlier paper (*1*) the authors reported work on Mo(VI) and Tc(VII) extraction with tetraalkyl ammonium iodides from alkaline media.

EXPERIMENTAL

Alamine 336 was obtained from General Mills Corporation (U.S.A.) and was used as received. All other chemicals used in this study were of either E. Merck (G.R. Grade) or B.D.H. AnalaR quality. Extraction of molybdenum was studied from aqueous solutions of sulfuric and nitric acids. In both cases Alamine 336 in a suitable diluent formed the organic phase, after proper preequilibration. A weighed amount of ammonium molybdate, tagged with ^{99}Mo, was dissolved in acids of appropriate molarity, which were used as the aqueous phases. The molybdenum concentration in the aqueous phase in most of the experiments was kept constant at 1×10^{-3} *M*. Measurements were made by following the γ-activity of the tracer ^{99}Mo, both in the aqueous and organic phases. In the case of technetium, ammonium pertechnetate obtained from Oak Ridge National Laboratory was used. Its extraction from acid solutions was followed by measuring the optical density at 290 nm (a wavelength characteristic of pertechnetate ion) of the aqueous phase before and after the extraction. All the experiments were performed at 25 ± 1 °C by equilibrating the organic and aqueous phases in the volume ratio of 1:1 for 10 min and then separating the phases by centrifugal method.

RESULTS AND DISCUSSIONS

Extraction of Molybdenum

Studies from Sulfuric Acid System

Variation of Amine Concentration. The sulfuric acid concentration was kept constant at 1.0 *M* while the concentration of Alamine 336 in benzene was varied from 0.001 to 0.05 *M*. It was observed that the extraction of molybdenum increased from 18 to 90% with an increase of amine concentration.

Variation of Acid Concentration. In this set of experiments the amine concentration was kept constant at 0.003 *M* in benzene, and the sulfuric acid concentration was varied from 0.01 to 1.0 *M*. It was found that the extraction of molybdenum decreased from 96 to 50% with an increase of acid concentration.

Effect of Bisulfate/Sulfate Ions. To investigate whether the supression of molybdenum extraction at increased sulfuric acid concentration was due to the increase in H$^+$ concentration or due to competition from bisulfate or sulfate ions, the concentration of the latter was varied by the addition of ammonium sulfate to the aqueous acidic phase. The experiments were performed at a constant sulfuric acid concentration of 1.0 *M*. The amine concentration in benzene was kept constant at 0.003 *M*. The extraction of molybdenum initially increased from 49 to 66% with an increase in the sulfate ion concentration and then gradually decreased to 56%. These results indicated that in the acid range studied the extraction of molybdenum was influenced by bisulfate/sulfate ions. The extraction decreased due to the competition of these anions for the protonated amine species.

When a basic solution containing only $(MoO_4)^{2-}$ and ammonium or alkali metal ions is acidified, the molybdate ions condense in definite steps to form a series of polymolybdate ions. It has been shown (*2*) that the paramolybdate ion, $Mo_7O_{24}{}^{6-}$, and octamolybdate ion, $Mo_8O_{26}{}^{4-}$, in equilibrium seem to account for most of the chemistry in acid solutions. In view of the highly charged and polymeric nature of the extracting molybdenum species, it will not be appropriate to use log-log plots to arrive at the number of protonated amine group bound to the extracting species. However, the above observations clearly indicated that the extraction of molybdenum decreased with the increase in acid concentration which may be ascribed to the conversion of paramolybdate to octamolybdate.

Studies from Nitric Acid System

Variation of Amine Concentration. In this set of experiments, the nitric acid concentration was kept constant at 0.1 *M* and amine concentration in benzene was varied. The results showed a pattern similar to the observations made from sulfuric acid solutions. The extraction of molybdenum increased from 8 to 85%.

Variation of the Acid Concentration. At a fixed concentration of Alamine 336 (0.003 *M*), the extraction of molybdenum was studied by varying the acid concentration in the aqueous phase. It was observed that the percentage extraction decreased from 87 to 20% with an increase of nitric acid concentration from 0.01 to 0.5 *M*, similar to the results in sulfuric acid solutions.

Effect of Nitrate Ion Concentration. Alamine 336 concentration was kept constant at 0.003 *M* in benzene and the concentration of nitrate ions was varied from 0.01 to 0.07 *M* using ammonium nitrate in the aqueous phase of fixed nitric acid molarity (0.01 *M*). Once again the percentage extraction of molybdenum decreased from 87 to 59% with an increase in anion concentration.

It is apparent that the extraction behavior of molybdenum from nitric acid solutions with Alamine 336 in benzene is similar to the extraction behavior in sulfuric acid solutions, and the same explanation would hold good.

Effect of Change in Diluents

To study the effect of a change in diluents for Alamine 336, xylene, cyclohexane, and kerosene were selected for comparison with benzene from sulfuric acid solutions. (In fuel reprocessing operations, one of the diluents employed is Shell Sol T. Hence extraction studies from nitric acid medium were extended to cover this diluent also.) It was observed that the extraction of molybdenum from sulfuric acid and nitric acid decreased when aliphatic diluents were used as compared to aromatic or cyclic diluents. This fact was observed even when the extraction was studied at different acid concentrations with these diluents. In the case of each diluent, the extraction decreased with an increase of acid concentration, as expected. The decrease in the extraction with the aliphatic diluents indicated that extraction is through the formation of polymolybdate aggregates in the aqueous phase which are preferentially extracted into the aromatic or cyclic diluents containing amine salts. Such diluents are known for their ability to stabilize polymeric species (*3*).

Extraction of Technetium

The extraction of technitium (as pertechnetate) with Alamine 336 was similarly studied as a function of the nitric acid* concentration as well as that of the diluents (listed in the previous paragraph). Concentrations of technetium in the aqueous phase and Alamine 336 in the organic phase were kept constant at 5×10^{-4} and 0.003 *M*, respectively. The results are shown in Table 1.

It was observed that the percentage extraction of technetium decreases with an increase of acid concentration in the experiments where benzene, xylene, and Shell Sol T were used as the diluents for the amine. As in the case of molybdenum, these results also indicated that the acidity was an important factor in the extraction of technetium. But in the case of the other two diluents, viz., cyclohexane and kerosene, the percentage extraction of technetium initially increased with an increase of acid concentration up to 0.05 *M*. After reaching a maximum at this acid concentration, the extraction decreased with a further increase of acid in the aqueous phase. Thus nitric acid at higher concentration did influence the extraction pattern of pertechnetate. The diluent effects are difficult to comprehend in this case.

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*Even from 0.01 *M* sulfuric acid solution, pertechnetate was extracted up to 98%. Hence further detailed work was done from that medium.

TABLE 1

Effect of Change in Diluents on the Extraction of Technetium from Nitric Acid Solutions with Alamine 336 (0.003 *M*) in Diluents

HNO_3 conc (*M*)	% Extraction				
	Benzene	Xylene	Cyclohexane	Kerosene	Shell Sol T
0.01	93.8	96.6	57.3	70.1	82.1
0.03	84.0	87.9	86.1	86.0	75.4
0.05	77.8	84.3	87.3	86.6	71.7
0.07	73.1	80.5	86.3	84.6	67.4
0.1	64.2	75.9	84.9	83.4	59.3

Extraction of Molybdenum in Presence of Technetium

Since molybdenum is usually accompanied by technetium at comparable concentrations in reactor coolant water, it was worthwhile to study the extraction behavior of molybdenum in the presence of technetium. The aqueous phase of varying nitric acid concentration consisted of a mixture of 5×10^{-4} *M* each of Mo and Tc; as in the previous experiments the organic phase was Alamine 336 0.003 *M* in benzene. For comparison, the extraction of molybdenum alone was also studied under the identical conditions. The results (Table 2) showed that the presence of technetium did not have any significant influence on the extraction pattern of molybdenum.

TABLE 2

Extraction of Molybdenum in the Presence of Technetium from Nitric Acid Solutions (Aqueous phase: Mo 5×10^{-4} *M*, Tc 5×10^{-4} *M*; Organic phase Alamine 336 0.003 *M* in benzene)

HNO_3 conc (*M*)	% Extraction	
	MO + Tc	Mo alone[a]
0.01	90.5	93.3
0.03	77.6	82.5
0.05	66.9	67.6
0.07	51.8	54.5
0.1	32.8	32.2

[a] Concentration of molybdenum employed is different from what has been used in all other work.

CONCLUSIONS

The major conclusions of these studies are:

(1) At constant acid concentration, molybdenum extraction from sulfuric acid and nitric acid solutions increased with an increase of amine concentration in the range of 0.001 to 0.05 *M* in the organic phase.

(2) Molybdenum extraction decreased with an increase in sulfuric acid and nitric acid concentration in the range of 0.01 to 1.0 *M* and 0.01 to 0.5 *M*, respectively.

(3) Sulfate ions initially enhanced the extraction up to 1.03 *M*, but a further increase in sulfate ions decreased the extraction gradually. A gradual decrease of extraction was observed when nitrate ion concentration was increased in nitric acid solutions.

(4) Using various diluents (other than benzene) such as xylene, cyclohexane, kerosene, and Shell Sol T, it was observed that extraction of Mo from sulfuric acid and nitric acid solutions decreased in aliphatic diluents as compared to aromatic or cyclic diluents.

(5) The presence of Tc did not have a significant influence on Mo extraction.

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