

Ionic Equilibria and Ion Exchange of Molybdenum(VI) from Strong Acid Solution

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Ion exchange experiments of molybdenum(VI) from strong HCl and H₂SO₄ solution have been done to investigate the existence of anionic complexes. The concentration of HCl and H₂SO₄ was changed from 1 to 9 M. From the data on the complex formation of molybdenum in aqueous solution, a new distribution diagram of Mo(VI) was constructed in the pH range from zero to 10. AG 1 X-8, an anion exchange resin, and Diphonix, a cation exchange resin were used in the loading experiments. Ion exchange results indicate that anionic complexes of Mo(VI) begins to form from 3 M HCl and 1 M H₂SO₄ solution and the tendency to form anionic complexes is stronger in HCl than in H₂SO₄ solution. Our results can be utilized in the analysis of Mo(VI) in strong acid solution and in the design of a process to separate Mo(VI).

Key Words : Molybdenum(VI), Strong acid, Ion exchange, Distribution diagram

Introduction

Molybdenum is a strategically important refractory metal. Its main usage is an alloying agent for super alloy as well as a medicine for human and plants.¹⁻³ Moreover, molybdenum is a key component in the manufacture of hydrodesulfurization (HDS) catalysts which are used in the refining of pure petroleum from crude oil.³ The composition of spent HDS catalysts is 10-30% molybdenum, 1-12% vanadium, 0.5-6% nickel and 1-6% cobalt.⁴ Many studies have been reported to recover the valuable metals from the spent HDS catalysts.^{4,5} Roasting followed by sulfuric acid leaching have been recommended to treat the spent HDS catalysts since all the valuable metals dissolve into the leach solution.⁵

In the petrochemical industries, the surface of the spent catalysts containing cobalt is glutinous. Therefore, these spent catalysts are first washed by water and this treatment step removes nickel and vanadium from the surface of the spent catalysts. In our study on the recovery of cobalt from the spent catalysts after washing with water, most of molybdenum and 90% of cobalt were dissolved by leaching them with 3 M HCl solution at 90 °C without any heat treatment.

In order to recover cobalt with high purity, it is necessary to separate cobalt and molybdenum from the leaching solution of the spent catalyst. Cobalt has a strong tendency to form complexes with chloride ion, such as CoCl₃⁻ and CoCl₄²⁻.⁶ It has been reported that Mo(VI) exists as cationic polynuclear complexes in acid solution with solution pH from zero to 2.⁴ However, few data have been reported on the nature of Mo(VI) complexes and on the complex formation constant in the solution with pH lower than zero. Information on the distribution of Mo(VI) species and on the predominant species under strong acid condition is valuable in designing a process to separate molybdenum and cobalt.

Moreover, these data can be utilized in analyzing solvent extraction of Mo(VI) from strong acid solution.

In this study, a new distribution diagram of Mo(VI) species was obtained by considering Mo(VI) complexes which have not been incorporated in the construction of the reported distribution diagram. Ion exchange experiments of Mo(VI) by using cationic and anionic resin were done to investigate the existence of anionic Mo(VI) complexes in strong HCl and H₂SO₄ solution where acid concentration was changed from 1 to 9 M.

Experimental

Molybdenum(VI) solution was prepared by dissolving Na₂MoO₄·2H₂O in doubly distilled water. Acid concentration in Mo(VI) solution was adjusted by using HCl (35%) and H₂SO₄. All reagents used in this study were of analytical grade. AG 1-X8 (Bio-Rad) and Diphonix (Eichrom) were used as an anionic and a cationic exchanger resin, respectively. These commercial resins were used as received without any treatment.

Batch loading experiments were carried out in a shaking incubator (HB-201SF, Hanbeak Scientific Co.) using 100 mL screwed cap bottle. The temperature of the shaking incubator was controlled to 25 °C in batch experiments. Molybdenum solutions of 50 mL were bottle rolled for 24 hours after putting resin. After filtering the resin, the concentration of Mo(VI) was measured by ICP-OES (Spectro Arcos). The concentration of molybdenum in the resin was obtained by mass balance.

The results were expressed as loading percentage of molybdenum, which is defined as the percentage of the equilibrium mass of metal in the resin to the initial mass of metal in the aqueous phase.

Loading percentage of metal =

$$\left(1 - \frac{\text{equilibrium mass of metal in solution}}{\text{initial mass of metal in solution}}\right) \times 100 \quad (1)$$

Results and Discussion

Distribution Diagram of Mo(VI) in Aqueous Solution.

Mononuclear species of Mo(VI) is known to form when the concentration of Mo(VI) is lower than 10^{-4} M.⁷ However, when the concentration of Mo(VI) is higher than 10^{-4} M, formation of polynuclear species occurs in the pH range between 2 and 6.5.^{7,8} Nature of polynuclear species depends on solution pH and the concentration of Mo(VI).

Figure 1 shows the distribution diagram of Mo(VI) species reported in the literature.⁴ Reaction of Mo(VI) in aqueous solution can be regarded as complex formation between MoO_4^{2-} and hydrogen ion. In alkaline solution, the concentration of hydrogen ion is so small that most of Mo(VI) exists as MoO_4^{2-} . This is evident in Figure 1 that the mole fraction of MoO_4^{2-} is almost unity when solution pH is higher than 6. When solution pH is lower than 6, various polymerization reaction occurs between MoO_4^{2-} and hydrogen ion and consequently diverse polynuclear species, such as $\text{Mo}_7\text{O}_{23}\text{OH}^{5-}$, $\text{Mo}_7\text{O}_{22}(\text{OH})_2^{4-}$ and $\text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-}$, are formed. Electrically neutral species begins to form with the further decrease of solution pH. Figure 1 shows that H_2MoO_4 exists in the pH range from zero to 4 and the maximum mole fraction of this species is around 0.15 at pH 1. Since the concentration of hydrogen ion is high in the solution with pH lower than 2, complexes with positive

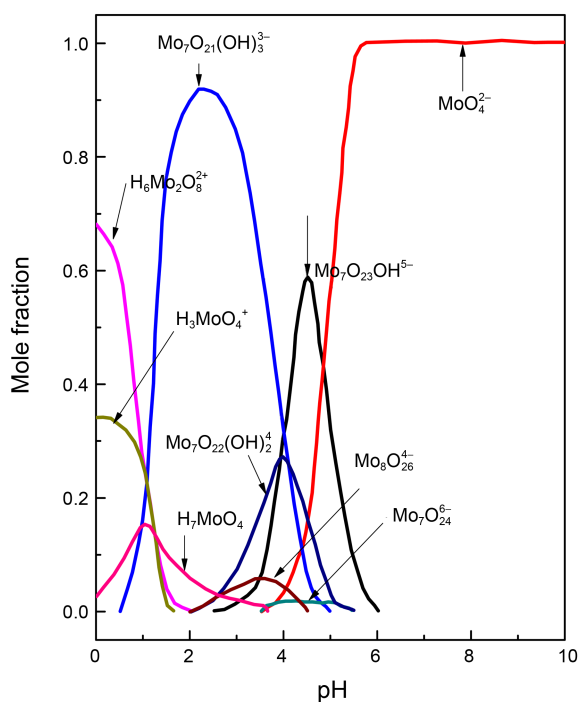


Figure 1. Distribution diagram of molybdenum species in aqueous phase as a function of pH reported in the literature.

charge begins to form in strong acid solution. According to Figure 1, H_3MoO_4^+ is formed at first with the decrease of solution pH and then $\text{H}_6\text{Mo}_2\text{O}_8^{2+}$ begins to form in strong acid solution.

Table 1 lists the complex formation constants of Mo(VI) reported by Cruywagen.^{7,8} In this table, formation constants for some new Mo(VI) containing species are reported. In this study, a new distribution diagram of Mo(VI) was constructed by considering the complex formation listed in Table 1. Mass balance for Mo(VI) was obtained from the complex formation reaction shown in Table 1 as follows

$$\begin{aligned} [\text{Mo}]_{\text{total}} = & [\text{MoO}_4^{2-}] + [\text{H}_3\text{MoO}_4^+] + [\text{MoO}_2\text{OH}^+] \\ & + 2[\text{Mo}_2\text{O}_5\text{OH}^+] + 2[\text{Mo}_2\text{O}_2(\text{OH})_6^{2+}] + 7[\text{Mo}_7\text{O}_{24}^{6-}] \\ & + 8[\text{Mo}_8\text{O}_{26}^{4-}] + 18[\text{Mo}_{18}\text{O}_{56}^{4-}] + [\text{HMoO}_4^-] \\ & + 7[\text{HMo}_7\text{O}_{24}^{5-}] + 7[\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}] + 7[\text{H}_3\text{Mo}_7\text{O}_{24}^{3-}] \\ & + 7[\text{Mo}_7\text{O}_{24}\text{OH}^{7-}] + 6[\text{H}_2\text{Mo}_6\text{O}_{21}^{4-}] + 8[\text{H}_3\text{Mo}_8\text{O}_{28}^{5-}] \\ & + 13[\text{HMo}_{13}\text{O}_{42}^{5-}] + [\text{MoO}_3] + [\text{H}_2\text{MoO}_4] \end{aligned} \quad (2)$$

In dilute solution, the activity of water can be regarded as unity. For simplicity, activity coefficient of species in Mo(VI) solution was assumed to be unity. With these assumptions, the equilibrium constant for the formation of MoO_2OH^+ is represented as follows

$$K_2 = \frac{[\text{MoO}_2\text{OH}^+]}{[\text{MoO}_4^{2-}][\text{H}^+]^3} \times a_{\text{H}_2\text{O}} = \frac{[\text{MoO}_2\text{OH}^+]}{[\text{MoO}_4^{2-}][\text{H}^+]^3} \quad (3)$$

Inserting the above expression for the equilibrium constants of various Mo(VI) species into the mass balance for Mo(VI) results in

Table 1. Stability constants for the formation of complexes of Mo(VI) in aqueous solution at 25 °C.^{7,8}

Formula	Reaction	Log K
H_3MoO_4^+	$\text{MoO}_4^{2-} + 3\text{H}^+ = \text{H}_3\text{MoO}_4^+$	$\log K_1 = 8.44$
MoO_2OH^+	$\text{MoO}_4^{2-} + 3\text{H}^+ = \text{MoO}_2\text{OH}^+ + \text{H}_2\text{O}$	$\log K_2 = 8$
$\text{Mo}_2\text{O}_5\text{OH}^+$	$2\text{MoO}_4^{2-} + 5\text{H}^+ = \text{Mo}_2\text{O}_5\text{OH}^+ + 2\text{H}_2\text{O}$	$\log K_3 = 18$
$\text{Mo}_2\text{O}_2(\text{OH})_6^{2+}$	$2\text{MoO}_4^{2-} + 6\text{H}^+ = \text{Mo}_2\text{O}_2(\text{OH})_6^{2+} + 2\text{H}_2\text{O}$	$\log K_4 = 19$
$\text{Mo}_7\text{O}_{24}^{6-}$	$7\text{MoO}_4^{2-} + 8\text{H}^+ = \text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O}$	$\log K_5 = 52$
$\text{Mo}_8\text{O}_{26}^{4-}$	$8\text{MoO}_4^{2-} + 12\text{H}^+ = \text{Mo}_8\text{O}_{26}^{4-} + 6\text{H}_2\text{O}$	$\log K_6 = 71$
$\text{Mo}_{18}\text{O}_{56}^{4-}$	$18\text{MoO}_4^{2-} + 32\text{H}^+ = \text{Mo}_{18}\text{O}_{56}^{4-} + 16\text{H}_2\text{O}$	$\log K_7 = 171$
HMoO_4^-	$\text{MoO}_4^{2-} + \text{H}^+ = \text{HMoO}_4^-$	$\log K_8 = 3.57$
$\text{HMo}_7\text{O}_{24}^{5-}$	$7\text{MoO}_4^{2-} + 9\text{H}^+ = \text{HMo}_7\text{O}_{24}^{5-} + 4\text{H}_2\text{O}$	$\log K_9 = 57$
$\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$	$7\text{MoO}_4^{2-} + 10\text{H}^+ = \text{H}_2\text{Mo}_7\text{O}_{24}^{4-} + 4\text{H}_2\text{O}$	$\log K_{10} = 60$
$\text{H}_3\text{Mo}_7\text{O}_{24}^{3-}$	$7\text{MoO}_4^{2-} + 11\text{H}^+ = \text{H}_3\text{Mo}_7\text{O}_{24}^{3-} + 4\text{H}_2\text{O}$	$\log K_{11} = 62$
$\text{Mo}_7\text{O}_{24}\text{OH}^{7-}$	$7\text{MoO}_4^{2-} + 7\text{H}^+ = \text{Mo}_7\text{O}_{24}\text{OH}^{7-} + 3\text{H}_2\text{O}$	$\log K_{12} = 46$
$\text{H}_2\text{Mo}_6\text{O}_{21}^{4-}$	$6\text{MoO}_4^{2-} + 8\text{H}^+ = \text{H}_2\text{Mo}_6\text{O}_{21}^{4-} + 3\text{H}_2\text{O}$	$\log K_{13} = 49$
$\text{H}_3\text{Mo}_8\text{O}_{28}^{5-}$	$8\text{MoO}_4^{2-} + 11\text{H}^+ = \text{H}_3\text{Mo}_8\text{O}_{28}^{5-} + 4\text{H}_2\text{O}$	$\log K_{14} = 67$
$\text{HMo}_{13}\text{O}_{42}^{5-}$	$13\text{MoO}_4^{2-} + 21\text{H}^+ = \text{HMo}_{13}\text{O}_{42}^{5-} + 10\text{H}_2\text{O}$	$\log K_{15} = 119$
MoO_3	$\text{MoO}_4^{2-} + 2\text{H}^+ = \text{MoO}_3 + \text{H}_2\text{O}$	$\log K_{16} = 7.2$
H_2MoO_4	$\text{MoO}_4^{2-} + 2\text{H}^+ = \text{H}_2\text{MoO}_4$	$\log K_{17} = 7.36$

$$\begin{aligned}
 [\text{Mo}]_{\text{total}} = & [\text{MoO}_4^{2-}] + K_1[\text{MoO}_4^{2-}][\text{H}^+]^3 \\
 & + K_2[\text{MoO}_4^{2-}][\text{H}^+]^3 + 2K_3[\text{MoO}_4^{2-}]^2[\text{H}^+]^5 \\
 & + 2K_4[\text{MoO}_4^{2-}]^2[\text{H}^+]^6 + 7K_5[\text{MoO}_4^{2-}]^7[\text{H}^+]^8 \\
 & + 8K_6[\text{MoO}_4^{2-}]^8[\text{H}^+]^{12} + 18K_7[\text{MoO}_4^{2-}]^{18}[\text{H}^+]^{32} \\
 & + K_8[\text{MoO}_4^{2-}][\text{H}^+] + 7K_9[\text{MoO}_4^{2-}]^7[\text{H}^+]^9 \\
 & + 7K_{10}[\text{MoO}_4^{2-}]^7[\text{H}^+]^{10} + 7K_{11}[\text{MoO}_4^{2-}]^7[\text{H}^+]^{11} \\
 & + 7K_{12}[\text{MoO}_4^{2-}]^7[\text{H}^+]^7 + 6K_{13}[\text{MoO}_4^{2-}]^6[\text{H}^+]^8 \\
 & + 8K_{14}[\text{MoO}_4^{2-}]^8[\text{H}^+]^{11} + 13K_{15}[\text{MoO}_4^{2-}]^{13}[\text{H}^+]^{21} \\
 & + K_{16}[\text{MoO}_4^{2-}][\text{H}^+]^2 + K_{17}[\text{MoO}_4^{2-}][\text{H}^+]^2 \quad (4)
 \end{aligned}$$

The concentration of MoO_4^{2-} at certain solution pH was obtained by solving Eq. (4) and then the concentration of other Mo(VI) species was calculated by using the equilibrium constant for the complex formation. Commercial software, MATLAB, was employed to solve Eq. (4). Distribution diagrams of 0.01 M Mo(VI) in the pH range from zero to 11 are shown in Figures 2 and 3. Figure 2 represents the distribution diagram of the major Mo(VI) species while Figure 3 represents that of minor species whose mole fraction is lower than 0.1.

In strong acid and alkaline solution, the predominant Mo(VI) species in Figures 1 and 2 are the same. In strong acid solution, $\text{H}_6\text{Mo}_2\text{O}_8^{2+}(\text{Mo}_2\text{O}_2(\text{OH})_6^{2+})$ is predominant while MoO_4^{2-} is predominant in solution with pH higher than 6. The most difference between the distribution diagram of Figure 1 and 2 occurs in the pH range from 1 to 5. Figure 1 shows that polynuclear species with negative charge, such as $\text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-}$, $\text{Mo}_7\text{O}_{22}(\text{OH})_2^{4-}$ and $\text{Mo}_7\text{O}_{23}\text{OH}^{5-}$ are predominant in this pH range. However, according to Figure 2, both mononuclear and polynuclear species with

negative charge, such as HMoO_4^- , $\text{Mo}_{18}\text{O}_{56}^{4-}$, $\text{Mo}_8\text{O}_{26}^{4-}$ and $\text{HMo}_7\text{O}_{24}^{5-}$, exist at the same pH range and the maximum of the mole fraction of these complexes is just 0.1.

According to Figure 1, 70% of Mo(VI) exists as $\text{H}_6\text{Mo}_2\text{O}_8^{2+}(\text{Mo}_2\text{O}_2(\text{OH})_6^{2+})$ and the other Mo(VI) exists as H_3MoO_4^+ in strong acid solution with pH zero. Mole fraction of H_2MoO_4 increases with the increase of solution pH. Figure 2 shows that $\text{Mo}_2\text{O}_2(\text{OH})_6^{2+}$ is the predominant species in strong acid solution with pH zero but its mole fraction at this pH is 0.4. Cationic complexes, such as $\text{Mo}_2\text{O}_5\text{OH}^+$ and MoO_2OH^+ , begin to form with the increase of solution pH.

Ion Exchange of Mo(VI) from Strong Acid Solution. It was reported that $\text{MoO}_2(\text{H}_2\text{O})_4^{2+}$ was the predominant species of Mo(VI) in solution with pH of -1 when the concentration of Mo(VI) was lower than 10^{-4} M.⁷ Moreover, it has been reported that $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ and $\text{MoO}_2\text{Cl}_4^{2-}$ are formed in 6 and 12 M HCl solution, respectively.⁹ In strong sulfuric acid solution, $\text{MoO}_2(\text{HSO}_4)_2$ and $\text{MoO}_2(\text{HSO}_4)_4^{2-}$ are known to exist.⁹ In strong HCl or H_2SO_4 solution, metal ions can form various complexes with chloride or sulfate ion. Therefore, it is probable that Mo(VI) can form anionic complexes with chloride or sulfate ion in strong acid solution. Information on the existence of anionic Mo(VI) species in strong acid solution is valuable in many respects. First, development of a technology for the separation of Mo(VI) depends on the charge of the molybdenum species at strong acid solution. Second, this information can be utilized in analyzing the thermodynamics of ion exchange of Mo(VI) from strong acid solution.

In order to investigate the existence of anionic Mo(VI) complexes in strong HCl and H_2SO_4 solution, ion exchange

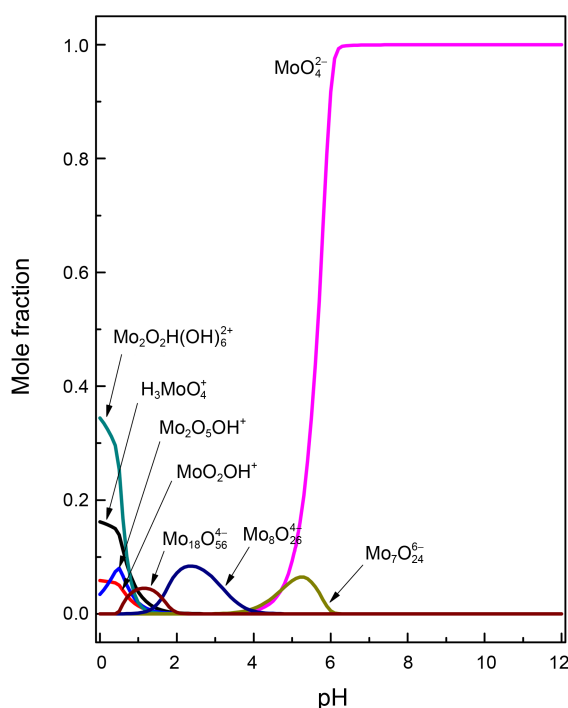


Figure 2. Distribution diagram of major molybdenum chemical species ($[\text{Mo(VI)}] = 0.01$ M).

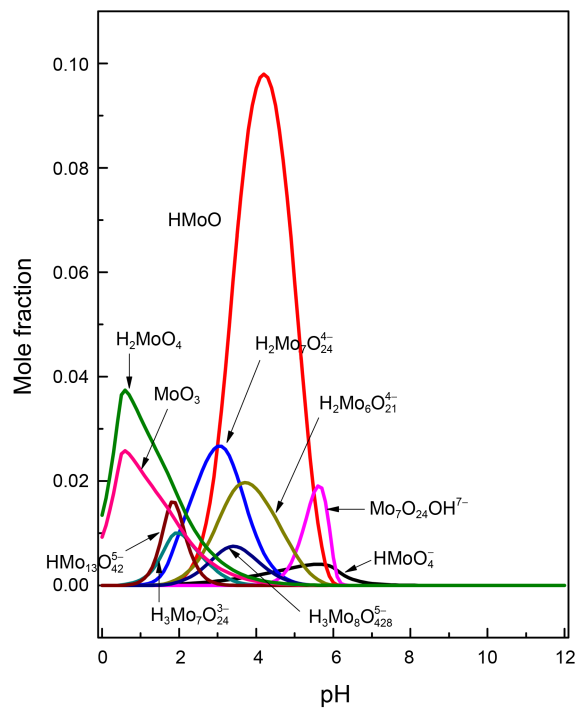


Figure 3. Distribution diagram of minor molybdenum chemical species ($[\text{Mo(VI)}] = 0.01$ M).

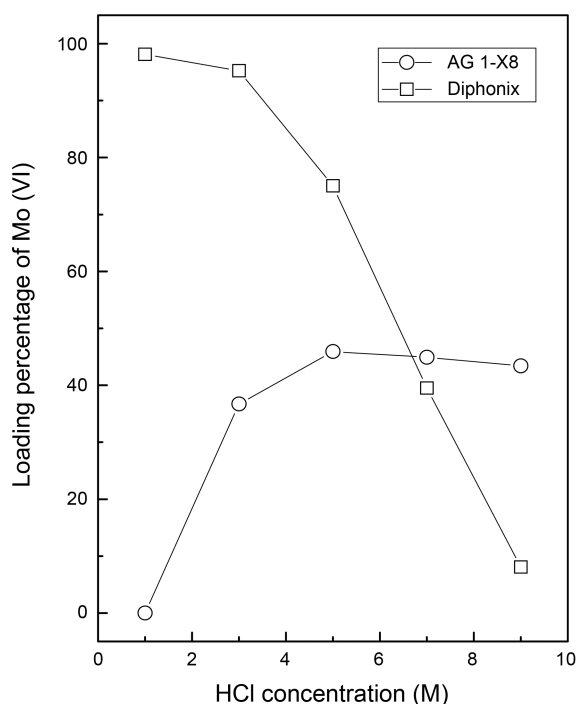


Figure 4. Variation of the adsorption percentage of Mo(VI) from hydrochloric acid solution by AG 1-X8 and Diphonix resin (Resin concentration: AG 1-X8 = 2 g/dm³, Diphonix = 20 g/dm³).

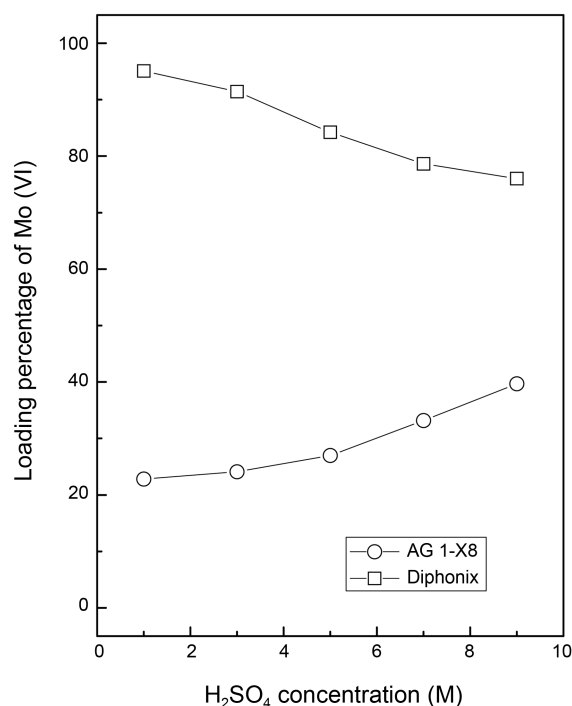


Figure 5. Variation of the adsorption percentage of Mo(VI) from sulfuric acid solution by AG 1-X8 and Diphonix resin (Resin concentration: AG 1-X8 = 2 g/dm³, Diphonix = 20 g/dm³).

experiments of Mo(VI) were done from strong acid solution by using cationic and anionic ion exchange resin. Diphonix resin was used as a cationic exchange resin, while AG 1-X8 resin was used for an anionic exchange resin. In these experiments, the concentration of HCl and H₂SO₄ was changed from 1 to 9 M. By considering the loading capacity of the two resins, the concentration of Diphonix and AG 1-X8 resin was kept at 20 and 2 g/dm³, respectively.

Loading percentage of Mo(VI) was calculated by using Eq. (1) from the experimental data and the results from HCl solution are shown in Figure 4. At 1 M HCl concentration, the loading percentage of Mo by Diphonix was around 99%, while that by AG 1-X8 was zero. This results mean that most of Mo(VI) exists as cationic form at 1 M HCl. The loading percentage of Mo by Diphonix decreased rapidly with the increase of HCl concentration when HCl concentration was higher than 3 M. On the contrary, the loading percentage of Mo by AG 1-X8 increased from zero to 45% as HCl concentration was varied from 1 to 5 M. There was little change in the loading percentage of Mo with the further increase of HCl concentration to 9 M. The data in Figure 4 indicate that anionic complexes are formed between Mo(VI) and chloride ion in strong acid solution where HCl concentration was higher than 3 M.

Figure 5 shows the results obtained from sulfuric acid solution. Unlike the results obtained from HCl solution, loading percentage of Mo by AG 1-X8 was higher than 20% at 1 M H₂SO₄ solution. Loading percentage of Mo by AG 1-X8 steadily increased with the increase of H₂SO₄ concentration. In the ion exchange by Diphonix resin, the loading

percentage of Mo at 1 M was 95% and steadily decreased with the further increase of H₂SO₄ concentration. When H₂SO₄ concentration was 9 M, loading percentage of Mo by Diphonix and AG 1-X8 was 80 and 42%, respectively. This implies that both cationic and anionic complexes of Mo exist at this strong H₂SO₄ solution.

Our results demonstrates that anionic complexes of Mo(VI) begins to form from 3 M HCl and 1 M H₂SO₄ solution. Further work is needed to identify the nature of anionic complexes and to determine the complex formation constant of the species from HCl and H₂SO₄ solution.

Conclusions

Distribution diagram of Mo(VI) was obtained by using the data on the complex formation of Mo in the pH range from zero to 10. Compared to the distribution diagram reported in the literature, there was some difference in the nature of predominant species and in the value of mole fraction of the predominant species in the pH range from zero to 5.

Ion exchange experiments of Mo(VI) from strong HCl and H₂SO₄ solution were done to investigate the existence of anionic complexes Mo(VI) in the concentration range from 1 to 9 M. From the variation in loading percentage of Mo with acid concentration, it is certain that anionic complexes of Mo(VI) begins to form from 3 M HCl and 1 M H₂SO₄ solution. Moreover, the tendency to form anionic complexes is stronger from HCl solution than from H₂SO₄ solution. This results can be used in developing a process to separate Co(II) and Mo(VI) from the leaching solution of spent

catalysts. Further work is needed to determine the nature of anionic complexes in strong acid solution.

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