

Synthesis and adsorptivity of acryloylmorpholine resin to various fission product elements in nitric acid media

NISHIDA Tetsuhiro, TANAKA Shotaro & NOGAMI Masanobu*

Department of Electric and Electronic Engineering, Faculty of Science and Engineering, Kinki University, Higashi-Osaka, Osaka 577-8502, Japan

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A novel silica-supported resin with a cyclic monoamide of polymerized 4-acryloylmorpholine (Silica-AM) was synthesized, and adsorptivity to metal ions of major fission products (FP) was examined in HNO₃ and HCl solutions. Silica-AM has a carbonyl oxygen atom outside of the 6-membered morpholine ring, and a cyclic structure that is different than other cyclic monoamide resins we have studied. These include polyvinylpyrrolidone (PVPP) and poly-*N*-vinyl- ϵ -caprolactam (VEC), both of which have coordinative carbonyl groups included in the ring. Silica-AM was similar to a cyclic monoamide we have reported because it exhibited adsorption to Pd(II) and Re(VII) in HNO₃ of a particularly low concentration range. Silica-AM has an ether oxygen atom included in the ring as well. Considering the difference in the chemical structures of Silica-AM and other cyclic monoamide resins, it was suggested that oxygen atoms in the carbonyl group and in ether may be main contributors to Silica-AM's respective adsorptions to Pd(II) and Re(VII), and Mo(VI) and Zr(IV). Our results imply that the contribution of the two types of oxygen atoms to adsorption is more observable in an HCl system. The contribution of the ether oxygen atom to the adsorption of Pd(II) was also suggested from our study on crystal prepared from 4-acetylmorpholine and palladium nitrate.

monoamide resin, acryloylmorpholine, FP, nitric acid

1 Introduction

Monoamide compounds are famous for extracting actinoid (IV) and (VI) species from aqueous nitric acid solutions. With this distinction in mind, we have synthesized several silica-supported polymer beads with the structure of a monoamide as the functional group for developing resins with selectivity to U(VI) in HNO₃ media, and examined their adsorptivities to various metal ions of fission products (FP) [1–4]. We have also investigated the adsorptivity of commercially available polyvinylpyrrolidone (PVPP), which is one of the cyclic monoamide resins and has a 5-membered pyrrolidone ring (Figure 1(a)) [5].

Because these resins have been studied for the selective

separation of U(VI) in HNO₃, it is desirable for them to adsorb no metal ions other than U(VI). In fact, few kinds of FP ions have been found to be adsorbed to the examined resins. Interestingly, it has also been revealed that the adsorptivity of the adsorbed FP ions differs depending on the chemical structure of the monoamide resins. Namely, a silica-supported resin consisting of *N,N*-dimethylacrylamide (Silica-DMAA), which is a chain monoamide (Figure 1(b)), exhibits no adsorption for major FP ions regardless of the concentration of HNO₃ [1]. However, PVPP shows weak adsorptions for Pd(II) and Re(VII), which are simulants of Tc(VII) in HNO₃ of lower concentration range [5]. It has also been revealed that another cyclic monoamide resin consisting of silica-supported poly-*N*-vinyl- ϵ -caprolactam (Silica-VEC), which has a 7-membered ring (Figure 1(c)), shows the characteristic of a cyclic monoamide such as PVPP for adsorptivity although this characteristic for VEC

*Corresponding author (email: mnogami@ele.kindai.ac.jp)

is lower than for PVPP [4].

The stability of PVPP [6] and water-soluble pyrrolidone derivatives which are supposed to be used for the selective precipitation of U(VI) species in HNO_3 media [7] against γ -ray irradiation have also been investigated in HNO_3 . Results show that the degradation of these compounds progresses differently from the observed degradation for chain-type monoamide extractants, in which the simple cleavage of the amide bond mainly occurs [8, 9]. Specifically, the degradation of pyrrolidone derivatives in HNO_3 by γ -ray irradiation starts from the cleavage of the pyrrolidone ring by the addition of oxygen atom originating from HNO_3 , followed by the formation of chain compounds by the successive addition of oxygen.

Considering the above information, the adsorptivity of cyclic monoamide resins to FP ions would be no less important than that the adsorptivity of U(VI) for developing resins with selectivity to U(VI) in HNO_3 . In the present study, a novel silica-supported resin with a monoamide of polymerized 4-acryloylmorpholine (Silica-AM; Figure 2) was synthesized; the adsorptivity to metal ions mainly for FP was examined before investigating the adsorptivity to U(VI). Poly-4-acryloylmorpholine is widely used as, among other things, a component of nanoparticles for drugs [10] and copolymer materials in the research field of solution chemistry [11]. AM has some interesting features for adsorbing metal ions from the viewpoint of the chemical structure: (1) It has a 6-membered ring. (2) Unlike PVPP and VEC, the carbonyl group is not included in the ring. (3) The ring has a coordinative ether oxygen atom. It is therefore expected that the adsorptivity of Silica-AM is more complicated than the adsorptivity of the resins shown in Figure 1, due to the adsorption by more kinds of metal ions.

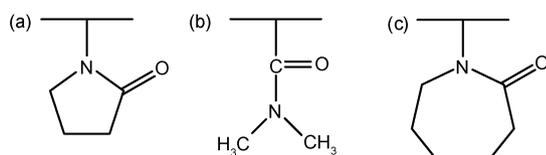


Figure 1 Chemical structure of monoamide resins previously studied. (a) PVPP; (b) DMAA; (c) VEC.

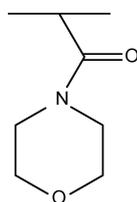


Figure 2 Chemical structure of polymerized AM.

2 Experimental

2.1 Synthesis of resin

AM was purchased from Wako Pure Chemical Industries, Ltd. (Japan) and divinylbenzene (DVB, purity 80%) was employed as a crosslinking agent. SILBEAD MST-8C from Mizusawa Industrial Chemicals, Ltd. (Japan) was sieved between 63 and 150 μm and used as a porous silica support. Silica-AM was synthesized by a single step of direct polymerization of the mixture of the porous silica support and oil (AM, DVB, pore-producing solvents, and initiators). The organic chemicals were used without further purification. The components of the mixture (Table 1) were determined by pre-polymerizations that used several combinations of pore-producing solvents. Under the mixing condition, the resin was supposed to have 8% crosslinkage. Polymerization of the mixture was performed similarly to the literature [1, 2, 4]. After the resin product was washed with acetone and water, characterization was performed by infrared (IR) spectroscopy and thermogravimetry (TG). For the TG, the adhesion ratio of the polymer to the silica was determined using an electric furnace in which the ambient temperature was raised to 1273 K.

Similarly to an earlier study [4], AM without a silica support was synthesized by bulk polymerization using the identical oil component in a separable flask. The resultant polymer was washed with acetone, dried, and ground using a mortar. After that, it was sieved between 63 and 150 μm .

2.2 Adsorptivity of synthetic resin

The adsorption rates for Silica-AM were measured by a batch method using Zr(IV), Pd(II), and Re(VII), and evaluated by the uptake of the metal ions per unit weight of the resin, excluding silica. Samples of the conditioned resin (0.2 g) and 0.1–6 mol/L HNO_3 solutions containing a 1 mmol/L metal ion (4 mL) were shaken at 298 K in a thermostatic shaking bath. Samples of the supernatant were taken after appropriate contact times of up to 24 h and the concentrations of the metal ion were measured using ICP-AES.

Adsorptivities of silica-AM to various FP ions from 0.1–6 mol/L HNO_3 at equilibrium were examined by a batch method using the same procedure as for the rate of adsorption (i.e., the initial concentration of each metal ion was 1 mmol/L and the contact time was 24 h). Adsorptivities were evaluated by the distribution ratio, K_d , defined as

Table 1 Components of raw materials for Silica-AM

Silica (g)	VEC (g)	DVB (g)	Pore producing solvents (g)	Initiators (g)
50.3	22.5	2.5	<i>N,N</i> -dimethylformamide: 20.2	2,2'-azobis(isobutyronitrile): 0.25 1,1'-azobis(cyclohexane-1-carbonitrile): 0.25

$$K_d(\text{mL/g}) = \frac{C_0 - C}{C} \times \frac{V}{W} \quad (1)$$

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, respectively, the volume of the solution and the weight of the resin, excluding silica. The C_0 and C for each metal ion were determined by ICP-AES. It is known that extractants and resins consisting of ether bonds such as crown ethers have affinity to some metal ions in hydrochloric acid media and that this affinity differs depending on the concentration of HCl [12, 13]. Therefore, we performed similar experiments using HCl solutions for comparison.

2.3 Preparation of crystal consisting of acetylmorpholine

To obtain information on the adsorption site of Silica-AM for Pd(II) in HNO_3 , a crystal consisting of 4-acetylmorpholine (AcM) and palladium nitrate was prepared. A 3 mol/L HNO_3 solution containing 50 g/L Pd(II) (Tanaka Kikinzoku Kogyo, Japan; 0.55 mL) and AcM (Aldrich, USA; 0.195 g) were added to the mixed solution of acetonitrile (5 mL) and heptane (0.05 mL). The mixture stood at ambient atmosphere for ca. 3 months, after which orange-colored needle-like crystals were obtained. The crystals were washed with hexane and air-dried, after which they were characterized by IR spectroscopy.

3 Results and discussion

3.1 Synthesis of resin

Polymerization of AM on the surface of the silica was confirmed by measuring IR spectra of Silica-AM. In the spectra, an increase in the intensity of the peak at around 1642 cm^{-1} , attributed to the stretching vibration of C=O bond of AM, was clearly observed. Generation of new peaks at around 3000 cm^{-1} , attributed to the alkyl groups of AM, was also observed. From the TG analysis, it was found that the weight decrease of the Silica-AM was 31.7%, from which the adhesion ratio was calculated as 93.2% based on the ratio of the organic components of the mixture before polymerization. This value was sufficiently enough as well as those for, e.g. Silica-DMAA resins [1].

3.2 Adsorptivity of synthetic resin

The adsorbed amount of Pd(II) onto Silica-AM, q_{Pd} , as a function of time is shown in Figure 3. The equilibrium was attained within approximately 2 h except for the sample of 0.1 mol/L HNO_3 ; in addition, the q_{Pd} values gradually increased from 4 h up to 48 h for the sample of 0.1 mol/L HNO_3 . These tendencies are similar to those of VEC [4] and

are much faster than those of PVPP, where q_{Pd} values for 30 h of contact were, respectively, ca. 80% and 30% higher than those for 1 h in 0.1 and 6 mol/L HNO_3 [5].

In our previous study, we observed differences in the color changes of the resin samples after we observed the adsorption of Pd(II) from HNO_3 of various concentrations. For VEC, with the adsorption of Pd(II), the color of the sample with 0.1 mol/L HNO_3 changed gradually from orange to dark brown; the samples of 3 and 6 mol/L HNO_3 remained orange [4]. For PVPP, the color change was observed in the samples of 3 mol/L HNO_3 and 0.1 mol/L HNO_3 . These color changes were explained by the reduction of Pd(II) to Pd(0) through the adsorption that originated from the strong coordination field generated by the N and O atoms in the polar group of PVPP [5]. In the present study, the tendency of the color change in the sample of AM without silica treated similarly to Silica-AM was found to be identical with that of VEC, which is in accordance with the results for the adsorption rate. It was difficult to observe such color changes for the samples of Silica-AM because all of the resins exhibited a light brown color due to the color of the silica support. These facts indicate that AM also has characteristics of a cyclic monoamide although the carbonyl group of AM is not included in the ring; in addition, the degree is compatible to that of VEC and lower than that of PVPP.

Adsorbed amounts of Zr(IV) and Re(VII) onto Silica-AM in 0.1 mol/L HNO_3 as a function of time are shown with the result of the above-mentioned Pd(II) in Figure 4. Adsorbed amounts of these metal ions are collectively described as q_{M} in the vertical axis. We found that equilibrium was attained within approximately 4 and 12 h for Re(VII) and Zr(IV), respectively. This result indicates that the slower adsorption rate for Pd(II) would be due to the nature of a cyclic monoamide of AM.

The K_d values of Silica-AM for various metal ions at 24 h of contact in HNO_3 solutions are shown in Figure 5. Zr(IV) and Mo(VI) were found to have the largest K_d values among the examined metal ions, more than 40 in 0.1 mol/L

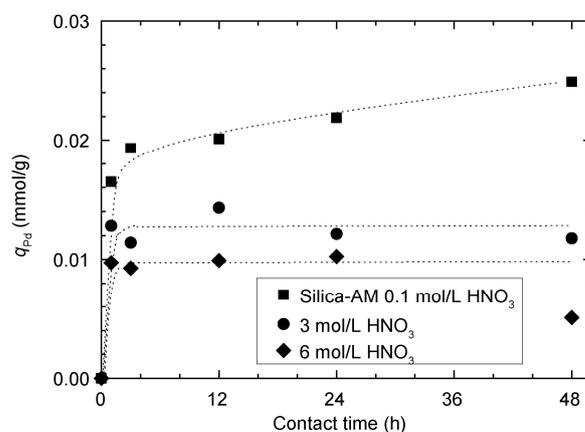


Figure 3 Plots of Pd(II) uptake onto Silica-AM vs. time.

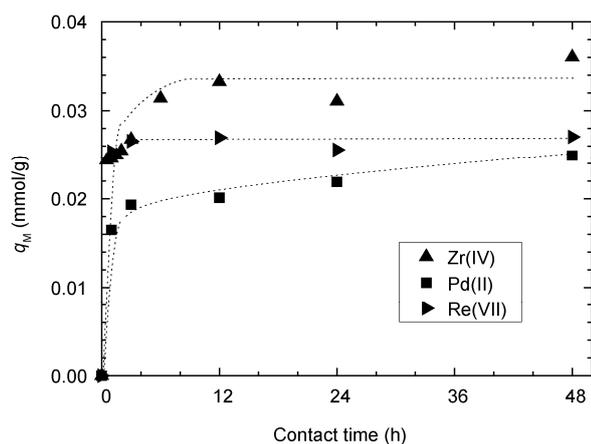


Figure 4 Plots of uptake of Zr(IV), Pd(II), and Re(VII) onto Silica-AM from 0.1 mol/L HNO_3 vs. time.

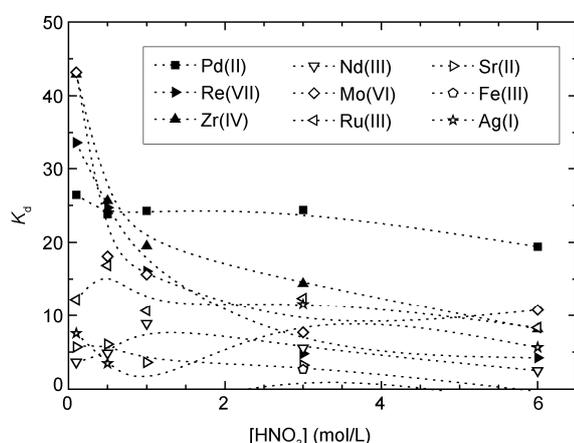


Figure 5 Dependence of concentration of HNO_3 on adsorption of Silica-AM to various metal ions.

HNO_3 , and also showed decreasing K_d values as the HNO_3 concentrations increased. Re(VII) and Pd(II) also showed decreasing K_d values with increasing HNO_3 concentrations; in addition, the dependence of the K_d values on the concentration of HNO_3 was much more easily observed in Re(VII) than in Pd(II), which is in accordance with the tendencies of PVPP and VEC [4, 5]. Pd(II) showed the highest adsorption in HNO_3 (higher than 1 mol/L). It can also be seen that Ru(III) was weakly adsorbed, regardless of the concentration of HNO_3 with K_d values of ca. 10. Very low adsorptions were observed for the other examined metal ions, however. Considering the difference in the chemical structure of silica-AM from the other cyclic monoamide resins, it is suggested that oxygen atoms of the carbonyl group and ether may be the main contributors to the adsorption of silica-AM to, respectively, Pd(II) and Re(VII), and Mo(VI) and Zr(IV).

The K_d values of Silica-AM for various metal ions at 24 h of contact in HCl solutions are shown in Figure 6. Re(VII) had the largest K_d values of ca. 70 in HCl (lower than

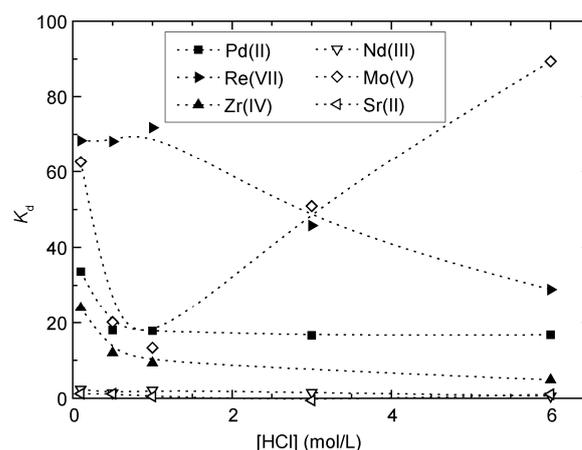


Figure 6 Dependence of concentration of HCl on adsorption of Silica-AM to various metal ions.

1 mol/L) as well as decreasing K_d values with increasing acid concentrations (as with HNO_3 media). These values are larger than those for HNO_3 media. For Mo(V), the K_d values increased with an increase in the concentration of HCl beyond ca. 1 mol/L. The large K_d values may partly result from the hydrolysis of Mo(V). It can be seen that Pd(II) and Zr(IV) have similar curves for adsorptivity with larger K_d values in 0.1 mol/L HCl, and that the adsorptivity is higher for Pd(II) than for Zr(IV). We did not investigate color change after adsorption of Pd(II) in 0.1 mol/L HCl using AM without silica in the present study.

As for the adsorptivities of other metal ions in HCl, Nd(III) and Sr(II) showed very little adsorption. It was also found that Fe(III) had no adsorption. Such adsorptivities observed in HCl media seem different than other types of adsorbents, which suggests that both of carbonyl and ether oxygen atoms in AM may contribute, to a greater or lesser extent, to the adsorption of metal ions. Clarification of the adsorption site in HCl media should be attempted in future studies.

3.3 Characterization of crystal

Figure 7 shows the IR spectrum of the crystal prepared from AcM and palladium nitrate with the IR spectrum of 4-acetylmorpholine. Low transmittance observed in a wide wavenumber range (below ca. 1000 cm^{-1}) for AcM resulted from using a set of CaF_2 discs for the measurement. It can be seen that the peak at 1649 cm^{-1} for 4-acetylmorpholine, attributed to the C=O stretching bond, shifted to 1623 cm^{-1} for the crystal. This indicates that the carbonyl oxygen atom coordinates to Pd(II), a result that corresponds to an earlier study which found that pyrrolidone derivatives and Pd(II) form nitrate complex where only the oxygen atom coordinates to Pd(II) and the nitrogen atom has no interactions with Pd(II) [14]. In addition, it is observed that the peak at 1115 cm^{-1} for AcM, attributed to the ether bond, shifted to

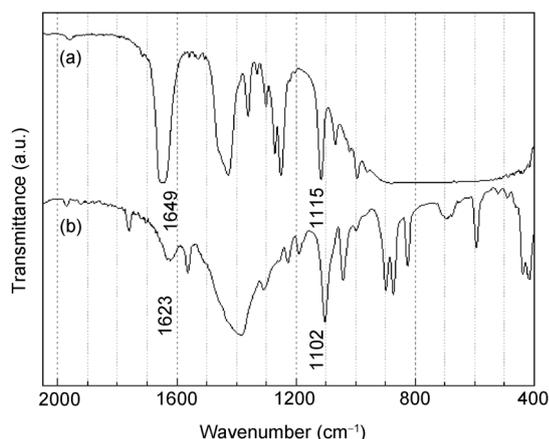


Figure 7 IR spectra of (a) AcM and (b) crystal prepared from AcM and palladium nitrate.

1102 cm^{-1} for the crystal. This suggests the contribution of the ether oxygen atom to the adsorption of Pd(II). So far, no more information is available for the obtained crystal. Another type of analysis, such as a single-crystal X-ray structure analysis, would be necessary for clarification of this point.

4 Conclusions

A newly synthesized cyclic monoamide resin of Silica-AM for selective separation of U(VI) in HNO_3 media was obtained and its adsorptivity to metal ions, mainly of FP, was examined in HNO_3 and HCl media. Although it is a different type of monoamide resin from those such as PVPP and VEC, Silica-AM showed characteristics of a cyclic monoamide because it similarly exhibited adsorption to Pd(II) and Re(VII) in HNO_3 in a particularly low concentration range. Considering the difference in the chemical structure of Silica-AM from other cyclic monoamide resins, we suggest that oxygen atoms of the carbonyl group and the ether may be the main contributors to the adsorption of Silica-AM to, respectively, Pd(II) and Re(VII), and Mo(VI) and Zr(IV). The results imply that the contribution of the two types of oxygen atoms to adsorption is more observable in

HCl system. The contribution of the ether oxygen atom to the adsorption of Pd(II) was also suggested from our study of the crystal prepared from AcM and palladium nitrate.

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