Molybdenum Isotope Fractionation in Basic Aqueous Solution Using Anion Exchange Chromatography

Yu TACHIBANA[1,*], Andri Rahma PUTRA[1], Shin OKUMURA[2], Toshitaka KANESHIKI[2], Masanobu NOGAMI[3], Tatsuya SUZUKI[1] and Masao NOMURA[2]

[1]Department of Nuclear System Safety Engineering, Graduate School of Engineering, Nagaoka University of Technology, 1603-1, Kamitomioka-machi, Nagaoka, Niigata 940-2188, Japan; [2]Laboratory for Advanced Nuclear Energy, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8550, Japan; [3]Department of Electric and Electronic Engineering, Kindai University, 3-4-1, Kowakae, Higashiōsaka-shi, Osaka 577-8502, Japan

The Mo(VI) isotope fractionation using well-known anion-exchange resins was investigated in aqueous solutions at 298 K. The weakly basic porous-type WA20 resin (WA20(Cl form)), PA316 resin, which is one of porous-type strongly basic anion-exchange resin (PA316(Cl form)), and benzimidazole-type anion-exchange resin embedded in high-porous silica beads, which has two types of functional groups consisting of 1-methylbenzimidazole and 1,3-dimethylbenzimidazole (AR-01(Cl form)) was used. The adsorption experiments of Mo(VI) species using WA20(Cl form), PA316(Cl form), and AR-01(Cl form) resins were performed by batch-wise techniques to evaluate the distribution coefficients (K_d) of Mo(VI) species in aqueous solutions ranging in pH value from 2.6 to 12.8 at room temperature. As a result, it was found that PA316(Cl form) and AR-01(Cl form) resin have high adsorption ability for Mo(VI) species in the broad pH range. On the other hand, the K_d values of WA20(Cl form) resin decreased sharply around neutral pH values. This adsorption tendency implies that the Mo(VI) isotope fractionation experiments in adsorption-desorption reactions are available. The isotope separation coefficients per unit mass (ε / ⊿*Mass*) of Mo(VI) species were obtained by using the isotope fractionation curve of Mo(VI) species with WA20(Cl form) resin. The ε / ⊿*Mass* values were compared with those obtained from acid conditions.

1. Introduction

Tc-99m, a metastable isomer of Tc-99, is of great interest from the viewpoint of the medical use of nuclear diagnostics due to the half-life of $T_{1/2}$ = 6.015 h and 143 keV [1]. It is the fact that our country depends on foreign countries such as Canada, Netherlands, and Belgium, etc. for Mo-99, a raw material of Tc-99m [2]. Nowadays, most Mo-99 is produced by using nuclear research reactors with highly enriched U-235, which has intrinsically some serious worries for nuclear proliferation. These reactors have been getting decrepit and the realistic costs for specialized facilities for chemical treatments, storages, and the disposal of large amounts of highly radioactive wastes are not reasonable [3]. Recently, some researchers have suggested that Mo-99 can be produced using the respective reactions of ^{98}Mo(n, γ)^{99}Mo, ^{100}Mo(n, 2n)^{99}Mo, and ^{100}Mo(p, x)^{99}Mo [2-4]. Before their nuclear reactions, it has also been required to enrich Mo-98 or Mo-100 isotope for preparation of the enriched Mo-99 isotope due to comparatively low natural abundance of Mo-98 and Mo-100 isotopes. The geochemists are particularly interested in the Mo isotope fractionation in chemical reaction [5-7]. Our present works which have examined the mechanisms of Mo isotope fractionation in solutions, may contribute to the understanding the nature of the isotope fraction of Mo in the natural world. Some researchers have studied the chemical enrichment of various nuclides by using chromatography [8-24]. In analogy of them, we have also performed some chromatographic isotope separation experiments of hexavalent Mo species using the synthesized benzimidazole-type anion-exchange resin embedded in high-porous silica beads (AR-01(Cl form)) and the weakly basic porous-type WA20 resin (WA20(Cl form)) in hydrochloric acid solutions (see Figure 1) [25] and their effect of different valence states on chromatographic fractionation of Mo isotopes in hydrochloric acid solutions was examined using Sn(II) [23-24]. It has been known that Mo species has various chemical forms in aqueous solutions and seven stable isotopes in nature [23]. In other words, the systematic understanding of adsorption and desorption behavior of Mo species is inevitable, compared with other elements. However, the chemical data on isotope fractionation of medium-heavy elements such as Mo are not well-known. Especially, little information on chromatographic isotope fractionation of Mo(VI) isotopes in basic aqueous solutions is available.

Judging from these viewpoints, we have investigated the Mo(VI) isotope fractionation behavior in the basic aqueous solutions using typical anion-exchange resins such as WA20(Cl form), PA316(Cl form), and AR-01(Cl form) resins.

2. Experimental

2.1 Reagents

$Na_2MoO_4 \cdot 2H_2O$ (Purity: 99.0 %), NaOH (Purity: 93.0 %), HCl (Purity: 35 %) were produced by NACALAI TESQUE, INC., Kyoto, Japan. The foregoing Mo(VI) salts were used without further purification. AR-01(Cl form) resin was synthesized and supplied from Laboratory for Advanced Nuclear Energy, Tokyo Institute of Technology, Tokyo, Japan [20]. Both of WA20(Cl form) and PA316(Cl form) resins were obtained from Mitsubishi Chemical Corporation, Tokyo, Japan and their structural details and chemical properties have been described elsewhere [25]. All chemicals for analyses were of special pure grade.

2.2. Sample preparations

The acidic and basic concentrations in solutions containing 1.0 mM (M = mol/dm^3) Mo(VI) species were adjusted to pH = 2.6 - 12.8 using HCl and NaOH for Mo(VI) adsorption experiments, whereas the concentration of NaOH and HCl was adjusted to 0.5 M for chromatographic experiments. The aqueous solutions with 0.5 M Mo(VI) species was also prepared. By mixing with ultrapure water (Specific electrical resistance: $\geq$ 18.2 MΩcm, total organic carbon: $\leq$ 3 ppb (ppb = ng/g)) produced with a Merck Millipore apparatus (Milli-Q Integral 3 Water Purification System), these sample solutions were carefully prepared to prevent any contamination. For Mo(VI) adsorption experiments, AR-01(Cl form), WA20(Cl form), and PA316(Cl form) resins and for Mo(VI) chromatographic experiments, WA20(Cl form) resin were used. The diameter of silica beads used for AR-01(Cl form) resin was 40 - 60 μm [20]. The quaternization ratio of AR-01(Cl form) resin was 58.8 % [20].

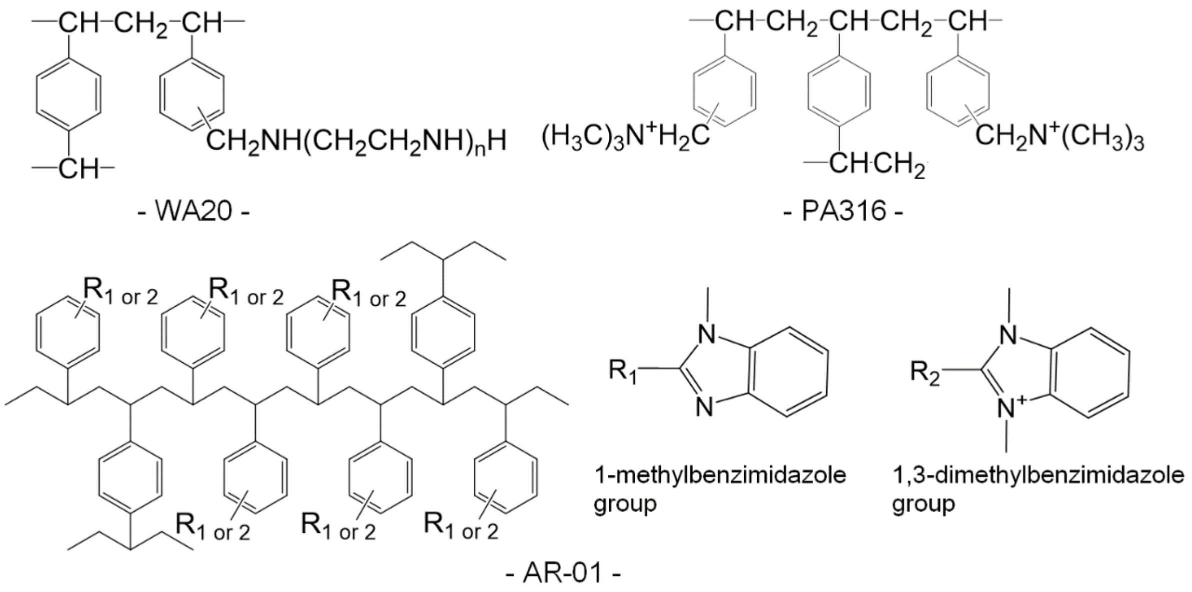

Figure 1. Structural formulas of anion-exchange resins used in the study.

2.3. Adsorption experiments of Mo(VI) species

The adsorption experiments of Mo(VI) species were carried out by batch-wise techniques to evaluate the distribution coefficients (K_d) using AR-01(Cl form), WA20(Cl form), and PA316(Cl form) resins in aqueous solutions of various pH values (pH = 2.6 - 12.8) at room temperature. These resins of 0.10 g were respectively added into 10.0 mL aqueous solutions containing 1.0 mM Mo (VI) species. The shaking time was 24 hours at room temperature. The concentration of Mo(VI) species was measured using ICP/MS (7700x, Agilent) after all samples were passed through a polytetrafluoroethylene-type membrane filter (Sartorius, pore size: 0.45 μm) to remove these resins.

2.4. Chromatography experiments of Mo(VI) species

For the Mo(VI) chromatographic isotope fractionation experiments, seven glass columns connected in series were used. All columns were equipped with water jacket made of glass. The length of one column was 1.0 m and its inner diameter was 8.0 mm. All apparatuses were connected in series with the polytetrafluoroethylene tubes with 2.0 mm inner diameter. The above-mentioned resins were packed into these glass columns. The total weight of WA20(Cl form) resin was 137.3 g. By using the circulator, the reaction temperature was kept constant at 298 K for WA20(Cl form) systems. The column chromatography experiments using aqueous solutions containing 0.5 M Mo(VI) species were performed under constant flow rate of 0.78 mL/min at 298 K. The flow rate was controlled by the high-pressure pump (NP-KX-210, Nihon Seimitsu Kagaku, Co., Ltd.). The order of mobile phase added into the columns was aqueous solution with 0.5 M Mo(VI) species (300 cm^3) and aqueous solution containing 0.5 M NaOH (4000 cm^3). WA20(OH form) resin was converted into WA20(Cl form) resin using 0.5 M HCl aqueous solution. The samples were taken every 10.0 g by using the fraction collector (CHF161RA, Advantech). The Mo(VI) concentration and their isotope ratios were measured by using ICP/MS described above. By varying the concentration of metal ions and kinds of solvents and their concentration, we have observed the effect of the Mo isotope discrimination in ICP/MS measurements [26]. Hence, the concentration of Mo(VI) species in the sample solutions was adjusted at ca. 10 ppb for the isotope ratio measurements. The 1.0 wt% HNO_3 solution was used as a diluent for all ICP/MS measurements. The Mo(VI) species adsorbed on the resins in the columns were completely removed by using 0.5 M NaOH after the chromatographic experiments.

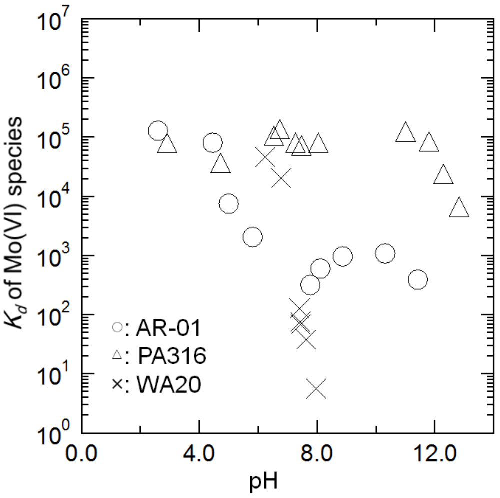

Figure 2. Plots of K_d of Mo(VI) species *vs.* pH at room temperature. [Mo(VI)] = 1.0 mM. Resin = 0.10 g.

3. Results and Discussion

3.1. Adsorption behavior of Mo(VI) species

The adsorption experiments of Mo(VI) species using WA20(Cl form), PA316(Cl form), and AR-01(Cl form) resins were performed by batch-wise techniques to evaluate the K_d values of Mo(VI) species in aqueous solutions in the pH 2.6 to 12.8 region at room temperature. The K_d values were calculated using the following Eq. (1).

$$K_d = \{C_r / C_s \times (V_s / V_r)\} = \{(C_0 - C_s) / C_s\} \times (V_s / V_r) \quad (1)$$

where C_r, C_s, C_0, V_s, and V_r are concentration of Mo(VI) species on resin at adsorption equilibrium, concentration of Mo(VI) species in solution after adsorption equilibrium, initial concentration of Mo(VI) species, volume of solution, and volume of resin, respectively.

As a result, it was found that PA316(Cl form) and AR-01(Cl form) resin have high adsorption ability for Mo(VI) species in the broad pH range while the K_d values of WA20(Cl form) resin decreased sharply around neutral pH values as shown in Figure 2. In the acidic aqueous solution around pH = 5, Mo(VI) exists as $Mo_7O_{23}^{4-}$, i.e., this Mo(VI) species can strongly adsorb on these resins. In case of pH = 6.5 or above, it was suggested that MoO_4^{2-} forms as a main species. These Mo(VI) species with comparatively high negative valence states such as $Mo_7O_{23}^{4-}$ and MoO_4^{2-} have generally high adsorption ability for these resins. Hence, the decrease of K_d values of Mo(VI) species using WA20(Cl form) and AR-01(Cl form) resins must be attributable to the acid dissociation constants of the functional groups in WA20(Cl form) and AR-01(Cl form) resins because these functional groups such as polyamine and 1-methylbenzimidazole are classified as a weakly basic anion exchange resin [25,27]. This adsorption tendency implied that the Mo(VI) isotope fractionation experiments in adsorption-desorption reactions using WA20(Cl form) resin are available.

Moreover, on the assumption that the 1 : 1 anion-exchange reaction is proceeded, Mo(VI) + WA20(Cl form) ⇌ WA20･Mo(VI) + Cl^- under the conditions; [Mo(VI)] = 1.0 mM, [WA20(Cl form)] = 0.10 g, we have investigated the adsorption mechanisms between WA20(Cl form) resin and Mo(VI) species in aqueous solutions in further detail. The thermodynamic parameters ($\varDelta H$, $\varDelta S$, and $\varDelta G$ values) for the adsorption of Mo(VI) species on WA20(Cl form) resin, ranging in Temp. = 278 - 333 K, were calculated from the linear plots of ln K_d against ($1/T$) using the following Van't Hoff equation (2) [28] and the obtained values were 1.5 ± 0.8, kJ / mol, 34 ± 3 J / (K･mol), and - 8.66 ± 0.01 kJ / mol at 298 K, respectively.

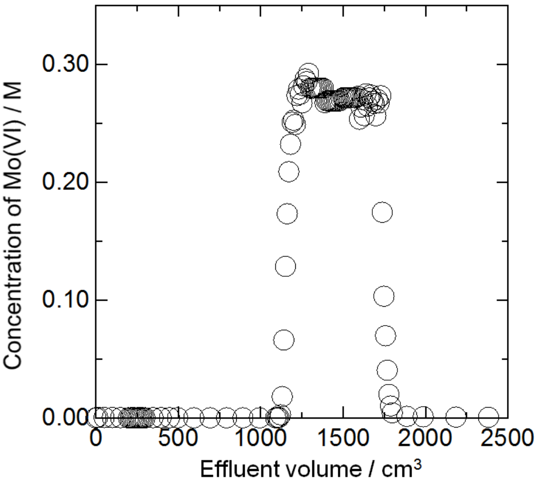

Figure 3. Profile of Mo(VI) concentration in the eluted fraction samples using WA20(Cl form) resin in aqueous solutions.

$$\ln K_d = -\varDelta G / R \cdot T = -\varDelta H / R \cdot T + \varDelta S / R \qquad (2)$$

Here, R and T represent gas constant and absolute temperature. This result indicates that the spontaneous adsorption processes between WA20(Cl form) resin and Mo (VI) species occur in aqueous solutions. The positive $\varDelta H$ values show the endothermic reactions of Mo(VI) species with WA20(Cl form) resin. It can be considered that Mo(VI) species is surrounded by plenty of water in aqueous solutions due to the comparatively high solubility for H_2O. When Mo(VI) species are adsorbed onto WA20(Cl form) resin, the hydration shell of Mo(VI) species must be broken before the adsorption reactions of Mo(VI) species with WA20(Cl form) resin proceed in aqueous solution. Thus, these dehydration processes are expected to require energy. On the other hand, the polyamine-type functional groups in WA20(Cl form) resin are generally regarded as hydrophobic groups. Therefore, it was found that the positive $\varDelta H$ values become very low, compared with those obtained from different adsorption systems [26]. In addition, the positive values of $\varDelta S$ also suggest an increase in randomness at the boundary between Mo(VI) species and WA20(Cl form) resin during the adsorption processes. In brief, this tendency implies that the randomness arises due to the destruction of hydration shell of Mo(VI) species superior to the adsorption of Mo(VI) species on the surface of WA20(Cl form) resin. The lower positive $\varDelta H$ values may cause the high effect of Mo(VI) isotope separation.

3.2. Chromatographic isotope fractionation of Mo(VI) species

The chromatography experiments for Mo(VI) isotope separation were carried out to evaluate the validation of our estimation in aqueous solutions at 298 K. Figure 3 shows the plateau of Mo(VI) concentration in the eluted fraction samples using WA20(Cl form) resin in aqueous solutions at 298 K. The amount of Mo(VI) species calculated from the plateau in Figure 3 is consistent with that obtained from the experimental condition. The typical isotope fractionation of Mo(VI) species is shown in Figure 4. In the figure, the notation of Mo isotope ratio deviation was defined as the isotopic ratios of

Mo-100/Mo-92 over effluent volume. The fractionation behavior of Mo-98/Mo-92 isotope ratio was similar to that of Mo-100/Mo-92 isotope ratio. The original isotope ratios of Mo-100/Mo-92 and Mo-98/Mo-92 were 7.89×10^{-1} and 1.88, respectively. It was found that the 100/92 Mo(VI) isotope ratios decrease sharply with increasing effluent volume and the Mo(VI) isotope ratios eventually approach the original values in case of the front band region. Therefore, this figure indicates that the heavier isotopes are disproportionately enriched in the solution phase. The depletion phenomena of the Mo(VI) isotope ratios were also confirmed in the rear band region. We have confirmed the three steps. In brief, first step exists when the elution volume is around 750 cm^3. Second step is in the range between ca. 1500 - 1600 cm^3, that is, the Mo(VI) original ratio. The effluent volume of third step was confirmed around 1750 cm^3. The existence of three steps indicates that there are three kinds of the Mo(VI) isotope fractionation in aqueous solutions. The chemical form of Mo(VI) species strongly depend on the pH in aqueous solutions [23]. The Mo(VI) species around pH = 5.5 and pH = 6.5 or above, form $Mo_7O_{23}^{4-}$ and MoO_4^{2-}, respectively. MoO_4^{2-} adsorbed on WA20(Cl form) resin was eluted using NaOH. The chemical reactions related to the present separation system can be expressed in the simplified form as follows:

$$Mo_7O_{23}^{4-} + WA20 \cdot Cl \rightleftarrows [WA20 \cdot Mo_7O_{23}]^{3-} + Cl^- \tag{A-1}$$
$$^{L}Mo_7O_{23}^{4-} + [WA20 \cdot {}^{H}Mo_7O_{23}]^{3-} \rightleftarrows {}^{H}Mo_7O_{23}^{4-} + [WA20 \cdot {}^{L}Mo_7O_{23}]^{3-} \tag{A-2}$$
$$MoO_4^{2-} + WA20 \cdot Cl \rightleftarrows [WA20 \cdot MoO_4]^- + Cl^- \tag{B-1}$$
$$^{L}MoO_4^{2-} + [WA20 \cdot {}^{H}MoO_4]^- \rightleftarrows {}^{H}MoO_4^{2-} + [WA20 \cdot {}^{L}MoO_4]^- \tag{B-2}$$
$$[WA20 \cdot MoO_4]^- + OH^- \rightleftarrows WA20 \cdot OH + MoO_4^{2-} \tag{C-1}$$
$$^{L}MoO_4^{2-} + [WA20 \cdot {}^{H}MoO_4]^- \rightleftarrows {}^{H}MoO_4^{2-} + [WA20 \cdot {}^{L}MoO_4]^- \tag{C-2}$$

where superscripts of H and L denote the heavier isotope and the lighter isotope, respectively. The isotope separation coefficients (ε) per unit mass (ε / $\Delta Mass$), which have been frequently used for the analysis of isotope fractionation using ion exchange chromatography and the corresponding height equivalent to a theoretical plate (HETP) derived from the theory of displacement type chromatographic enrichment in the isotopically transient state, are calculated by using the isotope fractionation curve of Mo-98 and Mo-100 in sample solutions. The equation can be expressed by Eq. (3, 4) [15,18,19-24].

$$\varepsilon / \Delta Mass = (\alpha - 1) / (Mass_H - Mass_L) = \Sigma (q_i |R_i - R_0| / \{Q \times R_0 (1 - R_0)\} / (Mass_H - Mass_L) \tag{3}$$
$$HETP = (\varepsilon / |k_s|) + (1 / k_s^2 \cdot L) \tag{4}$$

Here, α, $Mass_H$, $Mass_L$, q_i, R_i, and Q are the isotope fractionation factor, the mass of heavier isotope, the mass of lighter isotope, the amount of Mo in the fraction sample, the isotopic percentage of Mo, the total amount of adsorbed Mo species on the resin, respectively. The indication of fraction number is i = 0, 1, 2…. As a result, the calculated values of (ε / $\Delta Mass$) of Mo-100/Mo-92 and Mo-98/Mo-92 were found to be 1.0×10^{-4} and 8.7×10^{-5} in the front band region, respectively. These results imply that the (ε / $\Delta Mass$) values of Mo(VI) species are proportional to the reciprocal square of the atomic weight, which is called mass shift effect [8]. These *ε* / *⊿Mass* values were analogous to those obtained from acid conditions [23,24]. By contrast, as (*ε* / *⊿Mass*) values, 1.3 × 10^{-5} for Mo-100 /Mo-92 ratio and 8.3 × 10^{-6} for Mo-98 /Mo-92 ratio were calculated from the rear band region. In case of basic condition, the (*ε* / *⊿Mass*) values became much smaller. The slope coefficient, k_s value is experimentally determined by plotting of ln (r_i - r_0) against X_{Bi}. The r_0 and X_B values are the original isotopic ratio and the distance from the front boundary. This *r* value can be defined as Mo-98/Mo-92 and Mo-100/Mo-92 isotope ratios. The subscripts, *i* and *0* also denote the fraction number and original sample, respectively. Thus, the k_s values for Mo-98/Mo-92 and Mo-100/Mo-92 isotope ratios in aqueous solutions were calculated to obtain the HETP values and the analytical details of this equation have been described elsewhere [16]. As a result, the obtained HETP values was found to be more than 1.0 mm. The (*ε* / *⊿Mass*) values were small and the HETP values were large, much larger (*ε* / *⊿Mass*) values is needed to apply the present isotope separation system for nuclear medicine applications.

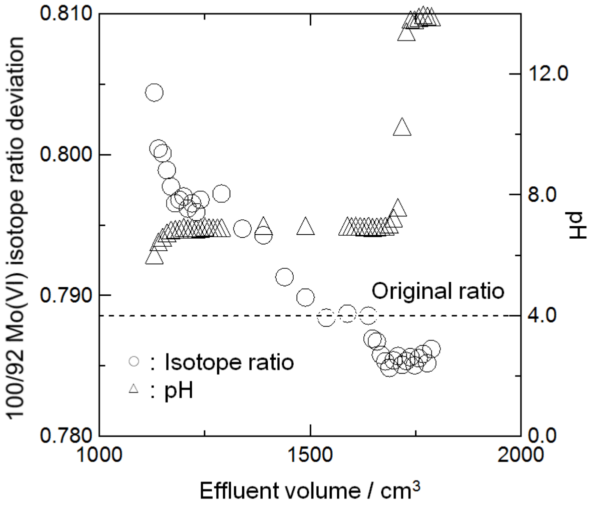

Figure 4. Profiles of Mo(VI) isotope ratios and their pH values in the eluted fraction samples using WA20(Cl form) resin in aqueous solutions.

4. Conclusion

The Mo(VI) isotope fractionation using well-known anion-exchange resins such as (WA20(Cl form)), (PA316(Cl form)), and (AR-01(Cl form)) resins, was investigated in aqueous solutions at 298 K. The adsorption experiments of Mo(VI) species using WA20(Cl form), PA316(Cl form), and AR-01(Cl form) resins were performed by batch-wise techniques to evaluate the K_d of Mo(VI) species in aqueous solutions in the pH 2.6 to 12.8 region at room temperature. As a result, it was found that PA316(Cl form) and AR-01(Cl form) resin have high adsorption ability for Mo(VI) species in the broad pH range while the K_d values of WA20(Cl form) resin decreased sharply around neutral pH values. This adsorption tendency implied that the Mo(VI) isotope fractionation experiments in adsorption-desorption reactions are available. The ε / *⊿Mass* values of Mo(VI) species were obtained by using the isotope fractionation curve of Mo(VI) species with WA20(Cl form) resin. The ε / *⊿Mass* values obtained from acidic and basic conditions were compared and we have confirmed that the ε / *⊿Mass* values under acidic condition become much larger.

Acknowledgement

This work was partially supported by Nagaoka University of Technology Presidential Research Grant (A) (No. 13).

References

1) M.J. Heeg, S.S. Jurisson, *Acc. Chem. Res.,* **32**, 1053-1060 (1999).
2) Y. Nagai, Y. Hatsukawa, *J. Phys. Soc. Jpn.*, **78**, 033201-1-033201-4 (2009).
3) A. Kimura, Y. Sato, M. Tanase, K. Tsuchida, *IOP Conf. Series: Mater. Sci. Eng.,* **18**, 1-4 (2011).
4) K. Gagnon, F. Bėnard, M. Kovacs, T.J. Ruth, P. Schaffer, J.S. Wilson, S.A. McQuarrie, *Nucl. Med. Biol.*, **38**, 907-916 (2011).
5) J. Barling, A.D. Anbar, *Earth Planet Sci. Lett.,* **217**, 315-329 (2004).
6) T. Golgberg, C. Archer, D. Vance, S.W. Poulton, *Geochim. Cosmochim. Acta*, **73**, 6502-6516 (2009).
7) T. Kashiwabara, Y. Takahashi, M. Tanimizu, *Geochem. J.*, **43**, e31-e36 (2009).
8) J. Bigeleisen, M.G. Mayer, *J. Chem. Phys.*, **15**, 261-267 (1947).
9) Y. Fujii, M. Aida, M. Okamoto, T. Oi., Sep. Sci. Technol., 20, 377-392 (1985).
10) J. Bigeleisen, *J. Am. Chem. Soc.*, **118**, 3676-3680 (1996).
11) M. Nomura, N. Higuchi, Y. Fujii, *J. Am. Chem. Soc.,* **118**, 9127-9130 (1996).
12) I.M. Ismail, M. Nomura, Y. Fujii, *J. Chromatogr. A*, **808**, 185-191 (1998).
13) M.D.A. Matin, M. Nomura, Y. Fujii, J. Chen, *Sep. Sci. Technol.*, **33**, 1075-1087 (1998).
14) S.H. Kim, M. Aida, M. Nomura, M.N. Rifaid, Y. Fujii, *J. Ion Exchange*, **11**, 26-31 (2000).
15) I.M. Ismail, A. Fukami, M. Nomura, Y. Fujii, *Anal. Chem.*, **72**, 2841-2845 (2000).
16) Y. Ban, M. Aida, M. Nomura, Y. Fujii, *J. Ion Exchange*, **13**, 46-52 (2002).
17) C. Marėchal, F. Albarėde, *Geochim. Cosmochim. Acta,* **66**, 1499-1509 (2002).
18) K. Hayasaka, T. Kaneshiki, M. Nomura, T. Suzuki, Y. Fujii, *Prog. Nucl. Energ.*, **50**, 510-513 (2008).
19) X. Ding, M. Nomura, T. Suzuki, Y. Fujii, *Prog. Nucl. Energ.,* **52**, 164-167 (2010).
20) T. Suzuki, M. Nomura, Y. Fujii, A. Ikeda-Ohno, T. Takaoka, K. Oguma, *J. Ion Exchange,* **21**, 328-333 (2010).
21) I.M. Ismail, M. Ibrahim, H.F. Aly, M. Nomura, Y. Fujii, *J. Chromatogr. A*, **1218**, 2923-2928 (2011).
22) T. Suzuki, Y. Tachibana, M. Nomura, Y. Fujii, *J. Plasma Fusion Res. Series*, **11**, 45-48 (2015).
23) Y. Tachibana, Y. Yamazaki, M. Nomura, T. Suzuki, *J. Radioanal. Nucl. Chem.,* **303**, 1429-1434 (2015).
24) Y. Tachibana, A.R. Putra, T. Kaneshiki, M. Nogami, T. Suzuki, M. Nomura, *Submitted to Energy Procedia.*
25) Information of structural details and chemical properties of WA20 and PA316 resins. http://www.diaion.com/en/products/ion_exchange_resins/index.html. Accessed 31 July 2017.
26) T. Suzuki, C. Kanzaki, M. Nomura, Y. Fujii, Rev. Sci. Instrum., **75**, 1931-1933 (2004).
27) G. Jerez, G. Kaufman, M. Prystai, S. Schenkeveld, K.K. Donkor, *J. Sep. Sci.*, **32**, 1087-1095 (2009).
28) P. Ilaiyaraja, K. Deb. A.K.S. Sivasubramanian, P.B. Venkatraman, *J. Hazard Mater.*, **250-251**, 155-166 (2013).