

# Syntheses and adsorption behavior of monoamide resins with porous silica support for selective recovery of uranium(VI) from nitric acid media

M. Nogami,<sup>1\*</sup> T. Ishihara,<sup>2</sup> K. Suzuki,<sup>1</sup> Y. Ikeda<sup>2</sup>

<sup>1</sup> Institute of Research and Innovation, 1201, Takada, Kashiwa, Chiba 277-0861, Japan

<sup>2</sup> Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1-N1-34, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

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Resins with monoamides as functional groups have been synthesized and their fundamental adsorption behaviors have been examined for selective recovery of uranium(VI) from nitric acid media. The resins synthesized with porous silica support showed greatly different adsorptions for U(VI) depending on the chemical structures of the functional group. Some resins show little or no adsorption for U(VI) from 0.1 to 6 mol/dm<sup>3</sup> HNO<sub>3</sub>. While, resins consisting of dimethylacrylamide (DMAA) showed an increasing adsorption with an increasing concentration of HNO<sub>3</sub> up to 9 to 12 mol/dm<sup>3</sup>. Other ions were not found to be adsorbed onto Silica-DMAA under similar solution conditions, which means that the resin is selective for U(VI) in HNO<sub>3</sub> media.

## Introduction

The resins with selectivity for U(VI) are useful in the field of radiochemistry and nuclear engineering. In fact, numerous chelating resins with selectivity for U(VI), e.g., amidoxime resins,<sup>1–3</sup> tannin,<sup>4</sup> resins with phosphono groups,<sup>5</sup> have been developed. Almost all of these resins show the highest adsorption for U(VI) from neutral aqueous solutions and very low adsorptions from acidic solutions because they have dissociative protons in the chemical structures. In many cases, however, U(VI) is supposed to be treated in nitric acid media, and the resins with selectivity for U(VI) under these solution conditions would be also useful.

On the other hand, it is known that some extractants, e.g., tri-*n*-butyl phosphate (TBP) and monoamides (RR'NCOR", R: alkyl group), extract tetravalent and hexavalent actinide ions from HNO<sub>3</sub> media in solvent extraction systems.<sup>6,7</sup> Besides, we found that some water-soluble monoamides like *N*-cyclohexyl-2-pyrrolidone (NCP) selectively precipitate with U(VI) from 1 to 7M (M = mol/dm<sup>3</sup>) HNO<sub>3</sub>.<sup>8</sup>

From the above, it is considered that the resins containing only one non-dissociative oxygen atom as the functional group like P=O in TBP and C=O in monoamides would possess selectivity for U(VI) in HNO<sub>3</sub> media. By using these resins, U(VI) would be adsorbed from relatively high concentrations of HNO<sub>3</sub> solutions and easily eluted with diluted HNO<sub>3</sub>. In addition, resins without phosphorus or sulfur as components are desired from the aspect of the treatment of waste resins.

In the present study, therefore, several resins with monoamides as the functional group have been synthesized, and the adsorption behaviors of the resins for U(VI) and other metal ions have been examined using HNO<sub>3</sub>.

## Experimental

### Syntheses of monoamide resins

The chemical structures of the functional groups of monoamide resins synthesized are shown in Fig. 1. Monoamides containing vinyl groups were used, all of them are commercially available. Divinylbenzene (DVB, purity 80%) was employed as a crosslinking agent.

The resins were synthesized by a single step of direct polymerization of the mixture of a porous silica support, a monomer containing monoamide groups, DVB, pore producing solvents, and initiators. The organic chemicals were used without further purification. The porous silica support has a uniform particle diameter of 50 μm with the pore size of 600 nm and the resins synthesized have also uniform particle diameter of ca. 50 μm.<sup>9</sup>

The components of the mixture in each resin are listed in Table 1. They were calculated in order that the pore volumes made by the pore producing solvents are 40% of the pore inside the silica, respectively. Polymerization of the mixture was performed in the similar method as described in the earlier paper.<sup>10</sup> The resin products were characterized by thermogravimetry (TG), infrared (IR) spectroscopy, and porosity analysis using a mercury porosimeter.

### Adsorption behavior of monoamide resins

Adsorption behavior of the monoamide resins for metal ions was examined by a batch method using 0.1 to 12M HNO<sub>3</sub> containing 10 mM of each metal ion, respectively, as the sample solution. U(VI) and other ions described below were used as metal ions:

Alkali and alkaline earth elements: Sr(II), Cs(I).

Rare earth elements: Ce(III), Sm(III), Dy(III).

\* E-mail: nogami@iri.or.jp

First transition elements: V(IV), Fe(III).

Second transition elements: Zr(IV), Mo(VI), Ru(III), Rh(III), Pd(II).

These are major fission products and elements forming oxo complexes like U(VI). In batch operations to measure the adsorption rates for U(VI), 10 g of the wet resin was immersed in 200 cm<sup>3</sup> of the sample solution followed by stirring at 298 K in a water bath. Aliquots of the sample solutions were taken in appropriate intervals. In the experiments of adsorption equilibrium, 1.0 g of the wet resin was immersed in 10 cm<sup>3</sup> of the sample solution followed by shaking for 1 hour at 298 K in a water bath. Atomic absorption spectrophotometry for Cs(I) and inductively coupled plasma – atomic emission spectroscopy for the others were used for the measurement of the concentration of the metal ions.

Adsorption behavior of the metal ions in the equilibrium experiments was evaluated by the distribution ratio,  $K_d$ ,

$$K_d = \frac{C_0 - C}{C} \cdot \frac{V}{W} \text{ cm}^3/\text{g dry resin} \quad (1)$$

where  $C_0$  and  $C$  denote the concentrations of the metal ion in the solution before and after contact with the resin, respectively,  $V$  and  $W$  represent the volume of the solution and the weight of the resin in dry form with silica, respectively.

## Results and discussion

### Syntheses of monoamide resins

The results of the decrease in weight of the resins by TG analysis up to 1273 K are shown in Table 2. The empirical values for Silica-DMAA and VPhI resins are a little smaller but close to those calculated from the ratio of the organic components of the mixture before polymerization, ca. 33 to 37wt%. In the case of Silica-VMAA resins, however, the empirical values were much smaller than the calculated ones. Polymerization of each monomer on the surface of the silica was confirmed by the IR spectra of the resins. Therefore, lower values of the organic component in Silica-VMAA resins are due to the insufficient adhesion of poly-VMAA on the silica after polymerization. Namely, it is considered that much larger amount of poly-VMAA was rinsed off during washing with acetone and water after polymerization.

Main pore sizes of the resins obtained from the porosity analysis are shown in Table 3. As previously expected, the resins except Silica-DMAA(2) possess large pores enough to be categorized into macroporous resins. Methyl benzoate had been found to be a good solvent for the DMAA-DVB mixture from the preliminary polymerization, and only Silica-DMAA(2), where the ratio of methyl benzoate is high, was expected to possess much smaller pores. Larger pore sizes in Silica-VMAA resins might be due to the insufficient conversion discussed in the TG analysis.

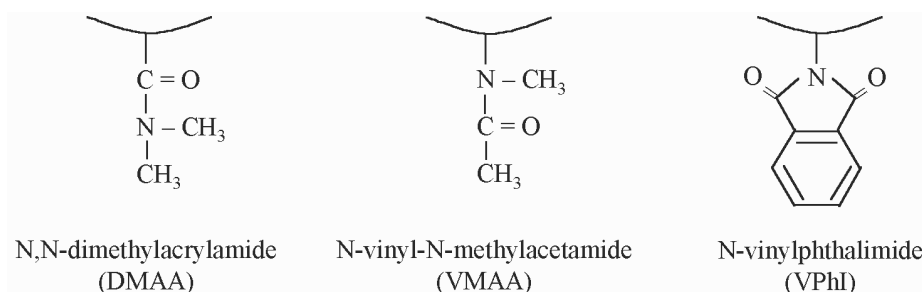


Fig. 1. Chemical structures of monoamide resins

Table 1. Components of raw material in monoamide resins

Resin	Crosslinkage, %	Silica, g	Monoamide monomer, g	DVB, g	Pore producing solvents, g
Silica-DMAA(1)	4	95	40.7	2.1	m-Xylene 8.7 heptane 20.8
Silica-DMAA(2)	4	95	42.3	2.2	Methyl benzoate 34.6 m-xylene 9.4
Silica-DMAA(3)	8	95	40.0	4.4	m-Xylene 9.1 heptane 21.5
Silica-VMAA(1)	4	95	40.6	2.1	Heptane 27.6
Silica-VMAA(2)	8	95	38.3	4.3	Heptane 27.5
Silica-VPhI	8	95	45.2	5.0	N,N-dimethylformamide 38.2

Table 2. Decrease in weights of resins by TG analysis

Resin	Calculated, %	Experimental, %
Silica-DMAA(1)	33.1	27.6
Silica-DMAA(2)	33.9	30.6
Silica-DMAA(3)	33.8	31.9
Silica-VMAA(1)	33.0	9.7
Silica-VMAA(2)	32.9	14.3
Silica-VPhI	36.7	33.0

Table 3. Main pore sizes of monoamide resins

Resin	Pore diameter, nm
Silica-DMAA(1)	220
Silica-DMAA(2)	10, 150
Silica-DMAA(3)	220
Silica-VMAA(1)	460
Silica-VMAA(2)	400
Silica-VPhI	120

### Adsorption behavior of monoamide resins

Adsorptions of Silica-DMAA resins for U(VI) from 3M HNO<sub>3</sub> as a function of time are shown in Fig. 2. The adsorption rates of Silica-DMAA(1) and (3) are fast enough to attain the adsorption equilibrium within 1 minute and the amounts of adsorbed U on them are almost identical. Silica-DMAA(2), on the other hand, shows slower adsorption rate because it is not macroporous.

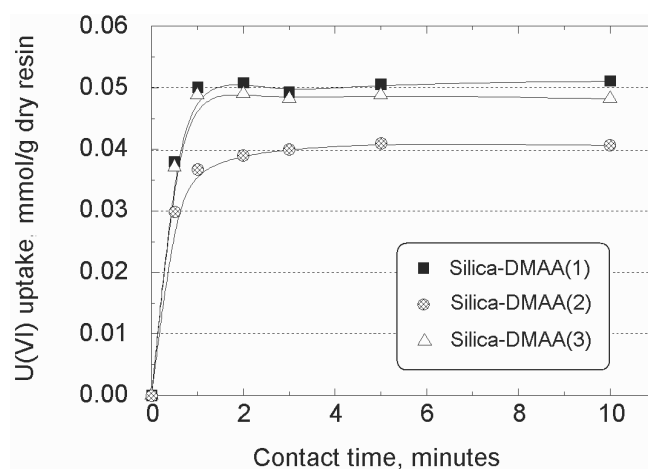
Adsorptions of the monoamide resins for U(VI) from HNO<sub>3</sub> solutions are shown in Fig. 3. In the case of Silica-DMAA resins, the  $K_d$  values are quite low in 0.1M HNO<sub>3</sub> and increase with increasing concentration of HNO<sub>3</sub>. The highest  $K_d$  values of them were ca. 60 around 9 to 12M HNO<sub>3</sub>. It has been revealed from Figs 2 and 3 that the crosslinkage of Silica-DMAA resins, (1) and (3), from 4 to 8% gives little difference to the adsorptions of U(VI). The lower adsorptions on Silica-DMAA(2) may be due to the much smaller pore sizes

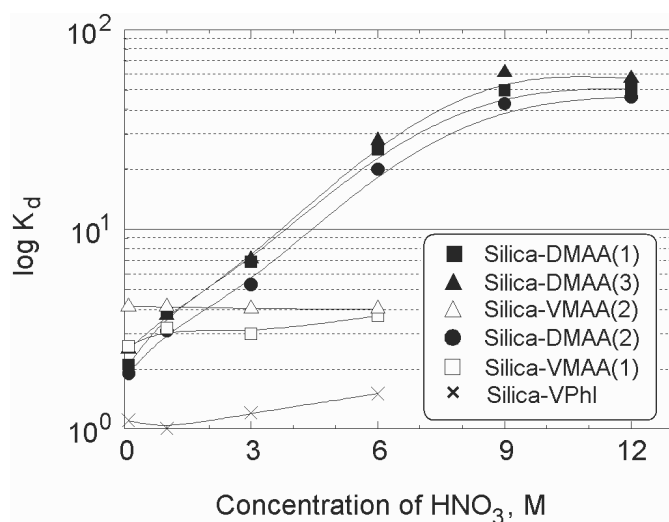
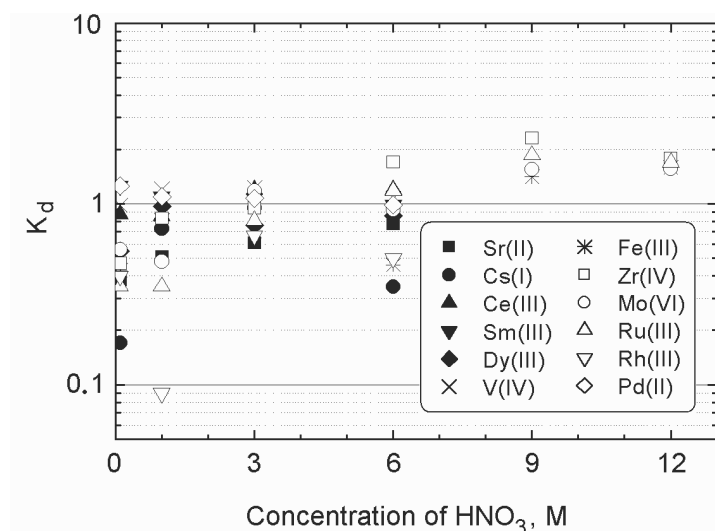
which make it difficult for uranyl ions to enter the inner side of the resin bead.

On the contrary, it is found that Silica-VMAA resins and Silica-VPhI show little or no adsorptions of U(VI), respectively.

Comparison of IR spectra of Silica-DMAA(1) before and after the U(VI) adsorption clarified that the peak at 1637 cm<sup>-1</sup> before adsorption is split into two peaks after adsorption and that one of them has a smaller wavenumber of 1595 cm<sup>-1</sup>. In addition, the peaks at 928, 1400 and 1500 cm<sup>-1</sup> originated from U=O bond in uranyl ions, free nitrates, nitrates when coordinated to uranyl ions, respectively, are found in the spectrum after adsorption. These results suggest that the probable adsorption mechanism of U(VI) onto Silica-DMAA resins might be the coordination of two oxygen atoms of the two amide groups to U(VI) comparable with monoamide extractants and NCP, forming UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DMAA)<sub>2</sub>.<sup>7,8</sup> No other mechanisms except the coordination of the amide oxygen atoms have been found for the U(VI) adsorption. The difference between Silica-DMAA resins and the other monoamide resins on the adsorption of U(VI) would be originated from the difficulty for the two oxygen atoms of Silica-VMAA and Silica-VPhI to coordinate to U(VI) due to the steric aspect. VPhI may be bulky actually, but VMAA seems not. Further investigations, e.g., of the basicity of the amide groups, would be necessary for clarification of the adsorption mechanisms of monoamide resins.

The adsorption experiments of elements except U(VI) were performed using Silica-DMAA(1). The results are shown in Fig. 4. The  $K_d$  values have been found to be up to ca. 2 for all the elements examined, which means that little or no adsorptions were measured. It can be considered, therefore, that Silica-DMAA resins are selective for U(VI) among naturally abundant metal ions in HNO<sub>3</sub> media.

Fig. 2. Adsorption of U(VI) on Silica-DMAA resins from 3M HNO<sub>3</sub> as a function of time

Fig. 3. Adsorption of U(VI) on monoamide resins from HNO<sub>3</sub> solutionsFig. 4. Adsorption of elements except uranium on Silica-DMAA(1) from HNO<sub>3</sub> solutions

It is known that TBP coextracts some metal ions, e.g., Tc(VII), with U(VI) from spent fuel dissolver solutions.<sup>11</sup> Adsorption behavior of other metal ions except U(VI) on Silica-DMAA resins from solutions containing multi elements together should be examined in the future.

### Conclusions

Several monoamide resins based on silica support were synthesized for the purpose of developing the resins with selectivity for U(VI) in the HNO<sub>3</sub> media. It was revealed that the adsorption behavior of the monoamide resins for U(VI) was largely influenced by the chemical structure of the monoamide functional

groups. Only Silica-DMAA resins have shown the U(VI) adsorption among the resins examined. Moreover, Silica-DMAA with macropores has shown the best adsorption behavior, where the  $K_d$  values for U(VI) are increased with increasing concentration of HNO<sub>3</sub> up to ca. 60. It was also found that Silica-DMAA has the selectivity for U(VI) as expected.

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