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Selective Separation of Vanadium from Molybdenum Using D_2EHPA-Immobilized Amberlite XAD-4 Resin

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ABSTRACT

This article presents the preparation of a new type of metal ion selective resin based on phosphoric acid functionality and its application on the separation of Mo and V ions. The metal ion selective resin can be prepared by immobilizing D_2EHPA onto the surface of porous Amberlite XAD-4 resin, employing a solvent–nonsolvent process. The amount of immobilized D_2EHPA is as high as 2.5 (mmole D_2EHPA/g of resin). Solvent extraction experiments indicated that D_2EHPA can extract more Mo ion than V ion. The separation of Mo and V ions is best accomplished at pH 6. Adsorption isotherm experimental results show that D_2EHPA-modified Amberlite XAD-4 resin can also adsorb more

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Mo ion than V ion. Within the range of experiment, the amount of adsorbed Mo ion can be as high as 0.04 (mole Mo/mole D_2EHPA), while the amount of adsorbed V ion is less than 0.01 (mole V/mole D_2EHPA). However, due to the formation of polyion in high concentration solution, the Mo ion distribution ratio between modified resin and liquid phase decreases with increasing Mo ion concentration. The initial concentration of Mo ion should be lower than 0.01 M to have effective separation results. The selective extraction results using series contacts of solution mixtures with resins further demonstrated the feasibility of D_2EHPA-immobilized Amberlite XAD-4 resin for the separation of Mo/V mixed ion solution. After only seven batches of contacts, the relative ion concentration of V ion increased from 67% to more than 96%, while the relative ion concentration of Mo ion decreased from 33% to less than 4%.

Key Words: Separation technology; Mo and V ions; Hydrometallurgy; D_2EHPA; Amberlite XAD4 resin; Spent catalyst.

INTRODUCTION

Waste hydroprocessing catalysts were identified as a potential source of Ni, Mo, and V.[1] Among these metals, Ni and Mo are the catalytic compounds of the waste hydroprocessing catalyst, while V is mainly from the petroleum crude. The presence of vanadium in petroleum crude is a problem in the hydroprocessing process, since catalysts can be poisoned by vanadium.[2] The spent catalyst can be regenerated for reuse or recycled for metal values. It is estimated that in the United States every year more than 26 million pounds of these metals are discharged in waste catalysts and less than half of these metals are recovered or recycled.[3] The recycling of valuable metals from spent catalysts generated by the petroleum industry has been intensively studied in the past few years.[4–6] One separation method is based on the selective dissolution of these metals from the spent catalyst. A two-step alkali–acid procedure was proposed for the selective dissolution of critical metals from spent catalyst.[6] Another way to recover these valuable metals is to unselectively dissolve these valuable metals using an acid solution followed by a metal ion separation process.[7–9]

Henry and Van Lierde[10] developed an electrochemically assisted ion exchange process for selective elution of vanadium co-adsorbed with molybdenum on Amberlite IRA 94S resin.

In our previous study,[11] it was demonstrated that Ni ion can be separated from Mo and V ions using Amberlite 200 ion exchange resin operating at pH 6. Zhang et al. showed that LIX63 can extract V and Mo from sulfuric acid solutions preferentially at pH 1.5, while the other coexisting metal ions remain in the aqueous solution.[4] TOA can be used to separate the V from Mo ions in the leaching solution.[12] Nevertheless, most of the proposed processes for Mo and V ions separation were mainly based on solvent extraction process, which suffered from the process inflexibility and possible secondary environmental concerns.

Extractant-modified ion exchangers show many advantageous over solvent extraction. These materials have high metal ions distribution and selectivity factors due to the impregnated extractant. These materials also have better equipment and operation simplicity due to solid-ion-exchange technology. Extractant-modified ion exchanger can be produced either by the impregnation of a porous carrier using a liquid extractant[13,14] or extractant introduction during porous matrix synthesis.[15] Applications of these systems in metal extraction and recovery[16–19] and analytical processes[20–22] have been investigated.

This study focused on the separation process of Mo ion from V metal ion. Vanadium and molybdenum have very similar chemical properties. These similarities effect similar responses to various solvent extraction systems, resulting in separation difficulty. The purpose of this research was to develop a new type of D_2EHPA extractant-immobilized Amberlite XAD-4 resin for the separation of V from Mo metal ion. In our previous study, it was reported that D_2EHPA can be impregnated into functionalized Amberlite 200 to prepare an extractant impregnated resin (EIR), which showed good V and Mo ions separation efficiency over 90%.[11] D_2EHPA has distinct metal ion extraction behaviors toward Mo and V ions. D_2EHPA effectively extracts V ion only at pH lower than 3, while the D_2EHPA can effectively extract Mo ion at pH as high as 6. Therefore, D_2EHPA was chosen as candidate extractant. Since D_2EHPA shows surface activity, a two-step solvent–nonsolvent procedure was proposed to immobilize D_2EHPA on Amberlite XAD-4 surface. In addition, since D_2EHPA is not soluble in aqueous solution, immobilized D_2EHPA can maintain good stability on Amberlite XAD-4 resin. Therefore, separation of V and Mo ions can be achieved by D_2EHPA-modified resin. The effects of pH and the amount of metal ions concentrations on metal ion adsorption behavior on D_2EHPA-modified Amberlite XAD-4 resin was investigated. Selective separation results further demonstrated the feasibility of using D_2EHPA-modified XAD resin for the separation of mixed V and Mo metal ions.

EXPERIMENTAL

Reagents and Chemicals

D_2EHPA [di(2-ethylhexyl)phosphoric acid] was provided by Daihachi Chemical Industry Co., Ltd. Japan. Amberlite XAD-4, size 20 to 50 mesh, was supplied by Fluka, Germany. Sodium hydroxide (NaOH, pellets GR for analysis) and ethanol (C_2H_5OH, absolute ACS) were from Merck, Inc. Metal ion synthetic solutions of known concentration were prepared by dissolving an appropriate salt in distilled and deionized water: sodium vanadate ($NaVO_3$) (Fluka), sodium molybdate dihydrate (Merck), nickel nitrate 6-hydrate (Ridel-de Haën). The pH was controlled by the addition of sulfuric acid and sodium hydroxide to control the pH at desired levels.

Solvent–Nonsolvent Immobilization Process

Cleaning of Amberlite XAD-4 Resin

In this study, Amberlite XAD-4, a hydrophobic resin, was subjected to a pretreatment sequence before the immobilization process. Amberlite XAD-4 was kept in contact with a 50% methanol–water solution containing 4-M HCl for 12 hours to eliminate impurities.[23] Amberlite XAD-4 was then immersed in distilled and deionized water for 12 hours to remove the residual methanol from the resin.

D_2EHPA Immobilization

Amberlite XAD-4 is a polystyrene-based and nonpolar resin without functionality. Water/ethanol mixture (50/50) can expand the matrix structure of Amberlite XAD-4 to some extent. In addition, water/ethanol mixture is also a solvent for D_2EHPA at a concentration as high as 20%. Therefore, the alkyl group of D_2EHPA will embed into the swollen resin, provided that the contact time is long enough. After the immobilization, the residual ethanol was removed by the addition of water. The hydrophobic characteristic of Amberlite XAD resin was changed to hydrophilic due to presence of the phosphoric acid group. The extractant-modified Amberlite XAD-4 resin was immersed in deionized water for 24 hours to further eliminate loosely bounded extractant inside the resin pores. The prepared resin was then ready for metal ion separation.

Determination of the Amount of Impregnated Extractant in Resin

The extractants investigated in this study were acid type. After washing the impregnated resin with distilled and deionized water, the amount of extractant was, then, determined using NaOH titration.

Metal Ions Extraction Isotherm

The extractions of V and Mo ions by modified resin were carried out using batch extraction isotherm experiments at 25°C. A known amount of resin was immersed in ion solutions with different ion concentration for 30 min at 25°C. The liquid phase was sampled to determine the ion concentration using an atomic adsorption spectrometer, Perkin Elmer AA 100.

The extraction of metal ions by D_2EHPA extractant was studied using liquid–liquid extraction. The extractant concentration was 20% using kerosene as a solvent. The volume ratio of aqueous phase to organic phase was 1:1. After 30 min of vigorous mixing, the aqueous phase was sampled and the metal ion concentrations in the aqueous solution were determined using an atomic adsorption spectrometer.

Metal Ion Selective Separation

Selective separation was conducted using a sequential contact of a metal ion solution with modified resin. Considering a series of contactors containing impregnated resin, a quantity of mixed ions solution was added to the first contactor (solid:liquid weight ratio equal to 1:5). After 30 min of mixing, the solution was decanted and added to the second contactor containing modified resin. The solid:liquid weight ratio was maintained at the same level by adjusting the amount of resin. The sequence was repeated for a series of ten contacts. The solution was sampled and the metal ion concentrations were determined after each contact.

RESULTS AND DISCUSSION

Conventional methods for the separation of Mo and V ions from the leaching solution of hydrodesulfurization waste catalyst are solvent extraction and, to a lesser extent, ion exchange.[7,24] In the ion exchange resin process, Mo and V ions are both adsorbed at pH 4 on to a tertiary amine resin, such as Amberlite IRA 94S.[10] After washing, V is selectively eluted with a reductive acid solution, then, Mo is eluted with a concentrated ammoniacal eluant.[10] Most of the ion exchange separation processes for Mo and V ions are based on the different elution behavior of these two metal ions. In this study, a new type of resin with D_2EHPA as the complexing functional group was prepared for the separation of Mo and V metal ions. The separation mechanism was based on the different adsorption affinity of Mo and V by D_2EHPA immobilized on Amberlite XAD-4 resin.

Immobilization of D_2EHPA on Amberlite XAD-4

D_2EHPA contains two alkyl groups attached to a polar phosphoric acid group. It is, therefore, expected that D_2EHPA will posses some degree of surface active property. Since the Amberlite XAD-4 resin is a nonpolar polystyrene matrix resin, the alkyl group of D_2EHPA can be embedded into the polystyrene matrix of Amberlite XAD-4 resin by suitable blending process. Pre-experiment showed that water/ethanol mixture (50/50) can expand the matrix of Amberlite XAD-4 resin and is also a good solvent for D_2EHPA. Therefore, a solvent–nonsolvent process can immobilize D_2EHPA on the surface of Amberlite XAD-4 resin through the entanglement of the alkyl groups of D_2EHPA with polystyrene matrix of resin. The surface active nature of D_2EHPA was first demonstrated by measuring the surface tension of water/ethanol mixture (50/50) in the presence of D_2EHPA. The surface tension of water/ethanol/D_2EHPA mixture was determined by drop-weight method. Figure 1 shows the effect of D_2EHPA concentration on the surface tension of water/ethanol mixture (50/50). The results show that the surface tension first decreases with increasing D_2EHPA concentration. The surface tension reaches a lowest value of 2.06×10^{-2} (N/m) as D_2EHPA concentration equals 5%. Apparently, the decrease of surface tension is due to the surface active property of D_2EHPA. Then, the surface tension starts increasing slightly with further increases of D_2EHPA concentration. As D_2EHPA concentration exceeds 20%, a phase separation of the mixture was observed. This surface active behavior of D_2EHPA provides a potential application of D_2EHPA-immobilized Amberlite XAD-4 resin. Since Amberlite XAD-4 is polystyrene based nonpolar resin containing no functional group, modified Amberlite XAD-4 will exhibit D_2EHPA functionality for metal ions separation purpose.

The amount of immobilized D_2EHPA was determined by NaOH titration. Figure 2 shows the titration curve of D_2EHPA-immobilized resin. The D_2EHPA-modified Amberlite XAD-4 resin showed a typically weak

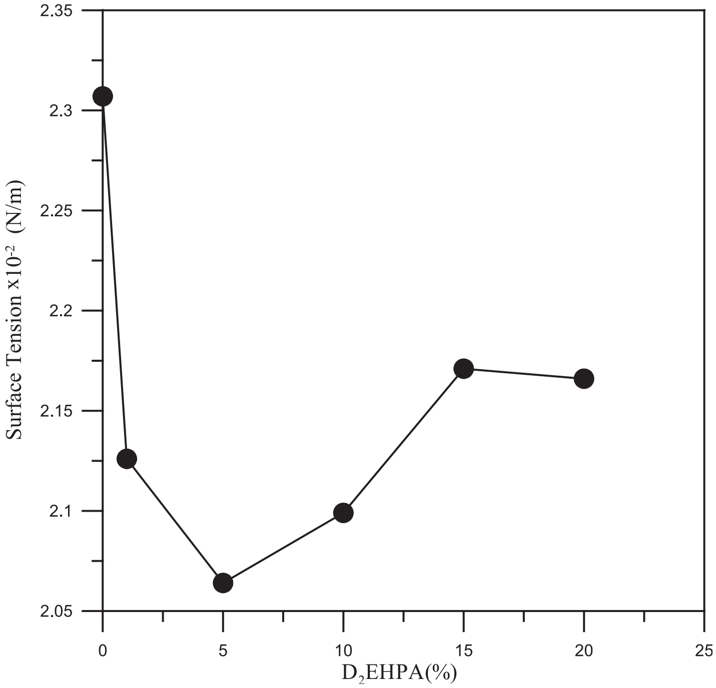

Figure 1. Effect of D_2EHPA concentration on the surface tension of water/ethanol mixture (50/50).

acid titration curve. From the titration curve, it is estimated that 1 g of Amberlite XAD-4 resin contains approximately 2.5 mmole of D_2EHPA. The level of functionality is comparable with many commercially available selective resins. This amount of D_2EHPA can provide the modified Amberlite XAD-4 resin with a high level of metal ion adsorption capability. It is also important to point out that after modification, the surface property of resin was changed from hydrophobic to hydrophilic surface due to the exposure of polar phosphoric acid group of D_2EHPA at the surface of resin. The water content of the modified resin was determined to be about 0.48 g/g of resin, indicating that most of the pores are filled with water since the porosity volume of Amberlite XAD-4 is about 50%, as specified by the provider (Fluka). The hydrophilic characteristic of D_2EHPA-modified resin is also an essential property for the extraction of metal ion from aqueous solution since more surface of the hydrophilic resin becomes accessible to the metal ion in aqueous solution for adsorption to take place.

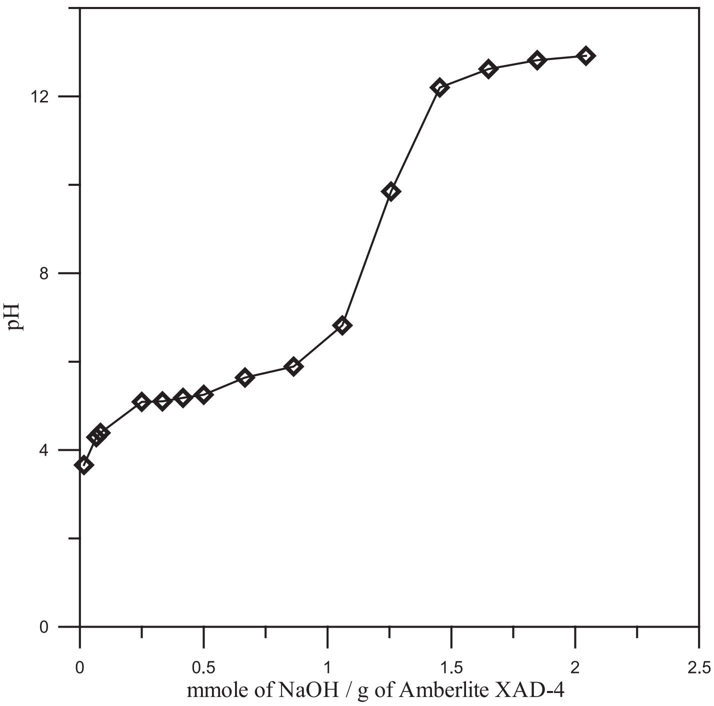

Figure 2. The titration curve of D_2EHPA-immobilized resin.

Extraction Behavior of Mo and V Ions by D_2EHPA Solvent Extraction

Extraction in Single-Ion Solution

Solvent extraction experiments of Mo and V ions using D_2EHPA were conducted to investigate the effects of pH and metal ion concentration on the extraction behavior of D_2EHPA. Pre-experiments showed that 20% (v/v) D_2EHPA in kerosene solution is the optimal concentration for the extraction phase (O/W = 1/1). The following extraction experiments were all conducted with this composition. Figure 3 shows the pH effect on the extractions of Mo ion and V ion (0.01 M) by D_2EHPA/kerosene solution. At pH 1, D_2EHPA can extract more than 95% of Mo ion from aqueous phase and the extraction of V ions is also as high as 64%. The extraction percentage of Mo remains higher than 95% for pH as high as 6. On the

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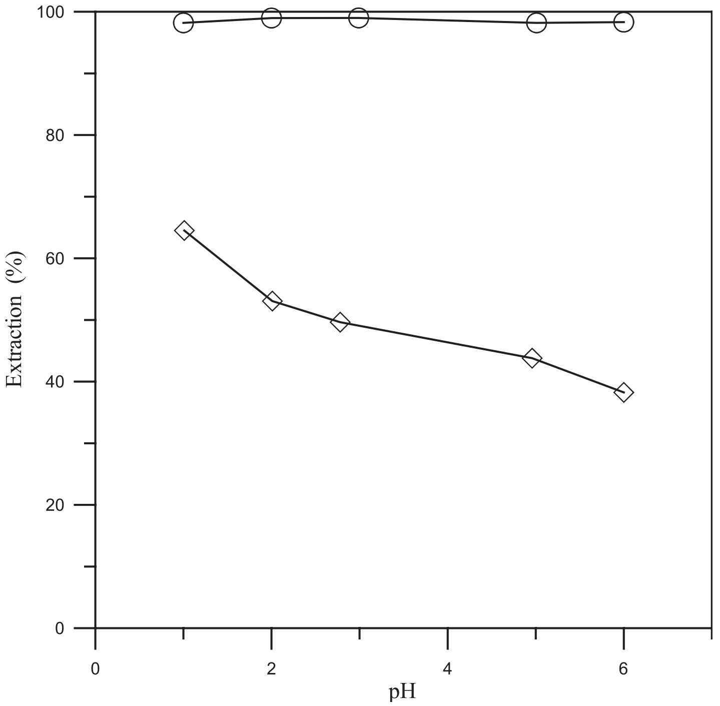

Figure 3. The pH effect on the extractions of Mo ion (○) and V ion (◇) by D_2EHPA/kerosene solution (25%). The initial concentrations of Mo and V ions are both equal to 0.01 M.

other hand, the extraction percentage of V decreases with increasing pH. At pH 6, the extraction percentage of V ion decreases to 40%. This observation is consistent with previous study.[8] Table 1 also shows the amount of metal ion extracted by per mole of D_2EHPA. The amount of extracted Mo ion remains about $0.017 \sim 0.018$ (mole Mo/mole D_2EHPA) for pH between 1 and 6. The amount of extracted V ion, on the other hand, decreases from 0.011 to 0.006 (mole V/mole D_2EHPA) for pH increases from 1 to 6. The extraction ratio for Mo over V, consequently, increases from 1.55 to 3.0. It is, therefore, expected that separation of V and Mo ions by D_2EHPA is more effective at pH 6 than at pH 1.

Metal ion concentration is also an important factor that affects the extraction efficiency. This is especially important for metal ions that can form polyions at higher concentration, such as Mo and V ions. Figure 4 shows the effects of initial metal ion concentration on the extraction of Mo

Table 1. Amount of metal ion extracted by per mole of D_2EHPA in the solvent extraction of single-ion solution.

V		Mo	
pH	Mole metal/mole D_2EHPA	pH	Mole metal/mole D_2EHPA
1.01	0.0107	1.01	0.0171
2.01	0.0089	2.02	0.0172
2.78	0.0081	2.99	0.0172
4.96	0.0071	5.01	0.0171
6.00	0.0060	6.00	0.0183

single ion solution at pH 1 and pH 6. At pH 1, the extraction percentage of Mo remains higher than 95% within the concentration range of the experiment. For pH 6, the extraction percentage of Mo ion is as high as 95% when the initial ion concentration is low. Then, the extraction percentage decreases slightly for initial Mo ion concentration higher than 0.01 M. The decrease of extraction percentage may be mainly due to the formation of Mo polyion at higher concentration level.[25] Figure 5 shows the initial concentration effects on the extraction percentage of V single ion solution at pH 1 and pH 6. For pH 1, the extraction percentage of V ion increases with increasing initial metal ion concentration and finally levels off at 78%. For pH 6, the extraction percentage of V ions first increases with increasing V initial concentration. Then, as initial V ion concentration higher than 0.02 M, the extraction percentage decreases slightly from 62% to 50%. Figure 6 shows the amount of metal ion extracted by per mole of D_2EHPA at pH 1 with respect to the equilibrium metal ion concentration in aqueous phase. The amounts of extracted Mo and V metal ions increase approximately linearly with increasing equilibrium metal ion concentration. It is clear that the extraction affinity of Mo ion is much higher than V ion. The slopes of Mo and V ions extraction curves are 70 and 5.3, respectively. The ratio of the slopes is as high as 13.2. Figure 7 shows the amount of metal ions extracted by per mole of D_2EHPA at pH 6 with respect to the metal ion equilibrium concentration in aqueous phase. The amounts of extracted Mo and V ion also increases with increasing equilibrium concentration. It is interesting to note that the slope of V ion extraction curve decreases from 5.3 to 1.6 as the pH increases from pH 1 to pH 6. The slope of Mo extraction curve decreases slightly from 70 to 65 as the pH increases from pH 1 to pH 6. The ratio of the slopes is as high

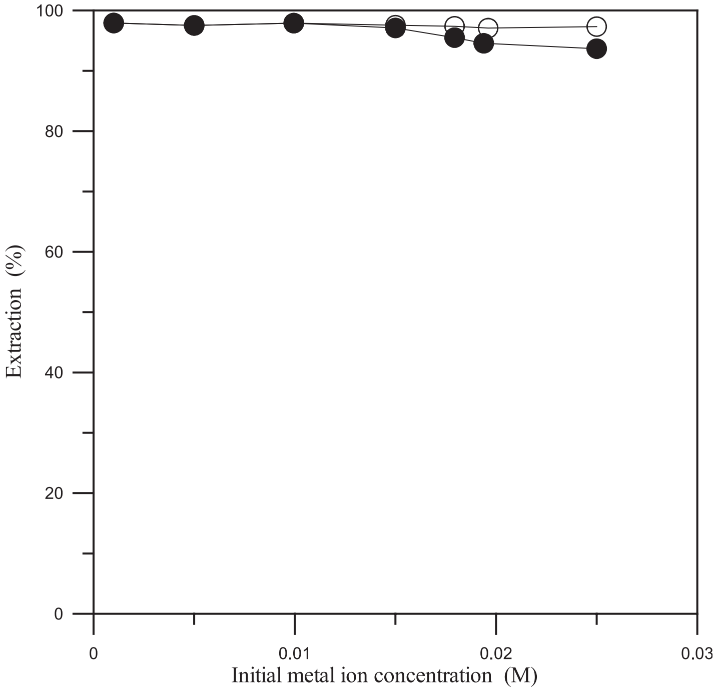

Figure 4. The effects of initial metal ion concentration on the extraction percentage of Mo single-ion solution at pH 1 (○) and pH 6 (●).

as 40.6, which is higher than that at pH 1. It is clear that D_2EHPA has a higher tendency to separate Mo ion from V ion at pH 6 than pH 1, provided that the metal ion concentration is low. From these extraction results, it was concluded that to achieve high separation efficiency of Mo and V ion, the D_2EHPA solvent extraction should be carried out at pH 6 and the initial concentrations of Mo and V ion solutions should be maintained below 0.01 M.

Extraction in Mo/V Mixed-Ion Solution

To study the interaction between Mo and V ions during separation, an extraction experiment was carried out to investigate the effect of pH on the extraction behavior of mixed Mo and V ions solution (Figure 8). The extraction percentage of Mo ion remains as a constant value (about 88%) within the pH range of experiments. The extraction of V ion shows high

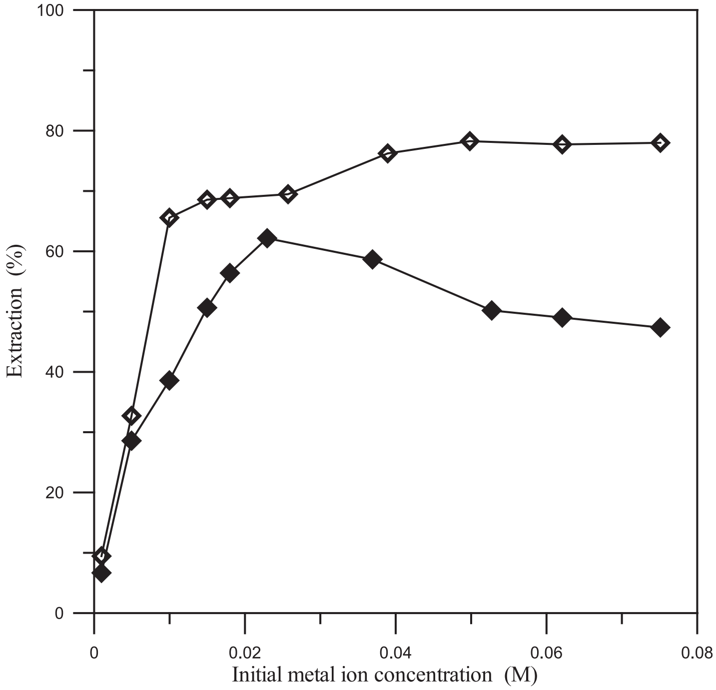

Figure 5. The effects of initial metal ion concentration on the extraction percentage of V single-ion solution at pH 1 (◇) and pH 6 (◆).

extraction percentage between pH 1 and 3. Then, the extraction percentage decreases with increasing pH value. Nevertheless, as a general trend, the extraction percentage of Mo decreases slightly, while the extraction percentage of V increases significantly, compared with the extraction results of single ion solution (see Figure 3). For example, at pH 6, the Mo extraction percentage is 96% for single ion solution and 88% for mixed ion solution. At pH 6, the V extraction percentage is 40% for single ion solution and 48% for mixed ion solution. This might be due to the reason that some Mo ions may form mixed ions with V.[25] Table 2 summarizes the results of extraction experiments in mixed ion solution.

Although the results of solvent extraction experiments indicate that Mo and V ions can be separated by solvent extraction, the process requires large amount of extractant and organic diluents (e.g., kerosene), which pose environmental concerns. The D_2EHPA-modified resin provides potential resolution for this problem.

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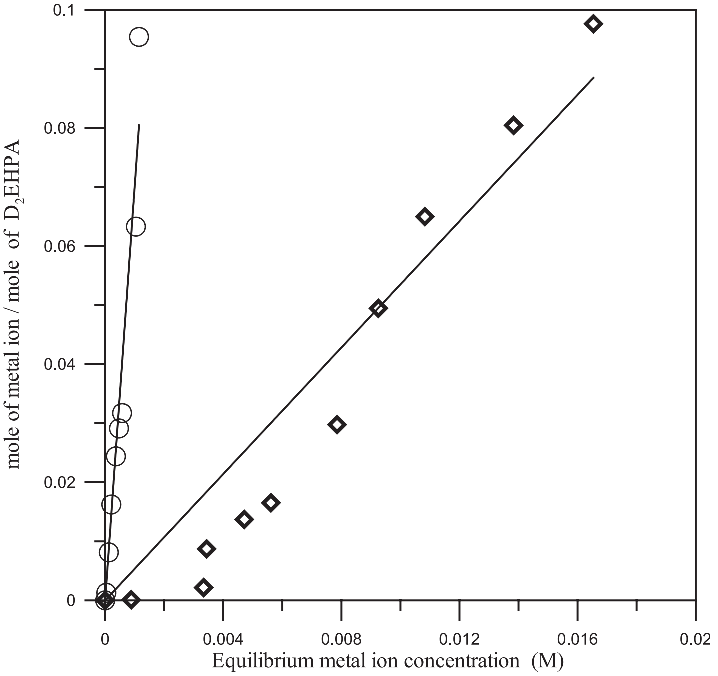

Figure 6. The amount of extracted metal ion by per mole of D_2EHPA at pH 1 with respect to the equilibrium metal ion concentration in aqueous phase. Mo (○), V (◇). The slope of Mo extraction curve is 70. The slope of V extraction curve is 5.3.

Adsorption of Mo and V Ions by D_2EHPA-Modified Amberlite XAD-4 Resin

As pointed out previously, the D_2EHPA solvent can extract Mo from Mo/V mixed solution while most of the V ions were left in the aqueous phase. It was expected that D_2EHPA-modified Amberlite XAD-4 resin would exhibit similar separation properties. Adsorption isotherm experiments were, therefore, conducted to study the adsorption behavior of V and Mo ions by D_2EHPA-modified Amberlite XAD-4 resin at pH 6.

Adsorption in Single-Ion Solution

The adsorption of Mo and V single ion solution was first investigated for the effect of initial metal ion concentration on the extraction percentage.

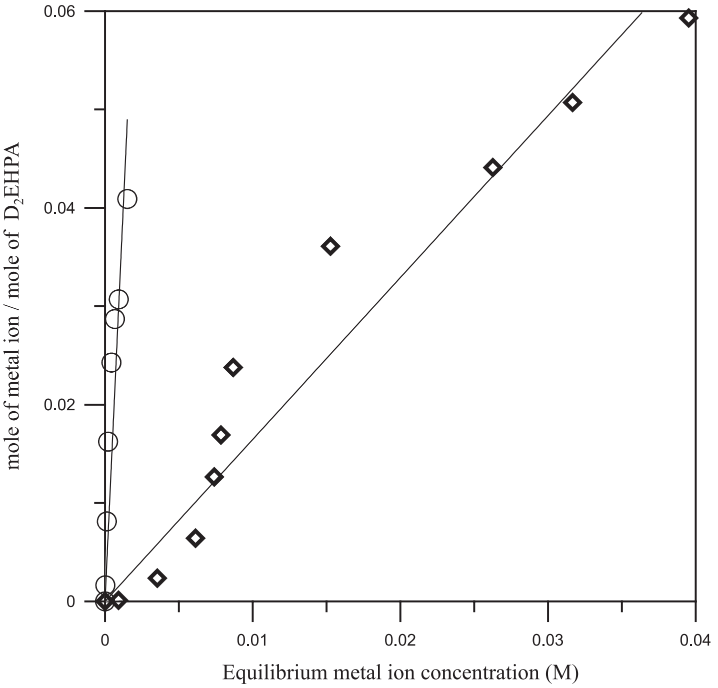

Figure 7. The amount of metal ions extracted by per mole of D_2EHPA at pH 6 with respect to the metal ion equilibrium concentration in aqueous phase. Mo (○), V (◇). The slope of Mo extraction curve is 65. The slope of V extraction curve is 1.6.

Similarly to the extraction behavior in solvent extraction system, the Mo extraction percentage in single Mo ion solution remains at very high level (94%) for low initial Mo ion concentration (not shown). The Mo extraction percentage, however, decreases as the initial Mo ion concentration is higher than 0.002 M. The V extraction percentage in single V ion solution first increases with increasing initial concentration to as high as 34% (initial V concentration equal to 0.004 M), then, the extraction percentage decreases with further increasing initial concentration. The extraction percentage of V is lower than that in solvent extraction system.

Figure 9 shows the amount of adsorbed V and Mo by per mole of immobilized D_2EHPA with respect to the equilibrium metal ion concentration in the aqueous phase at pH 6. The amounts of adsorbed Mo and V ions increase with increasing equilibrium metal ion concentrations. Since pre-experiment results showed that the unmodified hydrophobic Amberlite

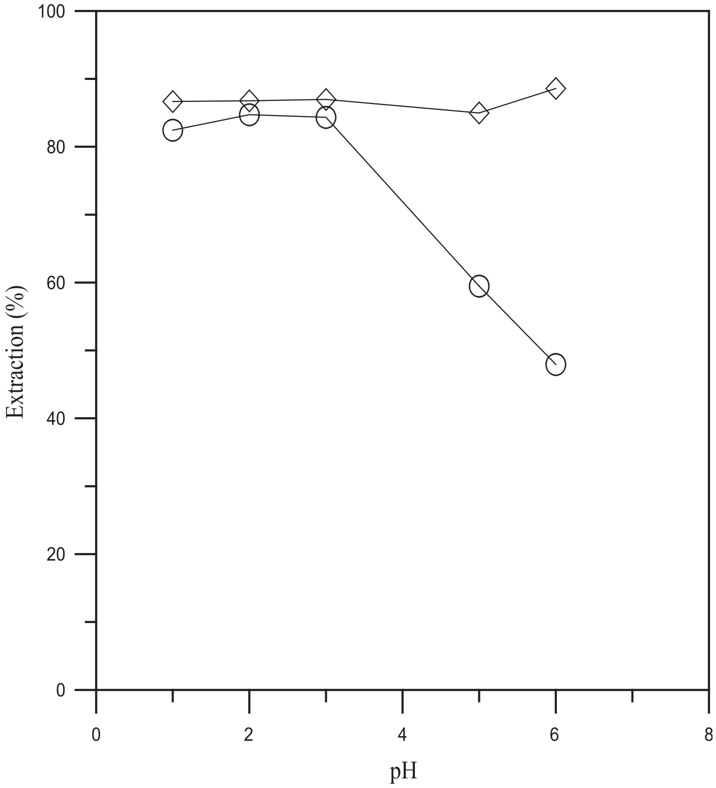

Figure 8. The effect of pH on the extraction percentage of mixed Mo (◇) and V (○) ions solution. The initial metal ion concentrations are both equal to 0.01 M.

XAD-4 resin does not adsorb Mo and V ions, the amount of adsorbed ions by modified resin is mainly due to the presence of immobilized-D_2EHPA. As expected from the solvent extraction of Mo and V ions, the modified Amberlite XAD-4 adsorbs more Mo ion than V ion. The amount of adsorbed Mo first increases with increasing equilibrium metal ion concentration. Then, as the equilibrium concentration of Mo ion reached 0.005 M, the amount of adsorbed Mo by per mole of D_2EHPA leveled off at 0.04 (mole Mo/mole of D_2EHPA). As pointed out previously in the discussion of D_2EHPA solvent extraction, this may be due to the formation of polyions at high metal ion concentration. The small pore size of Amberlite XAD-4 resin further prevents the penetration of more polyions into the resin. The amount of adsorbed V ions by per mole of D_2EHPA,

Table 2. Amount of metal ion extracted by per mole of D_2EHPA in the solvent extraction of mixed-ion solution.

pH	V (mole metal/mole D_2EHPA)	Mo (mole metal/mole D_2EHPA)
1	0.0124	0.0147
2	0.0136	0.0149
3	0.0137	0.0152
5	0.0099	0.0152
6	0.0079	0.0163

however, increased monotonically with increasing equilibrium metal ion concentration.

Conductivity experiments were carried out to verify the possible formation of polyions (Figure 10). By adopting the Fuoss–Onsager limiting law, the molar conductivity of Mo decreased almost linearly with increasing

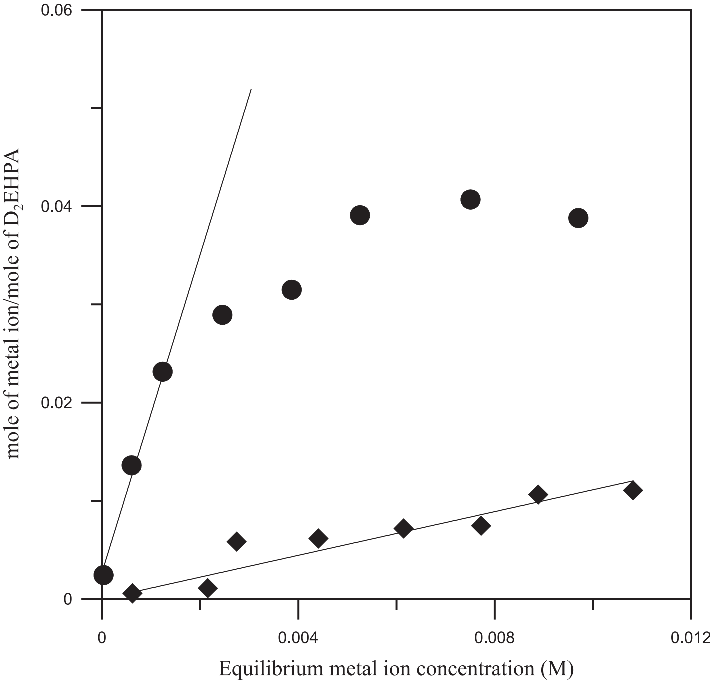

Figure 9. The amount of adsorbed V and Mo by a mole of immobilized D_2EHPA with respect to the equilibrium metal ion concentration. Single-ion solution, pH = 6. Mo (●), V (◆).

metal ion concentration at pH 6, indicating possible formation of Mo polyions at higher metal ion concentration. Figure 10 also shows the molar conductivity of V ions at different metal ion concentration. The molar conductivity of V solution maintains at 104.9 $S \cdot cm^2 \cdot mole^{-1}$ until the molar concentration equal to 0.01 M, then, the molar conductivity starts to decrease with further increasing metal ion concentration. The constant molar conductivity indicates that V ion does not associate to form polyion before 0.01 M. However, as the initial metal ion concentration further increases, V ions may also form polyions, resulting in the decrease of molar conductivity. The conductivity experiment showed that the molybdenum ions can form polymolybdate complexes in aqueous solutions.[25] Vanadium shows comparable behavior, but to a more limited extent.[25]

The equilibria of the metal polyions in aqueous solution are complicated and thus the distribution ratios in these systems in which such polymerized species are contained are also very complicated. In the low concentration region, the extraction is independent of the metal concentra-

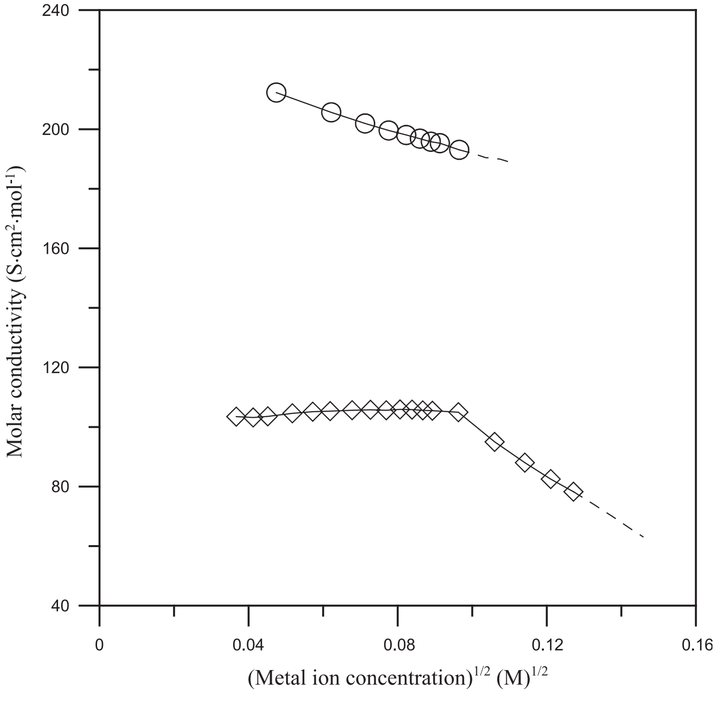

Figure 10. The conductivity of Mo (○) and V (◇) single metal ion solution at different ion concentration.

tion because all the metal species in both phases are monomeric. However, as the metal concentration increases, the extraction curve changes considerably and this can be explained as resulting from the formation of polyion complexes. Figure 11 shows the distribution ratio ($D = [\mathrm{Metal}]_{\mathrm{resin,\ total}}/[\mathrm{Metal}]_{\mathrm{aq,\ total}}$) of Mo and V ions with respect to equilibrium metal ion concentration in single ion solution. The Mo distribution ratio decreases with increasing equilibrium Mo concentration. Although the equilibrium of the formation of Mo polyions is complicated, still it is seen that when polyions complexes are formed in the aqueous phase, the distribution ratio decreases as the total metal concentration increases.[26] The distribution ratio of V ion, on the other hand, is almost constant. From the analysis of adsorption equilibria, it can be readily demonstrated that the distribution ratio is independent of the total solute concentrations as long as the degree of polymerization is not significant.[26] The experimental results were consistent with this polyions model.

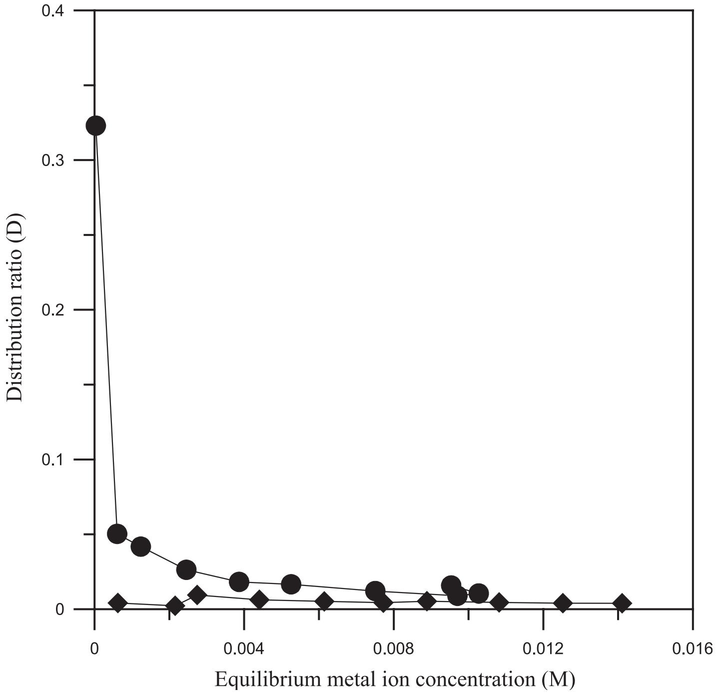

Figure 11. The distribution ratio ($D = [\mathrm{Metal}]_{\mathrm{resin,\ total}}/[\mathrm{Metal}]_{\mathrm{aq,\ total}}$) of Mo (●) and V (◆) ions with respect to equilibrium metal ion concentration in single-ion solution.

Adsorption in Mixed-Ion Solution

As pointed out in the solvent extraction of mixed Mo/V solution, the tendency of the formation of Mo-V mixed ions may further complicated the extraction behavior. Adsorption isotherm experiments were conducted on mixed ion solution. Figure 12 shows the amount of adsorbed V and Mo by per mole of immobilized D_2EHPA in the modified Amberlite XAD-4 resin at pH 6. The amounts of adsorbed Mo and V ions increased with increasing equilibrium ion concentrations in the mixed ion solution. The amount of adsorbed Mo ion leveled off at about 0.01 (mole Mo/mole D_2EHPA), as the equilibrium metal ion concentration reached 0.003 M, which is lower than that in single Mo ion solution (i.e., 0.04 mole Mo/mole D_2EHPA, see Figure 9). Figure 12 also shows that similarly to solvent extraction system, there is a maximum adsorption of V ion as equilibrium metal ion concentration is about 0.012 M. It is interesting to note that the amounts of

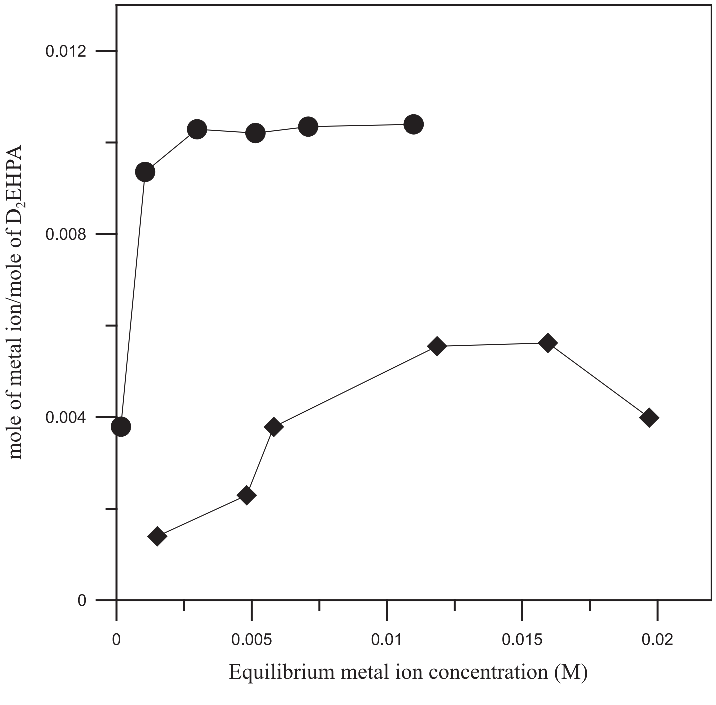

Figure 12. The amount of adsorbed V and Mo by a mole of immobilized D_2EHPA with respect to the equilibrium metal ion concentration. Mixed-ion solution, pH = 6. Mo (●), V (◆).

adsorbed Mo and V are smaller than those in single ion solution. The total amount of adsorbed Mo and V metal ions in mixed solution is even less than the amount of adsorbed Mo ion in single ion solution, based on the same equilibrium Mo ion concentration. This may be due to formation of Mo-V mixed ions, which lower the adsorption affinity of both Mo and V ions by immobilized D_2EHPA.

Figure 13 shows the distribution ratio (D) of Mo and V ions with respect to equilibrium Mo and V ion concentrations in aqueous phase of mixed ion solution. The Mo distribution ratio decreases with increasing Mo ion equilibrium concentrations. This is due to the formation of Mo polyions in the aqueous phase. Similarly to the adsorption of V ions in single ion solution, the V distribution ratio remains approximately constant. The metal distribution ratios in mixed ion solution are smaller than those in single ion

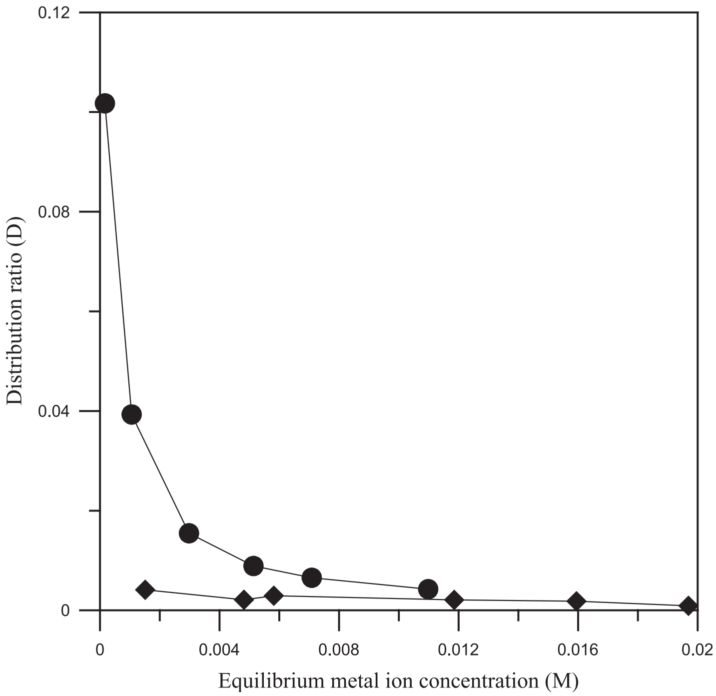

Figure 13. The distribution ratio ($D = [\text{Metal}]_{\text{resin, total}}/[\text{Metal}]_{\text{aq, total}}$) of Mo (●) and V (◆) ions with respect to equilibrium Mo and V ion concentrations in mixed-ion solution.

Table 3. Selectivity of Mo and V ions $\{([Mo]_{resin}[V]_{aq})/([Mo]_{aq}[V]_{resin})\}$ in mixed-ion solution by D_2EHPA-modified resin.

Initial metal ion concentration (M)		
Mo	V	Selectivity of Mo and V ions $\{([Mo]_{resin}[V]_{aq})/([Mo]_{aq}[V]_{resin})\}$
0.001	0.002	24.73
0.003	0.006	18.50
0.005	0.010	5.30
0.007	0.014	4.24
0.009	0.018	4.14
0.010	0.020	4.60

The molar ratio of Mo/V was maintained at 0.5.

solution, apparently due to the formation of Mo-V mixed ions. Table 3 summarizes the selectivity of Mo/V ions $\{([Mo]_{resin}[V]_{aq})/([Mo]_{aq}[V]_{resin})\}$ in mixed solution with respect to the initial metal ion concentration in the mixed ion solution, for constant Mo/V initial molar ratio (1:2). It is interesting to note that although the initial molar concentration of V is twice as much as Mo, the selectivity of Mo/V is still high. However, the selectivity decreased with increasing Mo and V concentrations.

Separation of Mo and V Mixed Solution by Batch Process

The application of D_2EHPA-modified Amberlite XAD-4 resin on the separation of Mo and V mixed ion solution was demonstrated by batch separation process. A mixed Mo/V solution was subjected to a sequential contact with modified Amberlite XAD-4 resin at pH 6. Solid–liquid ratio was maintained at 1:5 in each contactor. The concentration of Mo and V ions in the liquid phase was measured after the adsorption equilibrium was established. Figure 14 shows the batch separation of Mo and V ions in a mixed ion solution with initial concentrations equal to 0.01 M and 0.02 M, respectively. After ten batches of contacts, the relative ion concentration of V ion increased from 67% to 94%, while the relative ion concentration of Mo ion decreased from 33% to 6%. The purified liquid contained V ion concentration as high as 0.0063 M. More than 37% of initial V metal ion is remained in the purified liquid. According to the results of dependence of distribution ratio on equilibrium metal ion concentration (see Figure 13), it is clear that if the initial concentration of Mo and V ions is lower, the

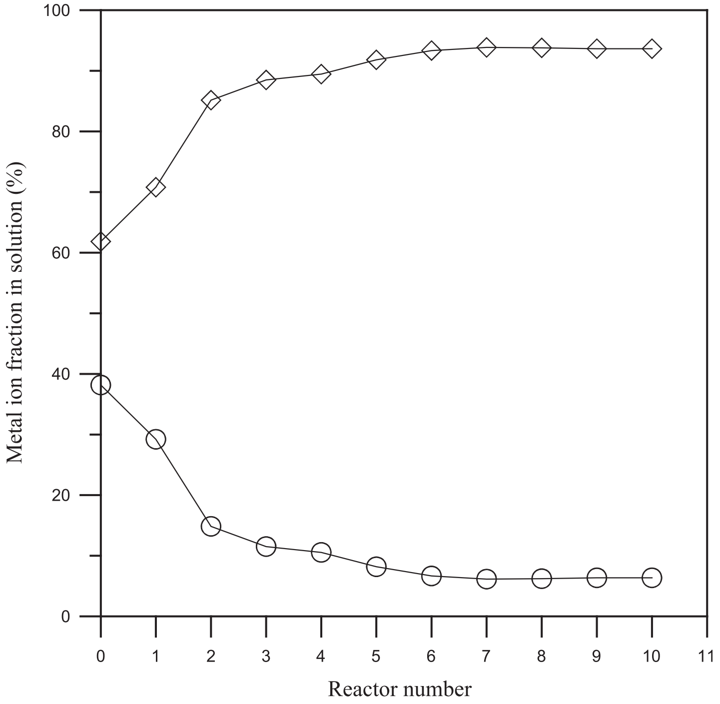

Figure 14. The batch separation of Mo and V ions in a mixed-ion solution. Initial concentrations [Mo] = 0.01 M (○), and [V] = 0.02 M (◇).

difference between the distribution ratios of Mo and V ions will be much more significant. Therefore, it is expected that better separation efficiency can be obtained if the initial metal ion concentration is low. Additional batch separation process was carried at lower metal ion initial concentration. Figure 15 shows the batch separation of Mo and V mixed ion solution with initial concentration equal to 0.001 M and 0.002 M, respectively. After only seven batches of contacts, the relative ion concentration of V ion increased from 67% to more than 96%, while the relative ion concentration of Mo ion decreased from 33% to less than 4%.

These results of batch separation process provide important equilibrium information for understanding the performance of continuous column experiments. However, apparently kinetic phenomena will also have profound effects on the application of D_2EHPA modified resin in separation column. Especially, the formation of polyions will affect the diffusion of

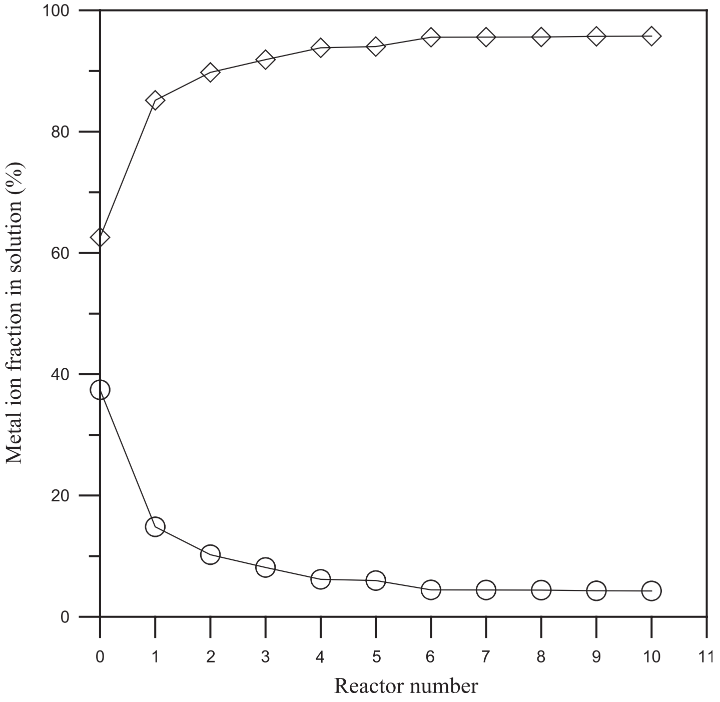

Figure 15. The batch separation of Mo and V ions in a mixed-ion solution. Initial concentrations [Mo] = 0.001 M (○), and [V] = 0.002 M (◇).

metal ions into the resin pores. Column experiments will be investigated in future study.

CONCLUSION

A new type of metal ion selective resin can be prepared by immobilizing D_2EHPA onto the surface of Amberlite XAD-4 resin by employing a solvent–nonsolvent process. The amount of immobilized D_2EHPA is as high as 2.5 (mmole D_2EHPA/g of resin). The immobilized phosphoric acid polar groups provide the resin with selective metal ion chelating functionality and change the hydrophobic surface into hydrophilic surface. Solvent extraction experiments indicated that D_2EHPA can extract more Mo ion than V ion. The ratio of the slopes of Mo and V ion extraction curve is

13.2 and 40.6 for pH 1 and 6, respectively. The separation of Mo and V ions is best accomplished at pH 6, provided that the Mo ion concentration is low.

Adsorption isotherm experimental results show that D_2EHPA-modified Amberlite XAD-4 resin can also adsorb more Mo ion than V ion. Within the range of experiment, the amount of adsorbed Mo ion can be as high as 0.04 (mole Mo/mole D_2EHPA), while the amount of adsorbed V ion is less than 0.01 (mole V/mole D_2EHPA). However, due to the formation of polyion in high concentration solution, the Mo ion distribution ratio decreases with increasing Mo ion concentration. In addition to the formation of Mo polyions, Mo will also associate with V ion to form mixed ions, which further complicated the adsorption behavior of modified resin. The initial concentration of Mo ion should be lower than 0.01 M to have effective separation results.

The selective extraction results using a series contacts of solution mixtures with resins further demonstrated the feasibility of using D_2EHPA-immobilized Amberlite XAD-4 resin for separating Mo/V mixed ion solution. After only seven batches of contacts, the relative ion concentration of V ion increased from 67% to more than 96%, while the relative ion concentration of Mo ion decreased from 33% to less than 4%. These results of batch separation process provide important equilibrium information for understanding the performance of continuous column experiments. Column experiments will be investigated in future study.

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