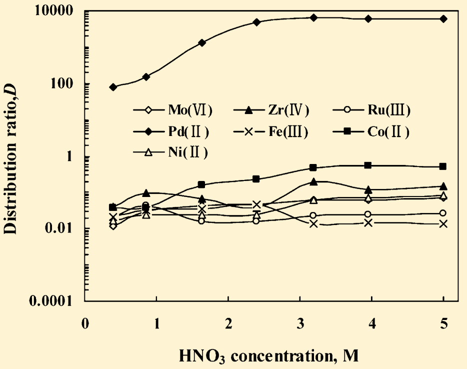
JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

New Insight into the Partitioning of Minor Actinides I: Extraction of Palladium and Some Typical Metals with a Multidentate Soft-Ligand 2,6-Bis(5,6-dinonyl-1,2,4-triazine-3-yl)pyridine

Anyun Zhang,*[†] Yaping Zhu,[†] and Zhifang Chai[†,‡]

[†]Department of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, P. R. China
[‡]Institute of High Energy Physics, Chinese Academy of Sciences, P.O. Box 918, Beijing 100049, P. R. China

ABSTRACT: A new multidentate soft-ligand 2,6-bis(5,6-dinonyl-1,2,4-triazine-3-yl)pyridine (NonBTP) was synthesized. The solvent extraction of Pd(II) and some typical metals Ru(III), Mo(VI), Fe(III), Co(II), Zr(IV), and Ni(II) with NonBTP/30 % 1-octanol—70 % 1-dodecane was investigated at 298 K. It was performed by examining the effects of contact time and the concentration of HNO_3 in the range of (0.42 to 5.11) M. NonBTP showed a strong extraction ability and high selectivity for Pd(II) over the tested metals, which had very weak or almost no extraction. The optimum acidity in the extraction of Pd(II) was around 3.0 M HNO_3. It was ascribed to the complexation of Pd(II), a weak Lewis acid and an electron-pair acceptor, with nitrogen inside NonBTP, a weak Lewis base and an electron-pair donor. The extraction of NonBTP for Pd(II) was an exothermic reaction. The composition of the extracted species was determined to be $Pd(NO_3)_2 \cdot 2NonBTP$. Considering the excellent complexation of minor actinides MAs(III) with NonBTP, the results are beneficial to simultaneous partitioning of MA(III) and Pd(II) from highly active liquid waste by the NonBTP-containing extraction system.



INTRODUCTION

It is known that one of the important purposes in the reprocessing of nuclear spent fuel is the partitioning and recovery of uranium and plutonium by 30 % tri-*n*-butyl phosphate/kerosene through the Purex or its modified extraction process.[1] As a result, an extremely complicated system, highly active liquid waste (HLW) with a high HNO_3 concentration, was produced. A variety of the fission and nonfission products (FPs) such as the long-lived minor actinides MAs(III), rare earths REs(III), heat generators Cs(I) and Sr(II), noble metals, Fe(II)—Fe(III), Mo(VI), Tc(VII), and Zr(IV), and so forth are contained in HLW.[2] To reduce the potential risk of HLW to the environment and human health, the elimination of the radionuclides to treatment and disposal of HLW are therefore significant. However, effective partitioning of relevant nuclides has always been one of the most challenging works these years. Most attention has been focused on the separation of MAs(III) such as Am(III) and Cm(III) from HLW because of the partitioning and transmutation (P/T) strategy.[3−9] Some attention is concentrated on the separation of heat emitting nuclides, Cs(I) and Sr(II).[10−15] Almost no attention has been focused on the partitioning of the long-lived Pd(II) from HLW.

Divalent palladium is one of the fission products in HLW. It is generated by the fission of uranium or plutonium in nuclear reactor or by β-decay of adjacent species. The radioactive ^{107}Pd with a half-life of $6.5 \cdot 10^6$ year is a soft β-emitter of 0.035 MeV energy. Its quantity in nuclear spent fuel is approximately (1 to 2) kg per ton. It was reported that the removal of Pd(II) from HLW might likely make the vitrification of HLW in final geological disposal easier. The effective elimination of Pd(II) from HLW is therefore valuable.

To separate the specific radionuclides Cs(I), Sr(II), MAs(III), Pd(II), and others, the advanced partitioning technologies entitled SPEC (Strontium/cesium Partitioning from HLW by Extraction Chromatography) and MPS (the long-lived MA (III) and Pd(II) Separation by extraction chromatography) processes have been developed recently.[16,17] Two heat generators Cs(I) and Sr(II) were separated utilizing two novel macroporous silica-based supramolecular recognition materials (SSRM), calix[4]arene-crown/SiO_2—P, and 4,4′,(5′)-di(*tert*-butylcyclohexano)-18-crown-6(DtBuCH18C6)/SiO_2—P.[18,19] The long-lived MA(III), Pd(II), and others showed no adsorption onto these macroporous silica-based materials and then flowed into effluent along with Pd(II), Zr(IV), Mo(VI), Rh(III), Ru(III), REs(III) (Y and from La to Lu), Na(I), K(I), Fe(III), MAs(III) (Am and Cm), and 2.0 M HNO_3 (noted as the MA-Pd-group). Subsequently, the long-lived Am(III), Cm(III), and Pd(II) in the MA-Pd-group were partitioned by the novel macroporous silica-based soft-ligand 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine (dialkyl-BTP) impregnated materials (SSLM) dialkyl-BTP/SiO_2—P as shown in Figure 1. The MA-Pd-group was separated into (1) REs(III), Mo(VI), Na(I), K(I), Ru(III), Rh(III), and Zr(IV) and so forth (nonadsorption group), (2) Pd, and (3) MAs(III), respectively, by

Received: December 25, 2011
Accepted: March 1, 2012
Published: March 15, 2012

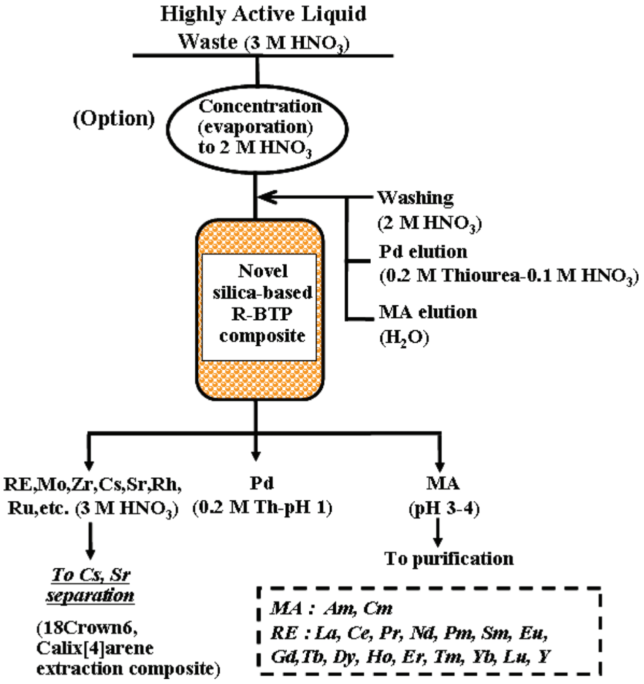


Figure 1. MPS: an advanced concept process of the MA(III) and Pd(II) Separation together from HLW by extraction chromatography utilizing the novel macroporous silica-based soft-ligand material.

using 0.2 M thiourea/0.1 M HNO_3 and 0.01 M HNO_3/1.0 M $NaNO_3$ as eluents. However, the preliminary investigations such as the complexation mechanism, the composition of the complex of Pd(II) with these novel macroporous silica-based nitrogen-containing soft-ligand materials, and the others have not been reported yet. Seeking an effective pathway to make the complexation of Pd(II) with dialkyl-BTP clear is therefore valuable.

Solvent extraction is one of the conventional separation technologies. It is effective for the determination of the complexation and complex composition of metals with chelating agents. Dialkyl-BTP as shown in Figure 2 is a multicoordinate soft-ligand containing seven nitrogen atoms. The results showed that it had an excellent extraction ability and selectivity for trivalent MAs(III) over all of the REs(III).[20−22] Similar to dialkyl-BTP, some derivatives of bipyridines also exhibited the same extraction properties for MAs(III) and REs(III).[23−25] On the other hand, in terms of the traditional Lewis theory of acid−base reactions, nitrogen in dialkyl-BTP or the derivative of bipyridine has a much better coordination ability for the elements in the d-block in the periodic table of elements. It is therefore predicted that some fission products Zr(IV), Ru(III), and Mo(VI) might also have a more or less adverse impact on the separation of MAs(III) and Pd(II). From this viewpoint, utilizing the principle and experimental method of the solvent extraction to investigate the complexation of Pd(II) with dialkyl-BTP is meaningful. However, regarding the complexation of Pd(II) with dialkyl-BTP or the derivatives of bipyridines either in chromatographic separation with a stationary phase or in solvent extraction has not been reported yet. The composition of the complex of Pd(II) with dialkyl-BTP or the derivatives of bipyridines in HNO_3 medium has not been understood.

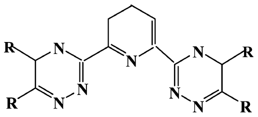


Figure 2. Chemical structure of 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl) pyridine (dialkyl-BTP).

To understand the complexation of Pd(II), the purpose of the present work was to obtain some valuable experimental data by solvent extraction. The main objective was focused on: (1) synthesis of a new multidentate soft-ligand 2,6-bis(5,6-dinonyl-1,2,4-triazine-3-yl)pyridine (NonBTP), which was performed by a multistep reaction; (2) investigation of the extraction properties of some typical fission and nonfission products Ru(III), Zr(IV), Mo(VI), Fe(III), Co(II), and Ni(II) with a NonBTP-containing mixture composed of 30 % 1-octanol and 70 % 1-dodecane. It was carried out by examining the effects of contact time, the HNO_3 concentration in the range of (0.42 to 5.11) M, and temperature, and (3) determination of the optimum concentration of HNO_3 in the extraction of Pd(II), the extraction mechanism, and the complex composition of Pd(II) with NonBTP. The possibility and feasibility of application of the NonBTP-containing extraction system in partitioning of MA(III) and Pd(II) together from HLW were evaluated.

■ EXPERIMENTAL PROCEDURE

Materials. The metal nitrates $ZrO(NO_3)_2 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$, $M^{II}(NO_3)_2$ (M^{II} = Co and Ni), and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ used were of analytical grade. Palladium nitrate solution with 4.5 wt % of Pd(II) was provided by the Tanaka Noble Metal Co. Inc., Japan. Ruthenium nitrosyl nitrate solution with 1.5 wt % of Ru(III) was provided by the Strem Chemicals (Newburyport, MA). The ionic strength (μ) in aqueous phase in the determination of the composition of the complex of Pd(II) was maintained by the addition of a stock solution of $NaNO_3$. The concentrations of the tested metals in HNO_3 solution were around $5.0 \cdot 10^{-3}$ M.

A soft-ligand with multinitrogen donors, 2,6-bis(5,6-dinonyl-1,2,4-triazine-3-yl)pyridine (NonBTP) as shown in Figure 3, was synthesized quantitatively by the multistep reactions. The diluents, 1-octanol and 1-dodecane, used in organic phase were available commercial products. To avoid the formation of the third phase in solvent extraction, a mixture composed of 30 % 1-octanol and 70 % 1-dodecane was used as the organic phase to dissolve NonBTP. Based on the excellent solubility of NonBTP, no any additive was used in organic phase. The other organic and inorganic reagents were of analytical grade and were used without further treatment.

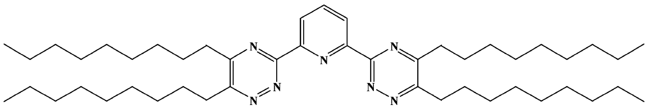


Figure 3. Molecular structure of 2,6-bis(5,6-dinonyl-1,2,4-triazine-3-yl) pyridine (Non-BTP).

Synthesis of NonBTP. The preparation of NonBTP was performed through three steps.[26] It was described as: (1) the synthesis of 2,6-pyridinedicarboxamide dihydrazone by the reaction of 2,6-pyridine with 85 % of hydrazine hydrate, performed for 30 h at 303 K and then recrystallized by water; (2) synthesis of a α-diketone $CH_3(CH_2)_7CH_2COCOCH_2(CH_2)_7CH_3$ by the reduction of $CH_3(CH_2)_7CH_2COOCH_2CH_3$ with sodium in xylene/diethyl ether and then oxidation of the resultant intermediate product with $Cu(CH_3COO)_2·H_2O$ in 70 % acetic acid medium, and (3) synthesis of NonBTP through the reaction of 2,6-pyridinedicarboxamide dihydrazone with $CH_3(CH_2)_7CH_2COCOCH_2(CH_2)_7CH_3$ in dichloromethane, carried out for 3 h at 313 K and then recrystallized with ethanol. The resultant NonBTP, a yellow product, was characterized by elementary analysis, ^{1}H NMR, and electrospray ionization mass spectrometry (EI-MS). The purity of NonBTP was determined to be more than 98.5 %. The synthesis technical route of NonBTP is shown in Figure 4.

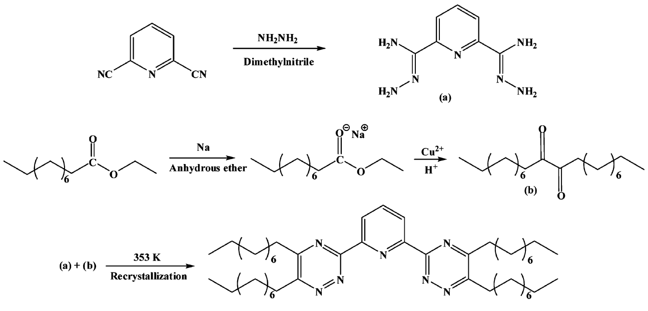


Figure 4. Technical route of synthesis of 2,6-bis(5,6-dinonyl-1,2,4-triazine-3-yl) pyridine (Non-BTP).

Measurement of the Distribution Ratio. The extraction of the tested metal with NonBTP was performed at 298 K except that of the experiment of the temperature effect. It was controlled using a TAITEC MM-10 model thermostatted water bath.

Equal volumes (5 cm^3) of a HNO_3 solution containing the tested metals as an aqueous phase and of a mixture composed of NonBTP, 30 % 1-octanol, and 70 % 1-dodecane as an organic phase, pre-equilibrated with HNO_3 of the same concentration without containing metals, were mixed into a ground glass-stopped equilibration tube, it was then shaken mechanically at 120 rpm. Preliminary studies showed that the extraction equilibrium was established within 30 min. To ensure that the equilibrium was reached fully, the contact time of two phases was extended to 90 min. The concentrations of NonBTP, the tested metal, and the ratio of aqueous phase to organic one were $2.0·10^{-2}$ M, $5.0·10^{-3}$ M, and 1:1. The concentration of HNO_3 in aqueous phase was in the range of 0.4 to 4.0 M. The ionic strength in aqueous phase was kept constant by the addition of a stock solution of $NaNO_3$. After the phases were centrifuged and separated, the concentrations of the tested metals in aqueous phase were determined using a Varian 700-ES model simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian, Inc., the United States of America) The distribution ratio (D) of the tested metals was calculated by the following equation:

$$D = C_{(\mathrm{o})}/C_{(\mathrm{a})} \tag{1}$$

In eq 1, $C_{(\mathrm{o})}$ and $C_{(\mathrm{a})}$ represent the equilibrium concentrations of the tested metals in organic phase and the aqueous phase, respectively.

RESULTS AND DISCUSSION

Dependence of the Tested Metal Extractions on Contact Time. It is known that in liquid−liquid solvent extraction, the effective extraction of metal ion is achieved by the formation of the extracted species between extractants and metal ions through the coordination bonding in organic phase. Therefore, the extraction ability and selectivity of extractants for metal ions strongly depends on the intensity of the chemical complexation. There are seven nitrogen atoms in the molecular structure of NonBTP. According to the Lewis theory of acid−base reactions, the Lewis bases donate pairs of electrons while acids accept them. A Lewis acid may be any ion or molecule that can accept a pair of nonbonding valence electrons, that is, a Lewis acid is an electron-pair acceptor. A Lewis base is any substance that can donate a pair of nonbonding valence electrons and is therefore an electron-pair donor. Based on the Lewis theory, Pd(II) located in d-block in the Periodic Table of Elements is considered to be an electron-pair acceptor, that is, a Lewis acid due to the unsaturated p-orbits, while the other tested metal ions are also thought as the Lewis acids. Opposite to Pd(II), the NonBTP molecule is an electron-pair donor, that is, a Lewis base. Because the nitrogen atom is a so-called soft-atom, NonBTP acts as a soft Lewis base. Since the hardness and softness of the Lewis acids of the tested metal ions including Pd(II) are different, so, the complexation of these metals with NonBTP in solvent extraction might be different. As a result, it might result in the different extraction ability and selectivity of NonBTP for these metal ions.

To understand the extraction behavior of NonBTP, a mixed organic solvent composed of 30 % 1-octanol and 70 % 1-dodecane was used to dissolve NonBTP. The dependence of the extraction of some typical fission and nonfission products Ru(III), Fe(III), Co(II), Zr(IV), Ni(II), Pd(II), and Mo(VI) with NonBTP/30 % 1-octanol−70 % 1-dodecane in 2.0 M HNO_3 with a change in contact time was investigated at 298 K. The results are shown in Figure 5.

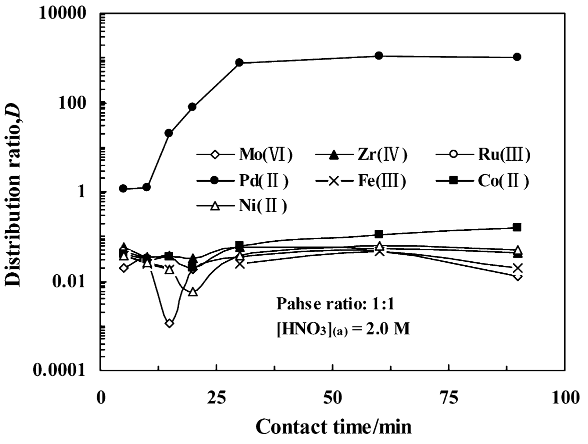


Figure 5. Dependence of the tested metals extraction with NonBTP on contact time in 2.0 M HNO_3 at 298 K.

With an increase in contact time, the extraction of Pd(II) with NonBTP increased quickly at initial 30 min and then kept constant, reflecting that it reached the extraction equilibrium. The distribution ratio (D) of Pd(II) in excess of 30 min was always greater than 765, while the tested metals Ru(III), Fe(III), Zr(IV), Co(II), Ni(II), and Mo(VI) showed weak or almost no extraction with NonBTP. The distribution ratios (D) of them at contact time of 90 min were always less than 0.1553. Such a low value in the distribution ratio resulted from the weak complexation of these metals with a nitrogen atom inside the NonBTP molecule.

According to the Lewis theory of acid−base reactions, the trivalent Fe(III) is considered to be a hard Lewis acid substance being capable of effective recognizing and accepting a pair of nonbonding valence electrons from a hard Lewis base with the electron-pair donor. So, no extraction of Fe(III) was ascribed to the lack of affinity of the soft-base nitrogen in NonBTP molecule for the hard-acid Fe(III). Namely, no effective complexation of NonBTP with Fe(III) resulted from the unmatched properties of the Lewis acid–base reaction. On the other hand, the tested Ru(III), Zr(IV), Co(II), Mo(VI), and Ni(II) are considered to be the intermediate Lewis acid in hardness. This made the properties of the Lewis acid–base reaction of these metals with NonBTP unmatched. As a result, almost all of the tested Ru(III), Fe(III), Zr(IV), Co(II), Ni(II), and Mo(VI) might have no adverse impact on the extraction of Pd(II).

Opposite to the tested metals mentioned above, the NonBTP/30 % 1-octanol–70 % 1-dodecane system showed a strong extraction ability for Pd(II). This is attributed to the chemical complexation of Pd(II) with NonBTP. Pd(II) was a soft Lewis acid containing an unsaturated d-orbital. It thus matched with that of a soft Lewis base. This makes it possible that the strong complexation might occur as Pd(II) acting as a soft Lewis acid accepted the pairs of nonbonding valence electrons from nitrogen in NonBTP, a soft-Lewis base. As a result, the stable complex of Pd(II) ion with NonBTP through N→Pd coordination bonding was formed. The strong extraction of Pd(II) was therefore considered to the effective complexation with NonBTP.

Based on the above discussion, the difference in the extraction of the tested metal ions exhibited that, in 2.0 M HNO_3, NonBTP had an excellent extraction ability and high selectivity for Pd(II) over all of the tested elements. Namely, the tested metals Ru(III), Fe(III), Zr(IV), Co(II), Ni(II), and Mo(VI) had no adverse impact on the extraction of Pd(II) with NonBTP. This is beneficial to the effective separation of Pd(II) from an acidic HLW utilizing NonBTP by solvent extraction.

Dependence of the Tested Element Extractions on the HNO_3 Concentration. In terms of the special molecular structure of NonBTP, the nitrogen atom inside NonBTP has a high affinity for HNO_3 to form the stable ammonium nitrates. It is therefore that the HNO_3 concentration would exhibit significant effect on the extraction of the tested metals with NonBTP. It was reported that HLW generated in reprocessing of nuclear spent fuel is a HNO_3 medium usually around the concentration of 3.0 M.[1] As a result, it is possible that the extraction of Pd(II) with NonBTP caused by the chemical complexation and the protonation of NonBTP with HNO_3 in the extraction process would be two competing reactions.

The impact of HNO_3 concentration in the range of (0.42 to 5.11) M on the extraction of Pd(II) and the other tested typical metals Ru(III), Fe(III), Zr(IV), Co(II), Ni(II), and Mo(VI) with NonBTP was investigated at 298 K. It was performed at a metal concentration of $5.0 \cdot 10^{-3}$ M, a phase ratio of 1:1, and contact time of 120 min. The corresponding results are illustrated in Figure 6.

As can be seen, with an increase in the concentration of HNO_3, the extraction of Pd(II) with NonBTP increased quickly from 0.42 M HNO_3 to 3.18 M HNO_3 and then basically kept constant to 5.11 M HNO_3. The distribution ratio (D) of Pd(II) was 80.78 in 0.42 M HNO_3, 1319 in 1.63 M HNO_3, 6447 in 3.18 M HNO_3, and 6452 in 5.11 M HNO_3. Meanwhile, the other tested metals Ru(III), Fe(III), Zr(IV), Co(II), Ni(II), and Mo(VI) showed weak or almost no extraction with NonBTP. The corresponding distribution ratios (D) of them were always less than 0.6. NonBTP had an excellent extraction ability and high selectivity for Pd(II) over all of the tested metals. The optimum acidity of the Pd(II) extraction in the experimental conditions was therefore determined to be around 3.0 M HNO_3.

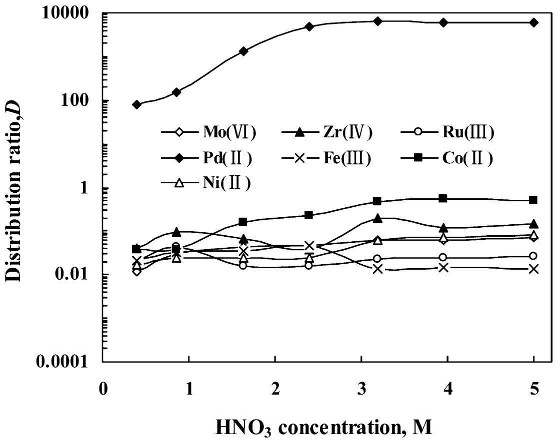


Figure 6. Dependence of the tested metal extractions with NonBTP on the concentration of HNO_3 in the range of (0.42 to 5.11) M at 298 K.

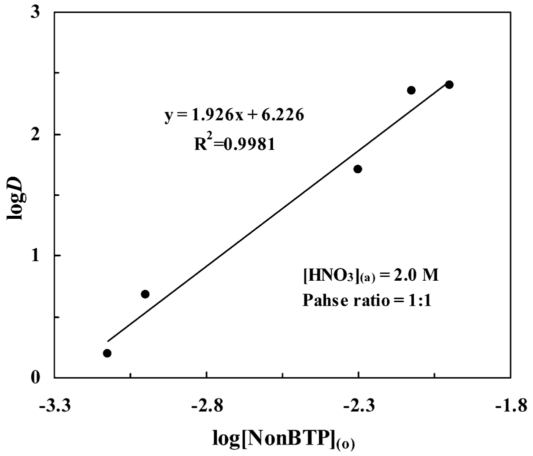


Figure 7. Relationship between log D and log$[\text{NonBTP}]_{(o)}$.

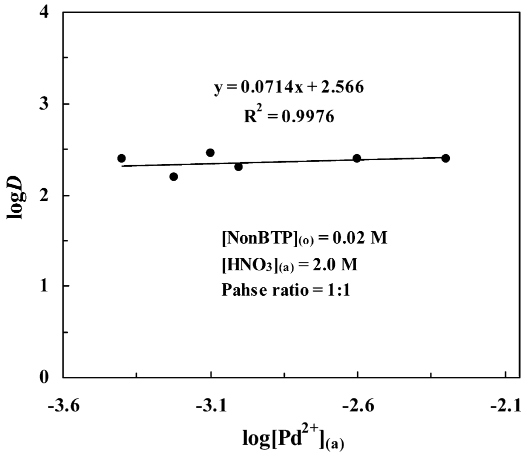


Figure 8. Relationship between log D and log$[\text{Pd}^{2+}]_{(a)}$.

Extraction Mechanism of Pd(II) with NonBTP. If one assumes that in HNO_3 medium, the composition of the extracted species of Pd(II) with NonBTP is *m*Pd-

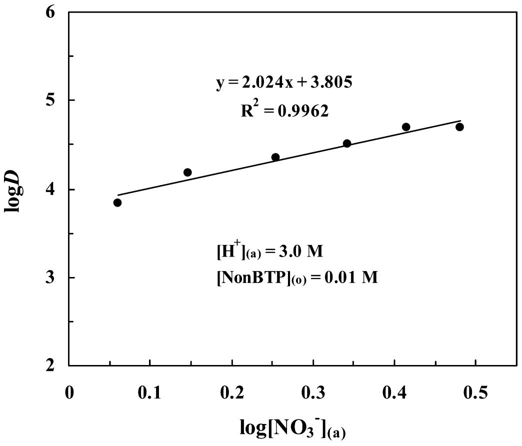


Figure 9. Relationship between log D and $\log[\mathrm{NO_3}^-]_{(a)}$.

$(NO_3)_2 \cdot n$NonBTP, then the extraction equilibrium of Pd(II) with the chelating extractant NonBTP is expressed as:

$$m\mathrm{Pd}^{2+}{}_{(a)} + 2m\mathrm{NO_3}^-{}_{(a)} + n\mathrm{NonBTP}_{(o)} \rightleftharpoons m\mathrm{Pd(NO_3)_2}\cdot n\mathrm{NonBTP}_{(o)} \qquad (2)$$

The extraction constant (K_{ex}) can be described as:

$$K_{ex} = [m\mathrm{Pd(NO_3)_2}\cdot n\mathrm{NonBTP}]_{(o)} / ([\mathrm{Pd}^{2+}]^m{}_{(a)}[\mathrm{NO_3}^-]^{2m}{}_{(a)}[\mathrm{NonBTP}]^n{}_{(o)}) \qquad (3)$$

The distribution ratio of Pd(II) (D) is

$$D = m[\mathrm{Pd(NO_3)_2}\cdot n\mathrm{NonBTP}]_{(o)}/[\mathrm{Pd}^{2+}]_{(a)} \qquad (4)$$

According to eqs 3 and 4, the relationship between the distribution ratio and the extraction constant can be described as:

$$\log D = n\log[\mathrm{NonBTP}]_{(o)} + (m-1)\log[\mathrm{Pd}^{2+}]_{(a)} + 2m\log[\mathrm{NO_3}^-]_{(a)} + \log mK_{ex} \qquad (5)$$

In terms of eq 5, the distribution ratio D was measured by varying the concentrations of NonBTP in organic phase at fixed the concentration of Pd(II) and the other experimental conditions. A plot of log D versus $\log[\mathrm{NonBTP}]_{(o)}$ yielded a straight line with a linear slope close to 2, that is, $n = 2$, as shown in Figure 7. Similarly, the influence of the Pd(II) concentration on the distribution ratio of Pd(II) was studied at constant concentrations of NonBTP and the others, and a plot of log D versus $\log[\mathrm{Pd}]_{(a)}$ is shown in Figure 8. The slope of the resultant straight line is close to 0. It showed that the extracted species of Pd(II) and NonBTP was a kind of mononuclear complex in metal under the experimental conditions, that is, $m = 1$. The effect of the concentration of $\mathrm{NO_3}^-$ on the distribution ratio of Pd(II) was investigated at the other fixed experimental conditions. A plot of log D versus $\log[\mathrm{NO_3}^-]_{(a)}$ got a straight line with a linear slope close to 2, that is, $2m = 2$, $m = 1$, as shown in Figure 9. A 1:2 type of the extracted species between Pd(II) and NonBTP was formed. The composition of the complex of Pd(II) with NonBTP was therefore determined to be $\mathrm{Pd(NO_3)_2}\cdot 2$NonBTP. The coordination number of Pd(II) in the complex $\mathrm{Pd(NO_3)_2}\cdot 2$NonBTP was 4.[27]

The reaction equation of the extraction of Pd(II) with NonBTP in the mixture of 1-octanol and 1-dodecane was represented as follows:

$$2\mathrm{Pd}^{2+}{}_{(a)} + 2\mathrm{NO_3}^-{}_{(a)} + \mathrm{NonBTP}_{(o)} \rightleftharpoons \mathrm{Pd(NO_3)_2}\cdot 2\mathrm{NonBTP}_{(o)} \qquad (6)$$

The equilibrium constant (K_{ex}) of the Pd(II) extraction was calculated, and the corresponding value $\log K_{ex}$ was 5.886. The chemical structure of the extracted species, $\mathrm{Pd(NO_3)_2}\cdot 2$NonBTP, is shown in Figure 10.

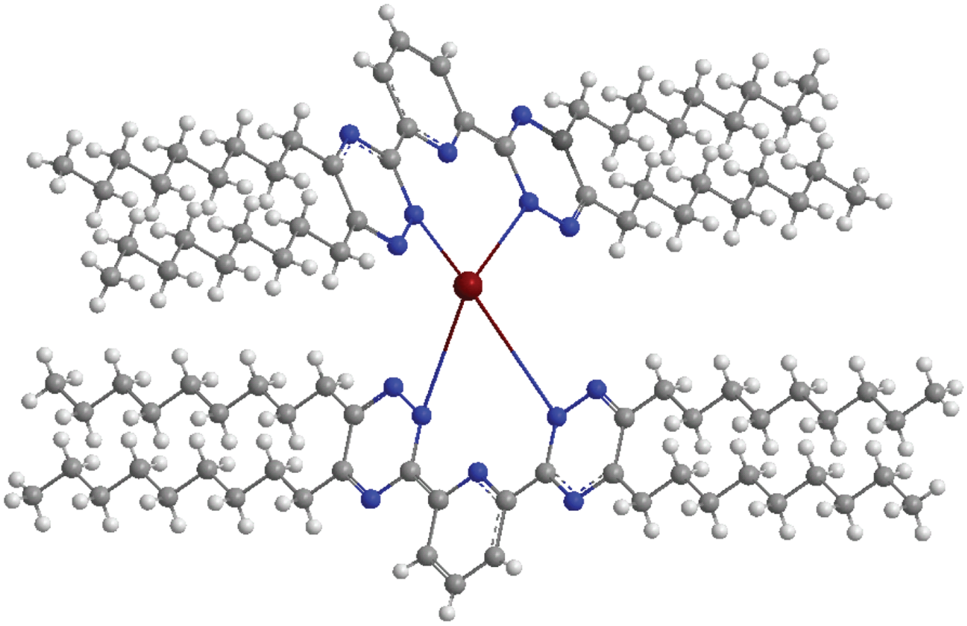


Figure 10. Structure of the extracted species of Pd(II) with NonBTP.

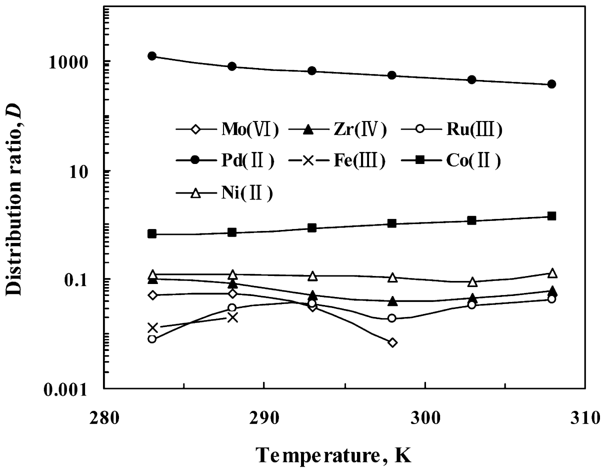


Figure 11. Dependence of the tested metals extraction with NonBTP on the operation temperature in the range of (283 to 308) K in 3.0 M HNO_3.

Dependence of NonBTP Extraction on Temperature.

The dependence of the extraction of NonBTP/30 % 1-octanol−70 % 1-dodecane system for the tested metals in 3.0 M HNO_3 with a change in temperature from (283 to 308) K was investigated. The results are depicted in Figure 11.

The extraction curve of Pd(II) decreased gradually with increasing the temperature. It indicated that, in 3.0 M HNO_3, the extraction of NonBTP for Pd(II) was an exothermic reaction. In other words, increasing the operation temperature in experimental conditions was adverse to the Pd(II) extraction. Therefore, the reasonable temperature in the Pd(II) extraction with NonBTP was considered to be at room temperature or at 298 K. Meanwhile, the extraction behavior of the other metals with NonBTP was different. The extraction of Co(II) showed a very slow increase with increasing the temperature, while the extraction of the others almost kept constant except for Mo(VI).

In terms of the linear slope of the plot of ln D vs 1/T as shown in Figure 12, the thermodynamic parameters, the change in enthalpy ($\Delta H°$), free energy ($\Delta G°$), and entropy ($\Delta S°$), of the extraction reaction of Pd(II) with NonBTP was calculated by the Arrhenius law $\mathrm{d}\ \ln D/\mathrm{d}T = \Delta H°/RT^2$ and Gibbs free energy $\Delta G° = \Delta H° - T\Delta S°$. The corresponding values were listed in Table 1.

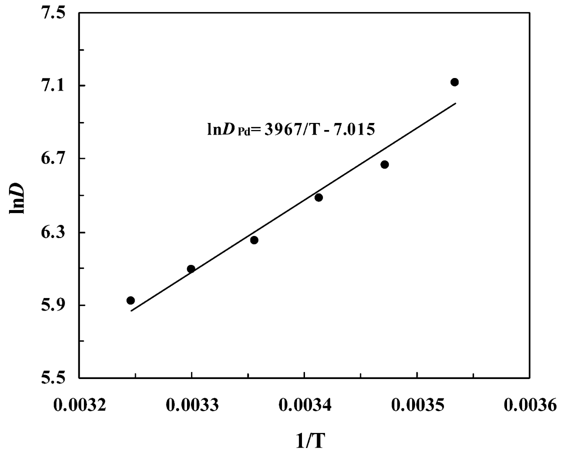


Figure 12. Relationship between ln D and $1/T$.

Table 1. Thermodynamic Parameters of the Extraction Reaction of Pd(II) with NonBTP

thermodynamic parameters	283 K	288 K	293 K	298 K	303 K	308 K
$\Delta H°$, kJ·mol^{-1}			−32.98			
$\Delta S°$, J·mol^{-1}K^{-1}	−12.48	−13.00	−13.02	−13.05	−12.86	−12.93
$\Delta G°$, kJ·mol^{-1}	−29.71	−29.16	−29.21	−29.13	−29.23	−29.27

■ CONCLUSION

In the treatment of HLW, most attention has been focused on partitioning of the long-lived MAs(III) such as Am(III) and Cm(III) as well as the heat-emitting nuclides Cs(I) and Sr(II), while almost no attention is concentrated on the separation of ^{107}Pd. To reduce the potential risk of HLW to environment, the simultaneous separation of MAs(III) and Pd(II) from HLW might be beneficial to the partitioning and transmutation (P/T) strategy. For this purpose, a multidentate soft-ligand 2,6-bis(5,6-dinonyl-1,2,4-triazine-3-yl)pyridine (NonBTP) was synthesized.

The extraction behavior of some fission and nonfission products Ru(III), Mo(VI), Pd(II), Fe(III), Co(II), Zr(IV), and Ni(II) with NonBTP/30 % 1-octanol−70 % 1-dodecane was studied at 298 K. The effects of contact time, the HNO_3 concentration in the range of (0.42 to 5.11) M, and temperature on the extraction of Pd(II) were investigated. The composition of the extracted species, the optimum extraction acidity, the extraction property, and mechanism of bivalent Pd(II) with NonBTP were evaluated. NonBTP showed an excellent extraction ability and high selectivity for Pd(II) over all of the tested metals. Some important parameters of chemical engineering in the Pd(II) extraction were obtained.

The results obtained considering of the strong complexation of MAs(III) with NonBTP are valuable for the simultaneous partitioning of MAs(III) and Pd(II) from HLW by the NonBTP-containing extraction system. Meanwhile, it is very valuable for understanding the adsorption mechanism as well as the adsorption−separation cycle in the advanced MPS (the long-lived MA(III) and Pd(II) Separation by extraction chromatography) process developed recently.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhangay@zju.edu.cn (A. Zhang). Tel./fax: +86 571 87953919.

Funding

This work was financially supported by the National Natural Science Foundation of China under Contract No. 20871103 and the Specialized Research Fund for the Doctoral Program of Higher Education under Contract No. 20090101110043.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors wish to thank Mr. Dilantha Thushara Sabasinghe for his assistance in writing this paper.

■ REFERENCES

(1) Madic, C. Overview of the Hydrometallurgical and Pyrometallurgical Processes Studied World-Wide for the Partitioning of High Active Nuclear Wastes. *International Symposium NUCEF 2001*, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan, 2001.

(2) Choppin, G. R.; Nash, K. L. Actinide Separation Science. *Radiochim. Acta* **1995**, *70–71*, 225–236.

(3) Collins, E. D.; Renier, J. P. Systems Studies of Actinide Partitioning-Transmutation Recycle Methods. *Proceedings of International Conference Global 2005*, Tsukuba, Japan, Oct 9–13, 2005; p 235.

(4) Oigawa, H.; Minato, K.; Kimura, T.; Morita, Y.; Arai, Y.; Nakayama, S.; Nishihara, K. Present Status and Future Perspective of Research and Development on Partitioning and Transmutation Technology at JAERI. *Proc. Int. Conf. (Global 2005)*, Japan, Oct 9–13, 2005; p 207.

(5) Warin, D.; Boullis, B.; Mouney, H. Status of French Programme on Partitioning and Transmutation for Nuclear Waste Management. *Proceedings of International Conference Global 2001*, Paris, France, September 9–13, 2001; pp 59–66.

(6) Mathur, J. M.; Murali, M. S.; Nash, K. L. Actinides Partitioning-A Review. *Solvent Extr. Ion Exch.* **2001**, *19*, 357–390.

(7) Apichaibukol, A.; Sasaki, Y.; Morita, Y. Effect of DTPA on the Extractions of Actinides (III) and Lanthanides(III) from Nitrate Solution Into TODGA/n-Dodecane. *Solvent Extr. Ion Exch.* **2004**, *22*, 997–1012.

(8) Koma, Y.; Watanabe, M.; Nemoto, S.; Tanaka, Y. A Counter Current Experiment for the Separation of Trivalent Actinides and Lanthanides by the SETFICS Process. *Solvent Extr. Ion Exch.* **1998**, *16*, 1357–1367.

(9) Apichaibukol, A.; Sasaki, Y.; Morita, Y. Effect of DTPA on the extractions of actinides (III) and lanthanides(III) from nitrate solution into TODGA/n-dodecane. *Solvent Extr. Ion Exch.* **2004**, *22*, 997–1012.

(10) Zhang, A.; Kuraoka, E.; Kumagai, M. Development of the Chromatographic Partitioning of Cesium and Strontium Utilizing Two Macroporous Silica-Based Calix[4]arene-crown and Amide Impregnated Polymeric Composites: PREC Partitioning Process. *J. Chromatogr., A* **2007**, *1157*, 85–95.

(11) Zhang, A.; Hu, Q.; Chai, Z. Chromatographic Partitioning of Cesium by a Macroporous Silica-Calix[4]arene-crown Supramolecular Recognition Composite. *AIChE J.* **2011**, *56*, 2632–2640.

(12) Horwitz, E. P.; Chiarizia, R.; Dietz, M. L. A novel strontium-selective extraction chromatographic resin. *Solvent Extr. Ion Exch.* **1992**, *10*, 313–336.

(13) Dietz, M, L.; Ensor, D. D.; Harmon, B.; Seekamp, S. Separation and preconcentration of cesium from acidic media by extraction chromatography. *Sep. Sci. Technol.* **2006**, *41*, 2183–2204.

(14) Riddle, C. L.; Baker, J. D.; Law, J. D.; McGrath, C. A.; Meikrantz, D. H.; Mincher, B. J.; Peterman, D. R.; Todd, T. A. Fission Product Extraction (FPEX): Development of a Novel Solvent for the Simultaneous Separation of Strontium and Cesium from Acidic Solutions. *Solvent Extr. Ion Exch.* **2005**, *23*, 449–461.

(15) Mincher, B. J.; Mezyk, S. P.; Bauer, W. F.; Elias, G.; Riddle, C.; Peterman, D. R. FPEX γ-Radiolysis in the Presence of Nitric Acid. *Solvent Extr. Ion Exch.* **2005**, *25*, 593–601.

(16) Zhang, A.; Hu, Q.; Chai, Z. SPEC: A New Process for Strontium and Cesium Partitioning Utilizing Two Macroporous Silica-Based Supramolecular Recognition Agents Impregnated Polymeric Composites. *Sep. Sci. Technol.* **2009**, *44*, 2146–2168.

(17) Zhang, A.; Xue, W.; Chai, Z. Preparation of a Macroporous Silica-Pyridine Multidentate Material and Its Adsorption Behavior for Some Typical Elements. *AIChE J.* **2012**, in press.

(18) Zhang, A.; Wang, W.; Chai, Z.; Kumagai, M. Separation of Strontium Ions from a Simulated Highly Active Liquid Waste Using a Composite of Silica-Crown Ether in a Polymer. *J. Sep. Sci.* **2008**, *31*, 3148–3155.

(19) Zhang, A.; Wei, Y. Z.; Hoshi, H.; Koma, Y.; Kamiya, M. Partitioning of Cesium from A Simulated High Level Liquid Waste by Extraction Chromatography Utilizing A Macroporous Silica-Based Supermolecular Calix[4]arene-Crown Impregnated Polymeric Composite. *Solvent Extr. Ion Exch.* **2007**, *25*, 389.

(20) Kolarik, Z.; Müllich, U.; Gassner, F. Selective Extraction of Am(III) and Eu(III) by 2,6-Ditriazolyl- and 2,6-Ditriazinylpyridines. *Solvent Extr. Ion Exch.* **1999**, *17*, 23–32.

(21) Kolarik, Z.; Müllich, U.; Gassner, F. Extraction of Am(III) and Eu(III) Nitrates by 2,6-Di(5,6-Dipropyl-1,2,4-Triazin-3-yl)Pyridines. *Solvent Extr. Ion Exch.* **1999**, *17*, 1155–1170.

(22) Kolarik, Z. Extraction of Selected Mono- to Tetravalent Metal Ions by 2,6-Di(5,6-Dialkyl-1,2,4,-Triazin-3-yl)Pyridines. *Solvent Extr. Ion Exch.* **2003**, *21*, 381–397.

(23) St. Mark, R.; Foreman, J.; Michael, J. H.; Andreas, G.; Madic, C.; Weigl, M. An Investigation into the Extraction of Americium(III) Lanthanides and d-Block Metals by 6,6-Bis-(5,6-Dipentyl-[1,2,4]-Triazin-3-yl)-[2,2]Bipyridine(C_5-BTBP). *Solvent Extr. Ion Exch.* **2005**, *23*, 645–662.

(24) Retegan, T.; Ekberg, C.; Dubois, I. Extraction of Actinides with Different 6,6′-Bis(5,6-Dialkyl-1,2,4-Triazin-3-yl)-2,2′-Bipyridines (BTBPs). *Solent Extr. Ion Exch.* **2007**, *25*, 417–431.

(25) Nilsson, M.; Andersson, S.; Drouet, F.; Ekberg, C.; Foreman, M.; Hudson, M.; Liljenzin, J. O.; Magnusson, D.; Skarnemark, G. Extraction Properties of 6,6′-Bis-(5,6-Di-pentyl-1,2,4-Triazin-3-yl)-2,2′-Bipyridinyl (C5-BTBP). *Solent Extr. Ion Exch.* **2006**, *24*, 299–318.

(26) Liu, Y. Preparation of a Few Novel Macroporous Silica-Based Soft-Ligand Materials and Their Adsorption Properties for Metals. Master's Dissertation, Zhejiang University, China, March 2011.

(27) Nadeem, S.; Rauf, M. K.; Ahmad, S.; Ebihara, M.; Tirmizi, S. A.; Bashir, S. A.; Badshah, A. Synthesis and Characterization of Palladium(II) Complexes of Thioureas. X-ray Structures of [Pd(N,N′-dimethylthiourea)$_4$]$Cl_2 \cdot 2H_2O$ and [Pd(tetramethylthiourea)$_4$]Cl_2. *Transition Met. Chem. (Dordrecht, Neth.)* **2009**, *34*, 197–202.