A Effect of 7-bromo Substituent on Solid-Phase Extraction of Molybdenum(VI) With Hydrophobic 8-Quinolinol Derivatives-Impregnated Resin from Strong Acid Solutions

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Abstract
Solid-phase extraction (SPE) of molybdenum(VI) with hydrophobic 8-quinolinol derivatives (HQs)-impregnated resin from strong acid solutions has been investigated. The HQs used were 5-octyloxymethyl-8-quinolinol (HO$_8$Q), 7-bromo-5-octyloxymethyl-8-quinolinol (HBrO$_8$Q), and 7-bromo-5-dodecyloxymethyl-8-quinolinol (HBrO$_{12}$Q). Various factors affecting the SPE behavior, such as the substituents of the HQs, acid concentration in the aqueous solution, the HQ concentration in the resin, and the stirring time, were clarified. It was observed that the introduction of the bromo-group at the 7-position of HO$_8$Q is very useful for the enhancement of the extractability for Mo(VI) from strong acid solutions. The reusability of the HBrO$_8$Q-Resin for the SPE of Mo(VI) was also investigated. In three consecutive recycles, the HBrO$_8$Q-Resin did not reduce the extractability for Mo(VI) at all.

Introduction

Molybdenum readily forms hard and stable carbides. For this reason, molybdenum is often used in the steel industry. In addition, molybdenum is used in electrodes, catalysts, and so on. Therefore, molybdenum is an indispensable element for industrial products. It is thought that molybdenum become more and more necessary with growth of the world economy. The world's supply of molybdenum ore is occupied by only a few countries, such as the United States, Chile, China and Peru [1]. The recycle of molybdenum from the used industrial products is hardly performed because it is not viable. The development of recycling technology is needed to maintain a stable supply of molybdenum in the future.

Solvent extraction is widely used to separate and concentrate metal ions from aqueous solutions. However, solvent extraction has some restrictions and drawbacks due to use of toxic and flammable organic solvents, the contamination of the aqueous solution by the organic solvent, and the production of organic solvent wastes. Solid-phase extraction (SPE) has a less use of the organic solvents than solvent extraction. Moreover, SPE has some advantages such as complete phase separation and high concentration of an analyte. There are some reviews on the SPE of the various metal ions [2,3]. Interesting studies of the SPE of Mo(VI) with hydrophobic extractants, such as 8-quninolinol [4,5], 1-(2-thiazolylazo)-2-napthol [6], pyrrolidinedithiocarbamate [7], and pyrocatechol violet [8] were reported. However, there were few studies on the SPE of Mo(VI) from strong acid solutions.

8-Quinolinol derivatives (HQs) have been known as good chelating reagents, because they can form the stable complexes with various metal ions [9,10]. In the solvent extraction, we previously found that 7-bromo-5-octyloxymethyl-8-quinolinol (HBrO$_8$Q) was a more useful extractant for Mo(VI) in the strong acid solutions than 5-octyloxymethyl-8-quinolinol (HO$_8$Q) [11]. The charge density on the nitrogen atom of HBrO$_8$Q is lower than that of HO$_8$Q, because the bromo-group of HBrO$_8$Q is electron-attracting. Therefore, HBrO$_8$Q is hard to relatively form the protonated species. It is thought that this HBrO$_8$Q's characteristic favors the formation of the complex with metal ions in strong acid solutions.

In this study, we investigate the SPE of Mo(VI) from strong acid solutions with the hydrophobic HQ-impregnated resins and clarify various factors affecting the SPE behavior, such as the substituents of the HQs, acid concentration in the aqueous phase, and the HQ concentration in the resin.

Experimental

Reagents

The structures of the HQs used in the SPE are illustrated in Fig. 1. HO$_8$Q and HBrO$_8$Q were synthesized according to the methods described in the previous works [12,13]. The synthetic and purification procedures of 7-Bromo-5-dodecyloxymethyl-8-quinolinol (HBrO$_{12}$Q) obeyed those of HBrO$_8$Q. The purities of HQs synthesized were confirmed by an elemental analysis, HPLC and ^{1}H-NMR.

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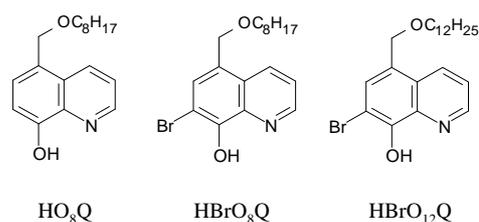

Figure 1. Structures of 8-quinolinol derivatives used in this study.

A molybdenum(VI) stock solution was prepared by dissolving hexaammonium heptamolybdate tetrahydrate (Kanto Chemical, GR) with water. High porous resin Diaion HP-20, which is a styrene-divinylbenzene copolymer, was obtained from Mitsubishi Chemicals Co. (Tokyo, Japan) and used as the solid phase. Physical properties of this resin are as follows: specific surface area, 500 m^2 g^{-1}; specific pore volume, 1.3 cm^3 g^{-1}; average pore diameter, 26.0 nm; particle size, 250-841 μm. Water was doubly distilled and further purified with Milli-Q (Millipore) equipment. All other chemicals were of analytical reagent grade.

Apparatus

Stirring of the mixture was performed with an *in vitro* shaker (SHAKER "MINI" SS-80, Tokyo Rikakiki Co. Ltd.) or a tube rotator (TR-350, AS ONE Corporation). The determination of Mo(VI) was performed with an inductively coupled plasma atomic-emission spectrometer (ICP-AES, Nippon Jurrell Ash ICAP-575) at 379.825 nm and 550 V. A UV-Vis spectrum was measured with a JASCO 560 spectrophotometer. The pH measurements were performed by a Radiometer PHM93 pH meter.

Preparation of HQ-impregnated resin

Resins were washed with methanol, 5 M NaOH, 6 M HCl, and acetone in ultrasonic cleaning equipment each for 10-15 min, and then dried. The dry resins (1.0 g) were immersed in an HQ acetone solution (8 ml). The concentrations ($[HQ]_{init}$) of HO_8Q, $HBrO_8Q$, and $HBrO_{12}Q$ in the acetone solutions used were 0.11, 0.03, and 0.01 M, respectively. The resins in the HQ acetone solution were stirred with the *in vitro* shaker for 15 min. Then, water (0.5 ml) was added to promote the impregnation of HQ onto the resin and stirred for another 30 min. After standing for 24 h, the resins were filtered and washed with 3 M NaOH, 2 M HCl, and water each for 10 min. The wet HQ-impregnated resins (HQ-Resins) prepared were preserved in water.

Property of HQ-impregnated resins

A 0.3-g portion of HQ-Resins was immersed in acetone (2.5 ml). After stirring for 1 h, the supernatant liquid was decanted. These procedures were repeated 2 times. The HQ acetone solution decanted was evaporated and HQ deposited was dissolved in chloroform. The HQ concentration in chloroform was determined by UV-Vis spectrophotometer to calculate the concentration of HQ on the HQ-Resin. The resins after the HQ removal were dried in an oven at 110 °C until a constant weight was obtained. Water content of resin was obtained from the difference in the weight of resin before and after dryness.

Elution of HQ from HQ-Resin by acid

The elution of HQ from the HQ-Resins by acid was performed as follows: Wet HQ-Resins (0.7 g) were immersed in 4 M HNO_3 solution (7 ml). After stirring for 6 h, the supernatant solution was taken out. The resulting solution was measured by UV-Vis spectrophotometer to determine the eluted amount of HQ from the HQ-Resins into the aqueous acid solution.

Solid-phase extraction procedure

An aqueous Mo(VI) solution (10 ml, 1.0 x 10^{-4} M) and wet HQ-Resins (1.0 g) were taken in a test tube with a glass stopper. After stirring for 6 h, the supernatant was decanted and the amount of Mo(VI) in the solution was measured by ICP-AES to obtain the extraction percentage ($\%E_{sp}$) of molybdenum(VI) to the HQ-Resins. The acid concentration was changed with HNO_3 or H_2SO_4 from 2 to 8 M.

The elution of Mo(VI) from the HQ-Resins was performed as follows: The resins after SPE were washed with water. In order to elute Mo(VI), they were stirred in 2 M aqueous ammonia (10 ml) for 1 h three times. The eluent was removed and the Mo(VI) concentration in the eluent was determined by ICP-AES. The recovery percentage ($\%R$) was calculated using the initial amount of Mo(VI) on the HQ-Resins and the amount eluted.

Reusability test of HQ-resin

The reusability of the $HBrO_8Q$-Resin was investigated in three consecutive recycles. The extractions were identical with the other batch tests. The SPEs of Mo(VI) were performed with 1.0 g $HBrO_8Q$-Resins containing 5.3 x 10^{-2} mol kg^{-1} $HBrO_8Q$ from 4 M HNO_3 solution (10 ml). Stripping of Mo(VI) from the $HBrO_8Q$-Resins was conducted by shaking the $HBrO_8Q$-Resins in 2 M aqueous ammonia (10 ml) for 1 h three times. The concentration of Mo(VI) in the solutions was measured by ICP-AES. The $\%E_{sp}$ and $\%R$ values in each experiment were determined from the concentration of Mo(VI) in the solution and the mass balance

Results and Discussion

Analysis of HQ-Resin

The wet HQ-Resin prepared as the solid-phase was evaluated in terms of the HQ concentration in HQ-Resin ($[HQ]_{wet}$ in mol kg^{-1}) and water content of resin ($[H_2O]_{wet}$ in %w/w) that are defined as follows:

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(1)

$$[\dot{HQ}]_{wet} = \frac{\text{Amount of HQ on Wet HQ-Resin (mol)}}{\text{Weight of Wet HQ-Resin (kg)}}$$

(2)

$$[H_2O]_{wet} = \frac{\text{Weight of water in Wet HQ-Resin (kg)}}{\text{Weight of Wet HQ-Resin (kg)}} \times 100$$

Table 1 demonstrates the results of the analysis of HQ-Resins. The $[HQ]_{wet}$ value became larger in the following order: $HBrO_{12}Q < HBrO_8Q < HO_8Q$. This order follows the order of the HQ concentration in acetone used to prepare the HQ-Resins. In the cases of $HBrO_8Q$ and $HBrO_{12}Q$, it was difficult to prepare the HQ-Resins containing a larger amount of $HBrO_8Q$ or $HBrO_{12}Q$ molecules, because the solubilities of $HBrO_8Q$ and $HBrO_{12}Q$ in acetone are lower than that of HO_8Q. The $[H_2O]_{wet}$ value was almost the same among three kinds of the HQ-Resins.

The elution of HQ from the HQ-Resins by acid was performed using the $HBrO_8Q$-Resins. The elution percentage of $HBrO_8Q$ was less than 1.4 %. Therefore, it is thought that the elution of HQ from the HQ-Resin by acid was able to be disregarded.

Solid-phase extraction behavior

SPE of Mo(VI) was performed using wet HQ-Resins. The $\%E_{sp}$ of Mo(VI) was defined as:

(3)

$$\%E_{sp}{}' = \frac{[Mo(VI)]_{init} - [Mo(VI)]_f}{[Mo(VI)]_{init}} \times 100$$

where the subscripts init and f denote the aqueous phases before and after the SPE, respectively. The effects of stirring time on the SPE of Mo(VI) from the HNO_3 and H_2SO_4 solutions with the HQ-Resins were investigated. Figure 2 shows the plots of $\%E_{sp}$ against the stirring time among each HQ-Resin. In all cases, the $\%E_{sp}$ of Mo(VI) from strong acid solutions gradually increased and reached a constant value at 6 h. Therefore, the stirring time in the subsequent extractions was fixed to 6 h.
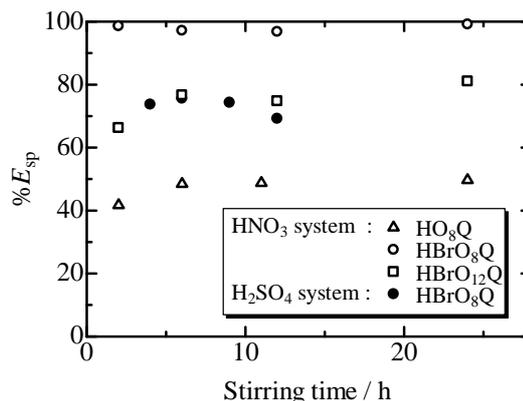

Figure 2. A. Ohashi, et. al.

The SPE behaviors of Mo(VI) from HNO_3 and H_2SO_4 solutions with HQ-Resins were investigated. Figure 3 shows the effect of acid concentration on the SPE of Mo(VI) with HQ-Resins. The HQ concentration in HQ-Resin used to the SPE was 0.11 mol kg^{-1} for HO_8Q, 5.5 x 10^{-2} mol kg^{-1} for $HBrO_8Q$, and 1.5 x 10^{-2} mol kg^{-1} for $HBrO_{12}Q$. Molybdenum(VI) was completely extracted with $HBrO_8Q$-Resins even from strong acid solutions of HNO_3 or H_2SO_4 as high as 4 M.
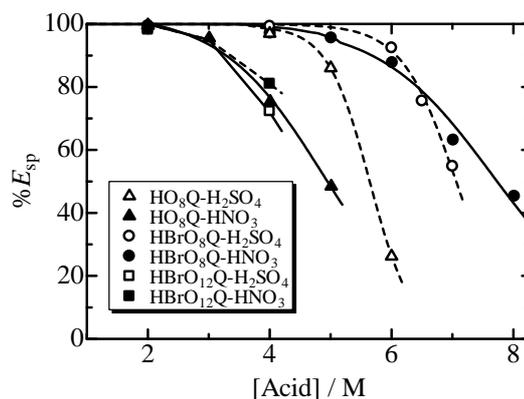

Figure 3. Effect of the acid concentration on the solid-phase extraction of Mo(VI) with the HQ-Resins. Weight of HQ-Resins, 1.0 g; $[Mo(VI)]$ = 1.0 x 10^{-4} M; $[HO_8Q]_{wet}$ = 0.11 mol kg^{-1}; $[HBrO_8Q]_{wet}$ = 5.4 x 10^{-2} mol kg^{-1}; $[HBrO_{12}Q]_{wet}$ = 1.5 x 10^{-2} mol kg^{-1}, volume of aqueous solution, 10 ml.

Table 1 HQ concentration in wet HQ-Resin prepared

HQ	$[HQ]_{init}$ / M	$[HQ]_{wet}$ / mol kg^{-1}	$[H_2O]_{wet}$ / %w/w
HO_8Q	0.11	0.13	64
$HBrO_8Q$	0.03	0.053	64
$HBrO_{12}Q$	0.01	0.014	63

HBrO$_8$Q-Resin demonstrated the higher extractability for Mo(VI) than HO$_8$Q-Resin, although the concentration of HBrO$_8$Q in the resin was about one-half of that of HO$_8$Q. This result implies that the introduction of the bromo-group at the 7-position of HO$_8$Q is very useful for the enhancement of the extractability for Mo(VI) from strong acid solutions. As mentioned above, HO$_8$Q tends to form the protonated species than HBrO$_8$Q does. The protonation of HO$_8$Q in acid concentration region may be difficult to form the complex with Mo(VI). The extractability of HBrO$_{12}$Q-Resin was lower than that of HBrO$_8$Q-Resin. This may be the result of the lower concentration of HBrO$_{12}$Q in the resin. The SPE of Mo(VI) was also investigated from 4 M HNO$_3$ with the HBrO$_8$Q-Resins and the HBrO$_{12}$Q-Resins of the same HQ concentration (1.5 x 10^{-2} mol kg^{-1}). In this case, the %E_{sp} value with the HBrO$_8$Q-Resins (71 %) was smaller than that with the HBrO$_{12}$Q-Resins (81 %). This implied that the extractability of the HBrO$_{12}$Q-Resin for Mo(VI) from the strong acid solutions is larger than that of HBrO$_8$Q-Resin in the case of the same HQ concentration. However, as mentioned above, it is difficult to prepare the HBrO$_{12}$Q-Resin of the higher HBrO$_{12}$Q concentration. Therefore, the subsequent extractions were performed using the HBrO$_8$Q-Resins.
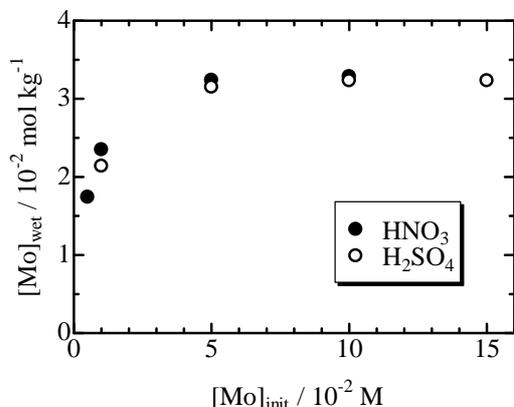

Figure 4. Relationship between the initial concentration of Mo(VI) and the concentration of Mo(VI) extracted onto the HBrO$_8$Q-Resins.
Weight of HBrO$_8$Q-Resins, 0.5 g; [HBrO$_8$Q]$_{wet}$ = 5.4 x 10^{-2} mol kg^{-1}; volume of aqueous solution, 5 ml.

Maximum loading tests of Mo(VI) were carried out using the HBrO$_8$Q-Resin (0.5 g) containing 5.4 x 10^{-2} mol kg^{-1} HBrO$_8$Q at 4 M HNO$_3$ and H$_2$SO$_4$ (Fig. 4). The initial concentration of Mo(VI) in the aqueous phase (5 ml) ranged from 0.005 to 0.15 M. The concentration of Mo(VI) loaded onto the HBrO$_8$Q-Resin ([Mo]$_{wet}$) became almost constant (3.2 x 10^{-2} mol kg^{-1}) in both HNO$_3$ and H$_2$SO$_4$ systems. From this value, [HBrO$_8$Q]$_{wet}$/[Mo]$_{wet}$, which is the number of coordinating ligands for a molybdenum(VI) ion, was calculated as 1.7. In the solvent extraction, it was well known that Mo(VI) was extracted with HQs into chloroform as MoO$_2$(Q)$_2$ [14]. Therefore, it is expected that Mo(VI) is extracted with HBrO$_8$Q into the polystyrene phase as MoO$_2$(BrO$_8$Q)$_2$ in the SPE.

It is important to accomplish an easy recovery of Mo(VI) from the HBrO$_8$Q-Resin. The elution behavior of Mo(VI) from wet HBrO$_8$Q-Resin was investigated. The recovery percentage (%R) of Mo(VI) from the HBrO$_8$Q-Resin after SPE was obtained with 2 M aqueous ammonia as 93 ± 2 % (n = 6). Relative high recovery percentage of Mo(VI) from the HBrO$_8$Q-Resin was able to be accomplished. Consequently, it was found that almost all Mo(VI) can be recovered from the HBrO$_8$Q-Resins after SPE.

Finally, the reusability of the HBrO$_8$Q-Resins was investigated. Figure 5 shows the results of SPE in three consecutive recycles. Molybdenum(VI) was quantitatively extracted with the HBrO$_8$Q-Resins and the extractability of the HBrO$_8$Q-Resins for Mo(VI) hardly dropped with the successive recycling. Moreover, almost all Mo(VI) can be recovered from the HBrO$_8$Q-Resins after SPE during each recycle. These results demonstrates that the SPE using the HBrO$_8$Q-Resins can be applied to the extraction method of Mo(VI) from a real sample such as industrial and nuclear liquid wastes.
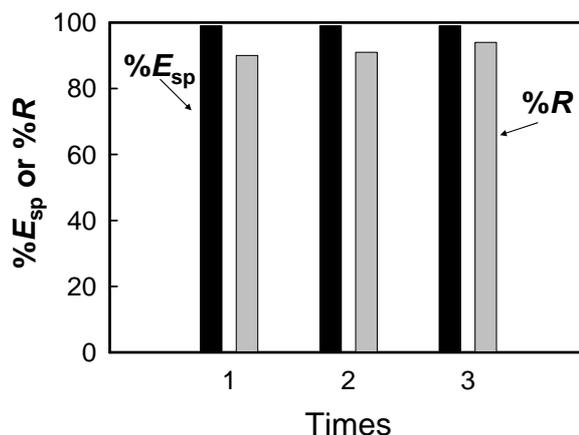

Figure 5. Result of recycle tests of the HBrO$_8$Q-Resin. Weight of HBrO$_8$Q-Resins, 1.0 g; [Mo(VI)] = 1.0 x 10^{-4} M; [HBrO$_8$Q]$_{wet}$ = 5.4 x 10^{-2} mol kg^{-1}; volume of aqueous solution, 10 ml. Extraction, 4 M HNO$_3$; elution, 2 M aqueous ammonia.

Conclusion

In the present study, the SPE of Mo(VI) with the HQs-Resins from strong acid solutions has been investigated. The effects of the substituents of the HQs on the extractability of Mo(VI) were clarified. The result obtained in this study demonstrates that the introduction of the bromo-group at the 7-position of HO$_8$Q is very useful for the enhancement of the extractability for Mo(VI) from strong acid solutions. The investigation on the reusability of the HBrO$_8$Q-Resins for the SPE of Mo(VI) demonstrates that the capability of the HBrO$_8$Q-Resins does not change with successive recycling steps. The SPE proposed in this study can be an alternative separation method of

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Mo(VI) from strong acid solutions in the conventional extraction.

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