

Extraction Behavior of Strontium from Nitric Acid Solution with *N,N,N',N'*-Tetraisobutyl Diglycolamide

S.-D. Ding^{a,*}, T. Yang^a, N. Liu^b and L. Zhang^a

^aCollege of Chemistry, Sichuan University, Chengdu, 610064, P. R. China

^bKey Laboratory of Radiation Physics and Technology of Education Ministry of China, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064, P. R. China

(Received 10 April 2009, Accepted 5 June 2009)

The extraction behaviors of strontium from nitric acid solution were investigated with *N,N,N',N'*-tetraisobutyl diglycolamide (TiBDGA). Effects of acidity, diluents, concentration of extractant and temperature on the distribution ratio of strontium (D_{Sr}) were examined. The stoichiometry of the extracted molecule was Sr^{2+} :TiBDGA of 1:3. The apparent extraction equilibrium concentration constant $\log K_{ex}$ was 3.25. The enthalpy change ΔH and entropy change ΔS were $-55.6 \text{ kJ mol}^{-1}$ and $-124 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The extraction is an exothermic process. Through two strip stages, strontium could be stripped effectively by 0.01 M nitric acid solution.

Keywords: *N,N,N',N'*-Tetraisobutyl diglycolamide, Strontium, Extraction, Diglycolamide, High level liquid waste

INTRODUCTION

⁹⁰Sr ($T_{1/2} = 28.5$ years) with long biological as well as radioactive half-lives is one of the important long-lived fission products (FPs) present in high level liquid waste (HLLW) solution generated during the reprocessing of the spent nuclear fuel. It is considered as one of the most hazardous FPs and harmful to the vitrification of HLLW due to its heat generation. Therefore, it is desirable to separate it from HLLW for the reprocessing of the spent fuel.

As a simple and effective method, solvent extraction is usually used in the process of the HLLW partitioning-transmutation for the reprocessing of the spent fuel. Schulz *et al.* [1] have made comments on this issue. The extraction of strontium from acidic HLLW solution is considered to be one of the most challenging topics in radiochemistry and chemical

industry. Employing appropriate oxygenated aliphatic solvents as diluents, Horwitz *et al.* [2] found that dicyclohexyl-18-crown-6 (DCH18C6) and its derivatives can effectively extract strontium from acidic solution, and established SREX (strontium extraction) technology for partitioning-transmutation [3]. By using bis(*t*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) as extractant and *n*-octanol as diluent, the separation and recovery of strontium was studied from the raffinate of TRUEX (transuranium extraction) technology. In this process, strontium is extracted from nitric acid solution ($>1.0 \text{ M HNO}_3$) using 0.2 M DtBuCH18C6 in *n*-octanol. Extracted strontium is readily stripped from the organic phase using either water or dilute HNO_3 ($<0.05 \text{ M}$). The results showed that 99.7% of the strontium initially present in a feed solution could be removed by only three extraction stages. Wang *et al.* [4,5] have studied the separation of strontium from the raffinate of TRPO (trialkyl phosphine oxide) technology utilizing 0.1 M DCH18C6 in *n*-octanol. In the simulated test,

*Corresponding author. E-mail: dsd68@163.com

with ten extraction stages and two scrubbing stages, more than 99.96% of strontium was extracted from the feed solution, and above 99.84% strontium was stripped out of the organic phase with four stripping stages. Kumar *et al.* [6,7] have investigated the extraction of strontium from nitric acid medium employing DCH18C6 in aliphatic alcohols as diluents. 80% n-Butanol-20% octanol (V/V) mixture was found to give higher distribution ratio of strontium (D_{Sr}) value as compared with other alcohols investigated. Extraction selectivity of strontium is excellent over lanthanides and cesium. In general, DCH18C6 and its derivatives have good extraction properties for strontium and excellent irradiation resistance.

Recent research shows that the extraction properties of some diglycolamide compounds are similar to those of crown ethers. Compared with crown ethers, the diglycolamide compounds are easier to be synthesized, much cheaper, and more practical. At present, there are some comprehensive reports on the extraction of actinide and lanthanide elements with diglycolamides [8-18]. Stephan *et al.* [8,9] have studied the extraction behaviors of strontium with some diglycolamides in the presence of large accompanying anions such as picrate. *N,N'*-Dimethyl-*N,N'*-diheptyl-diglycolamide shows a clear preference for the extraction of the alkaline-earth metal ions such as calcium and strontium ions. Alkali metal ions such as sodium and potassium ions are practically not extracted by the investigated diglycolamides. However, due to the existence of large accompanying anions, the practical applications of these extraction systems are hampered greatly. Manchanda *et al.* [10,11] have made an overview on the development of mono- and di-amides as alternate extractants in the back end of fuel cycle. By using *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) as an extractant from nitric acid solution as well as from simulated HLLW, the distribution behaviors of various metal ions *viz.* Am(III), Pu(IV), U(VI), Eu(III), Fe(II), Sr(II) and Cs(I) were studied. In the case of simulated HLLW at 3.0 M HNO₃, the distribution ratio values for Eu(III), Am(III), Pu(IV), U(VI), Sr(II) were 98, 62, 110, 6.2 and 0.08, respectively. The separation factor values for Pu/Sr, Eu/Sr and Am/Sr were 1375, 1225 and 775, respectively. Sasaki *et al.* [12] have investigated the extraction capacity of TODGA using the novel analytical method, which determines the limit of metal concentration in the organic phase (LOC). The LOC of Nd(III) by TODGA depended on

the HNO₃ concentration and temperature. Moreover, the LOC value rose by modifier *N,N*-dihexyl-octanamide which was employed to suppress the third liquid phase. The diglycolamide compounds exhibit good prospect to be used in the process of the HLLW partitioning- transmutation for the reprocessing of the spent fuel. Regarding the importance of separation of ⁹⁰Sr from HLLW, the extraction behavior of strontium with diglycolamide is of critical importance.

Accordingly, in the absence of large accompanying anions, the extraction behaviors of strontium from nitric acid solution were investigated in detail by using TiBDGA as an extractant in n-octanol-kerosene mixture as diluent. The extraction mechanism is described and the extraction equilibrium concentration constant as well as the extraction enthalpy and entropy obtained are presented.

EXPERIMENTAL

Reagents

TiBDGA was synthesized by making reference to literature [19]. Its chemical structure is shown in Fig. 1. The product obtained was characterized by IR, MS, ¹H NMR and elemental analysis. The infrared absorption spectrum was recorded on a Nicolet FTIR 170SX infrared spectrometer using KBr wafer. Mass spectrum was obtained with a 75 eV Kratos spectrometer. The ¹H NMR characterization was determined in CDCl₃ on a Varian Inova 400 MHz NMR spectrometer. The chemical shift values are reported relative to an internal trimethylsilane (TMS) standard. Elemental analysis was carried out at the Analytical and Testing Center at Sichuan University, Chengdu, China. The corresponding data are given as follows: IR (KBr, cm⁻¹)_{v,max}: 2959, 2873 (C-H), 1649 (C=O), 1468, 1427 (CH₂), 1128, 1080 (C-O); MS

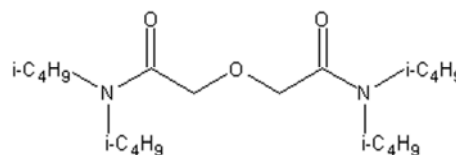


Fig. 1. Chemical structure of *N,N,N',N'*-tetraisobutyl diglycolamide.

m/z: 357 (M^{+1}); ^1H NMR (CDCl_3) δ : 0.88 (m, 24H, CH_3), 1.92 (m, 4H, CH), 3.16 (m, 8H, CH_2N), 4.36 (s, 4H, $\text{OCH}_2\text{C}=\text{O}$) ppm. Anal. Calcd. for $\text{C}_{20}\text{H}_{40}\text{N}_2\text{O}_3$ (356.5): C, 67.37; H, 11.31; N, 7.86; Found C, 67.3; H, 11.2; N, 7.8, all in %.

Sulfonated kerosene was prepared by making reference to literature [20]. Tracers $^{85,89}\text{Sr}$ were provided by China Institute of Atomic Energy with radiochemical purity of 99.3%. The other chemicals such as nitric acid and n-octanol purchased from Kelong Chemical Factory, Chengdu, China, were of analytical grade and used without further treatment.

Experimental Method

For distribution studies, 5.0 ml of organic phase (TiBDGA in various diluents) and equal aqueous phase volume of varying acidity (0.01-4.0 M) were equilibrated for 20 min in a mechanical shaker at constant temperature. The two phases were then centrifuged and assayed radiometrically. The acidity of the aqueous phase was subsequently determined by acid-base titration with 0.01 or 0.1 M NaOH solution. The organic phase acidity was also determined by titration in 1:1 (V/V) aqueous alcohol medium which had been neutralized to phenolphthalein indicator with 0.01 or 0.1 M NaOH solution. The distribution ratio of nitric acid (D_{H}) is defined as follows:

$$D_{\text{H}} = \frac{\text{HNO}_3 \text{ concentration of organic phase}}{\text{HNO}_3 \text{ concentration of aqueous phase}} \quad (1)$$

Assay of strontium equilibrium concentrations in each phase were carried out by gamma counting of $^{85,89}\text{Sr}$ employing a well type NaI(Tl) scintillation counter. The distribution ratio of strontium (D_{Sr}) was calculated from the counts of the radioactivities. D_{Sr} is defined as follows:

$$D_{\text{Sr}} = \frac{\text{Counts per minute per unit volume of organic phase}}{\text{Counts per minute per unit volume of aqueous phase}} \quad (2)$$

RESULTS AND DISCUSSION

Extraction of HNO_3

It is important to study the extraction behaviors of HNO_3 because the acid in the organic phase sometimes suppresses or enhances the objective metal cations and/or influences the back-extraction of the metal ion in the case of low acid stripping. The effect of aqueous nitric acid initial concentration $[\text{HNO}_3]_{\text{aq}}$ on distribution ratio of HNO_3 (D_{H}) is shown in Table 1.

In the absence of NaNO_3 as salting-out agent, D_{H} declines with the increase of the $[\text{HNO}_3]_{\text{aq}}$ until it levels on 1.0 M. Further increase of $[\text{HNO}_3]_{\text{aq}}$ gives rise to an increase of D_{H} . In the presence of the 3.0 M NaNO_3 , D_{H} is an approximate constant of 0.25 ± 0.02 . The higher and constant D_{H} value is ascribed to the salting-out effect of NaNO_3 , which is good for the extraction of nitric acid. Figure 2 indicates that the plot of D_{H} vs. the concentrations of TiBDGA is linear with a slope value of 1.0610, indicating that the stoichiometry of the extracted molecule is HNO_3 :TiBDGA of 1:1.

Effect of $[\text{HNO}_3]_{\text{aq}}$ Concentration

Figure 3 shows the effect of nitric acid concentration on the extraction of strontium. The value of D_{Sr} increases with the increase of $[\text{HNO}_3]_{\text{aq}}$ until it levels on 2.0 M and subsequently decreases with a further increase of acidity. The maximum D_{Sr} appears about 2.0 M $[\text{HNO}_3]_{\text{aq}}$. This phenomenon can be explained by the salting-out effect and competitive extraction of nitric acid. In the case of $[\text{HNO}_3]_{\text{aq}}$ below 2.0 M, the salting-out effect of HNO_3 is dominant, which leads to the increase of D_{Sr} . However, beyond this acidity, the competitive

Table 1. Extraction of HNO_3 with TiBDGA^a

$[\text{HNO}_3]_{\text{aq}}$ (M)	0.10	0.50	1.0	1.5	2.0	3.0
D_{H} (without NaNO_3)	0.07	0.07	0.06	0.09	0.10	0.14
D_{H} (with 3.0 M NaNO_3)	0.23	0.22	0.26	0.25	0.26	0.26

^a $[\text{TiBDGA}] = 0.20$ M; Aqueous phase: HNO_3 .

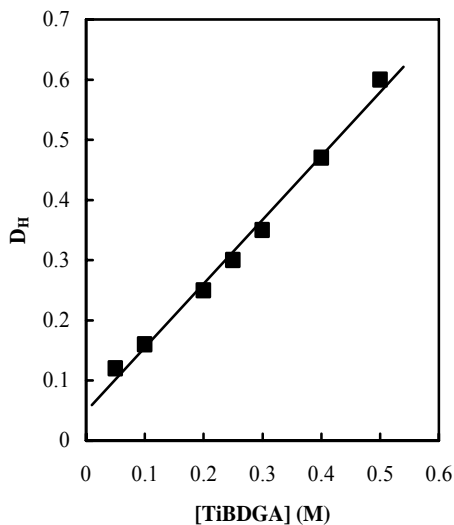


Fig. 2. Effect of TiBDGA concentration on distribution ratio of HNO_3 ; Aqueous phase: $[\text{HNO}_3] = 1.0 \text{ M}$, $[\text{NaNO}_3] = 3.0 \text{ M}$.

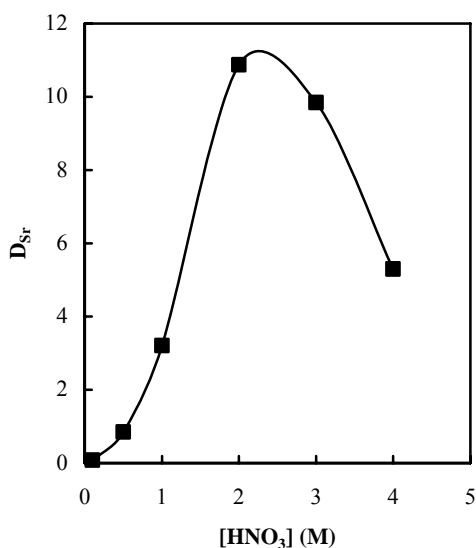


Fig. 3. Effect of nitric acid concentration in the aqueous phase on distribution ratio of strontium; $[\text{TiBDGA}] = 0.20 \text{ M}$; Aqueous phase: $[\text{Sr}(\text{NO}_3)_2] = 1.0 \times 10^{-3} \text{ M}$, HNO_3 .

extraction of HNO_3 is predominant, which results in a decrease of D_{Sr} .

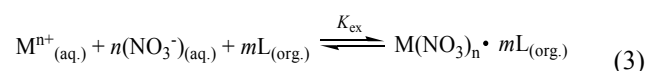
Effect of Diluents

Diluents are unable to extract metal ions from the aqueous phase, but they greatly affect the extraction behavior of the extractant. In order to optimize the diluents, the extraction of strontium was investigated employing diluents of varying dielectric constant *viz.* kerosene, toluene, chloroform, benzyl alcohol and n-octanol. The results (Table 2) indicate that D_{Sr} increases with the increase of dielectric constant of the diluents. n-Octanol with dielectric constant of 10.34 is a better diluent for strontium than the others investigated, but its high viscosity and density are disadvantageous to the operation of extraction.

In order to improve its hydromechanical properties and to help ease phase-separation, it is necessary to add appropriate modifying agents. As a cheap and commonly used solvent, kerosene is often employed as a modifier for organic phase [20]. Figure 4 shows the continuous decrease of D_{Sr} with increasing proportion of n-octanol in n-octanol-kerosene mixture. The D_{Sr} value reaches 8.79 in 20% n-octanol-80% kerosene (v/v), which increases by more than 2 times as compared with that in 100% n-octanol ($D_{\text{Sr}} = 4.08$). In the case of the proportion of n-octanol below 20%, there is the third phase and white precipitation (interfacial sewage), which is bad for the extraction of strontium. Therefore, the proportion of n-octanol should be more than 20% at least. Considering the relatively high D_{Sr} and the appearance of third phase, 40% n-octanol-60% kerosene (v/v) solution is suggested as the diluent for the following studies.

Effect of TiBDGA Concentration

Diglycolamides belong to neutral complex extractants. In the range of nitric acid concentration investigated, the main extraction reaction of diglycolamide with metal ion M^{n+} from nitric acid solution can be expressed as:



where the subscripts aq. and org. represent the aqueous and the organic phases, respectively. L represents diglycolamide. K_{ex}

Table 2. Effect of Diluent on the Distribution Ratio of Strontium^a

Diluents	Dielectric constant	Viscosity (cP)	Boiling point (°C)	D_{Sr}
Kerosene	2.0	-	170-270	0.05 ^b
Toluene	2.38	0.55	110.6	0.75
Chloroform	4.81	0.51	61.2	$<1.0 \times 10^{-3}$
Benzyl alcohol	13.10	7.76	205.5	4.56
n-Octanol	10.34	10.64	195.3	4.08

^a[TiBDGA] = 0.20 M; Aqueous phase: [HNO₃] = 1.0 M, [NaNO₃] = 3.0 M, [Sr(NO₃)₂] = 1.0×10^{-3} M. ^bSlight appearance of white precipitate.

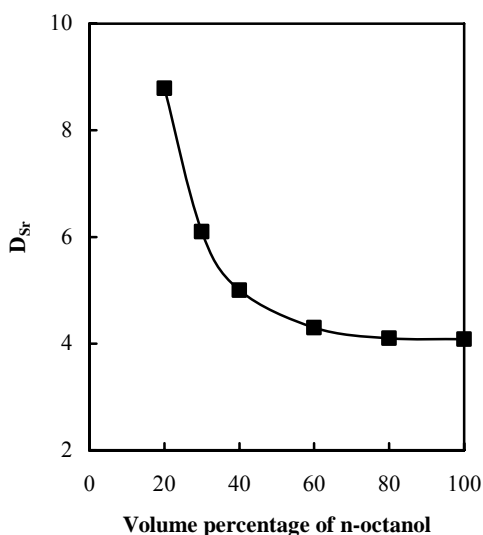


Fig. 4. Effect of n-octanol content on distribution ratio of strontium; [TiBDGA] = 0.20 M; Diluent: n-octanol-kerosene; Aqueous phase: [HNO₃] = 1.0 M, [Sr(NO₃)₂] = 1.0×10^{-3} M.

is the apparent extraction equilibrium concentration constant which is described as:

$$K_{ex} = \frac{[M(NO_3)_n \cdot mL]_{(org.)}}{[M^{n+}]_{(aq.)} \cdot [NO_3^-]_{(aq.)}^n \cdot [L]_{(org.)}^m} \quad (4)$$

The concentration terms, $[M(NO_3)_n \cdot mL]_{(org.)}$, $[M^{n+}]_{(aq.)}$,

$[NO_3^-]_{(aq.)}$, and $[L]_{(org.)}$, in Eq. (4) are given in molarity. The distribution ratio D_M , is defined as:

$$D_M = \frac{[M(NO_3)_n \cdot mL]_{(org.)}}{[M^{n+}]_{(aq.)}} \quad (5)$$

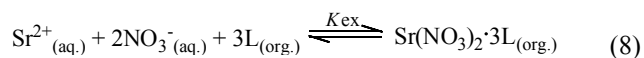
By substituting Eq. (5) into Eq. (4), and converting Eq. (4) into the logarithmic form, Eq. (6) and Eq. (7) are obtained:

$$\log K_{ex} = \log D_M - m \log [L]_{(org.)} - n \log [NO_3^-]_{(aq.)} \quad (6)$$

$$\log D_M = \log K_{ex} + m \log [L]_{(org.)} + n \log [NO_3^-]_{(aq.)} \quad (7)$$

Under the conditions of constant aqueous phase and constant temperature, the value of m can be determined from the linear regression plot of $\log D_M$ vs. $\log [L]_{(org.)}$. The value of m equals the slope value of the straight line.

The effect of original concentration of TiBDGA in the organic phase $C_{L(org.)}$ on D_{Sr} is studied in the range of 0.05-0.50 M. As shown in Fig. 5, plots of $\log D_{Sr}$ vs. $\log C_{L(org.)}$ are linear with a slope value of 3.2909, indicating that the extraction complex $Sr(NO_3)_2 \cdot 3L$ is generated between Sr^{2+} and TiBDGA. Therefore, the extraction equilibrium can be expressed as follows:



K_{ex} can be expressed as:

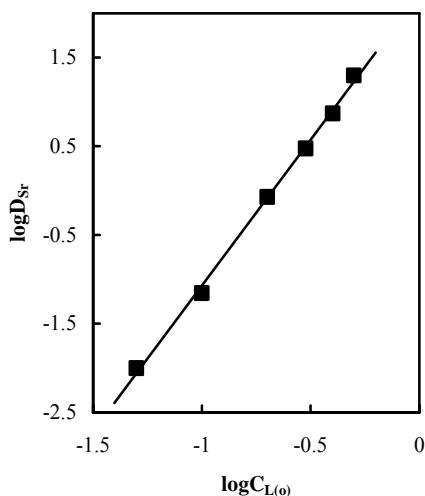
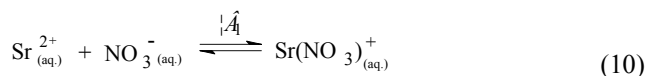


Fig. 5. Effect of extractant concentration on distribution ratio of strontium; Diluent: 40% n-octanol-60% kerosene (v/v); Aqueous phase: $[\text{HNO}_3] = 0.50 \text{ M}$, $[\text{Sr}(\text{NO}_3)_2] = 1.0 \times 10^{-3} \text{ M}$.

$$K_{\text{ex}} = \frac{[\text{Sr}(\text{NO}_3)_2 \cdot 3\text{L}]_{(\text{org.})}}{[\text{Sr}^{2+}]_{(\text{aq.})} \cdot [\text{NO}_3^-]_{(\text{aq.})}^2 \cdot [\text{L}]_{(\text{org.})}^3} \quad (9)$$

In the presence of nitrate ions, strontium ion in the aqueous phase can form a variety of complexes. However, under the experimental conditions, there are two main forms of strontium as Sr^{2+} and $(\text{SrNO}_3)^+$, whereas the form of $\text{Sr}(\text{NO}_3)_2$ is minute and can be ignored because of the almost total dissociation of $\text{Sr}(\text{NO}_3)_2$ in nitric acid solution. Thus, in the following deduction for D_{Sr} and K_{ex} , only the first complex is considered and the second complex is ignored. The first complexation equilibrium is as follows:



The complexation stability constant β_1 of 6.61 was taken from literature [21]. The total strontium $[\text{Sr}]_{(\text{aq.})t}$ in the aqueous phase was given by:

$$[\text{Sr}]_{(\text{aq.})t} = [\text{Sr}^{2+}]_{(\text{aq.})} + [\text{Sr}(\text{NO}_3)^+]_{(\text{aq.})} = [\text{Sr}^{2+}]_{(\text{aq.})} \{1 + \beta_1 [\text{NO}_3^-]_{(\text{aq.})}\} \quad (11)$$

Then, the distribution ratio of strontium, D_{Sr} , can be written from Eq. (9) and Eq. (11) as:

$$D_{\text{Sr}} = \frac{[\text{Sr}]_{(\text{org.})}}{[\text{Sr}]_{(\text{aq.})t}} = \frac{[\text{Sr}(\text{NO}_3)_2 \cdot 3\text{L}]_{(\text{org.})}}{[\text{Sr}^{2+}]_{(\text{aq.})} \{1 + \beta_1 [\text{NO}_3^-]_{(\text{aq.})}\}} = \quad (12)$$

$$K_{\text{ex}} [\text{NO}_3^-]_{(\text{aq.})}^2 \cdot [\text{L}]_{(\text{org.})}^3 \frac{1}{\{1 + \beta_1 [\text{NO}_3^-]_{(\text{aq.})}\}}$$

So K_{ex} can be written from Eq. (9) and Eq. (12) as follows:

$$K_{\text{ex}} = \frac{D_{\text{Sr}} \cdot \{1 + \beta_1 [\text{NO}_3^-]_{(\text{aq.})}\}}{[\text{NO}_3^-]_{(\text{aq.})}^2 \cdot [\text{L}]_{(\text{org.})}^3} = \frac{\{1 + \beta_1 [\text{NO}_3^-]_{(\text{aq.})}\}}{[\text{NO}_3^-]_{(\text{aq.})}^2} \cdot \frac{D_{\text{Sr}}}{[\text{L}]_{(\text{org.})}^3} \quad (13)$$

In Eq. (13), the equilibrium concentration of extractant approximately equals its initial concentration. Therefore, from the data of Fig. 5, the apparent extraction equilibrium concentration constant can be calculated as $\log K_{\text{ex}} = 3.25$ (Table 3).

Effect of Temperature

The introduction of a neutral complex into a solution phase involves a number of processes that can be associated with large changes in enthalpy (solvation processes) and in entropy (solvent orientation and restructuring), leading to considerable temperature effects [22]. To study the effect of temperature on the extraction of strontium, experiments were carried out by varying temperatures in the range of 288-313 K. Table 4 represents the extraction data obtained as a function of temperature. The D_{Sr} values decrease with increasing temperature.

The free energy change ΔG and entropy change ΔS were calculated from the thermodynamic relationship Eq. (14).

$$\Delta G = \Delta H - T\Delta S = -2.303RT \log K \quad (14)$$

The apparent extraction equilibrium concentration constant approximately equals thermodynamic equilibrium constant. The change of extraction equilibrium concentration constant K_{ex} with temperature is expressed as follows:

$$\log K_{\text{ex}} = -\frac{\Delta H}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S}{2.303R} \quad (15)$$

Extraction Behavior of Strontium from Nitric Acid Solution

Table 3. The Values of Extraction Equilibrium Constants for Strontium^a

$C_{L(org.)}$ (M)	0.05	0.1	0.2	0.3	0.4	0.5
D_{Sr}	0.01	0.07	0.85	2.99	7.45	19.88
$\log K_{ex}$	3.14	3.08	3.26	3.28	3.30	3.44
Average value: 3.25						

^a[TiBDGA] = 0.20 M; Aqueous phase: [HNO₃] = 0.50 M, [Sr(NO₃)₂] = 1.0 × 10⁻³ M.

Table 4. Effect of Temperature on Distribution Ratio of Strontium^a

Temperature (°C)	15	20	25	30	35	40
$1/T \times 10^3$ (K ⁻¹)	3.47	3.41	3.35	3.30	3.24	3.19
D_{Sr}	1.83	1.30	0.85	0.59	0.40	0.29
$\log K_{ex}$	3.60	3.45	3.26	3.10	2.94	2.80

^a[TiBDGA] = 0.20 M; Diluent: 40% n-octanol-60% kerosene (v/v); Aqueous phase: [HNO₃] = 0.50 M, [Sr(NO₃)₂] = 1.0 × 10⁻³ M.

Figure 6 shows that the plot of $\log K_{ex}$ vs. $1/T$ is a straight line. The enthalpy change ΔH for the extraction reaction can be calculated from the slope value of 2.9023, entropy change ΔS can be obtained from the intercept value of -6.4633. Thus, $\Delta H = -55.6 \text{ kJ mol}^{-1}$, $\Delta S = -124 \text{ J mol}^{-1} \text{ K}$, $\Delta G = -18.6 \text{ kJ mol}^{-1}$ (298 K). The negative value of ΔH reveals that the extraction of strontium from nitric acid solution with TiBDGA is an exothermic process and favorable with drop in temperature. The negative value of ΔS suggests that the degree of order increases during the extraction process. The highly ordered complex structure is formed between Sr(II) and the extractant ligand. The negative value of ΔG at room temperature indicates that the extraction reaction is spontaneous [23].

Stripping of Strontium

Stripping is the reverse of extraction, so it should be promoted by the factors that affect extraction negatively. Figure 3 shows that D_{Sr} is very low in the range of aqueous phase acidity below 0.5 M. The stripping of strontium from 0.20 M TiBDGA in 40% n-octanol-60% kerosene (v/v) organic phase was investigated using varying concentrations of HNO₃. The results are listed in Table 5. Almost quantitative

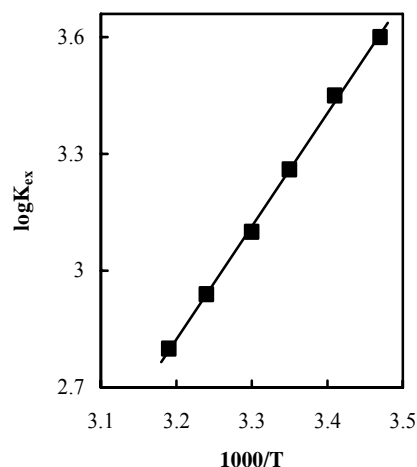


Fig. 6. Effect of temperature on distribution ratio of strontium; [TiBDGA] = 0.20 M; Diluent: 40% n-octanol-60% kerosene (v/v); Aqueous phase: [HNO₃] = 0.50 M, [Sr(NO₃)₂] = 1.0 × 10⁻³ M.

stripping of strontium can be achieved by deionized water, 0.01 or 0.05 M nitric acid solution in two stages. Considering the potential hydrolysis of other metal ions in practical applications, 0.01 M dilute nitric acid solution is

Table 5. Results of Stripping of Strontium^a

Strip stage		Stripping reagent				
		Deionized water	HNO ₃ (M)			
			0.01	0.05	0.10	0.50
1	D_{Sr}	0.22	0.20	0.29	0.37	1.00
	%E ^b	81.9	83.5	77.4	72.8	50.0
2	D_{Sr}	0.01 ^c	0.01	0.01	1.11	1.73
	%E ^b	96.3	94.9	93.9	89.8	57.8
3	D_{Sr}	- ^d	- ^d	- ^d	0.38	1.33
	%E ^b	- ^d	- ^d	- ^d	72.4	43.0

^a[TiBDGA] = 0.20 M; Diluent: 40% n-octanol-60% kerosene (v/v); Aqueous phase: deionized water or HNO₃ solution. ^bPercentage stripping-extraction. ^cAppearance of the third phase. ^dNo radioactive counting detected in aqueous phase.

recommended as stripping agent.

CONCLUSIONS

By using n-octanol-kerosene as the diluent, strontium can be extracted effectively with TiBDGA from nitric acid solution. With the increase of nitric acid concentration in aqueous phase, D_{Sr} increases at first and then decreases when the acidity exceeds 2.0 M. The plot of the concentration of extractant vs. D_{Sr} is linear with a slope value of 3.2909, indicating that the stoichiometry of the extracted molecule is Sr²⁺:TiBDGA of 1:3. The apparent extraction equilibrium concentration constant $\log K_{ex}$ is 3.25. D_{Sr} decreases with the increase of temperature. The enthalpy change ΔH and entropy change ΔS are -55.6 kJ mol⁻¹ and -124 J mol⁻¹ K⁻¹, respectively. The extraction is an exothermic process. 0.01 M Dilute nitric acid solution is recommended as stripping agent and strontium can be stripped effectively in two strip stages.

REFERENCES

- [1] W.W. Schulz, L.A. Bray, *Sep. Sci. Technol.* 22 (1987) 191.
- [2] E.P. Horwitz, M.L. Dietz, D.E. Fisher, *Solvent Extr. Ion Exch.* 8 (1990) 557.
- [3] E.P. Horwitz, M.L. Dietz, D.E. Fisher, *Solvent Extr. Ion Exch.* 9 (1991) 1.
- [4] J.C. Wang, C.L. Song, *Radiochim. Acta* 89 (2001) 151.
- [5] W.H. Duan, J.C. Wang, X.Z. Zhou, J. Chen, *Solvent Extr. Ion Exch.* 26 (2008) 783.
- [6] A. Kumar, P.K. Mohapatra, P.N. Pathak, V.K. Manchanda, *Talanta* 45 (1997) 387.
- [7] A. Kumar, P.K. Mohapatra, P.N. Pathak, V.K. Manchanda, *Radiochim. Acta* 88 (2000) 885.
- [8] H. Stephan, K. Gloe, J. Beger, P. Mühl, *Solvent Extr. Ion Exch.* 9 (1991) 435.
- [9] H. Stephan, K. Gloe, J. Beger, P. Mühl, *Solvent Extr. Ion Exch.* 9 (1991) 459.
- [10] V.K. Manchanda, P.N. Pathak, *Sep. Purif. Technol.* 35 (2004) 85.
- [11] S.A. Ansari, P.N. Pathak, V.K. Manchanda, *Solvent Extr. Ion Exch.* 23 (2005) 463.
- [12] Y. Sasaki, Y. Sugo, S. Suzuki, T. Kimura, *Anal. Chim. Acta* 543 (2005) 31.
- [13] Y. Sasaki, Y. Sugo, S. Suzuki, *Solvent Extr. Ion Exch.* 19 (2001) 91.
- [14] Y. Sasaki, G.R. Choppin, R. Gregory, *Radiochim. Acta* 80 (1998) 85.

Extraction Behavior of Strontium from Nitric Acid Solution

- [15] Y. Sasaki, T. Adachi, G.R. Choppin, *J. Alloy. Compd.* 271 (1998) 799.
- [16] H. Narita, T. Yaita, K. Tamura, *Radiochim. Acta* 81 (1998) 223.
- [17] L. Nigondl, C. Musikasc, C. Cuillerdiere, *Solvent Extr. Ion Exch.* 12 (1994) 261.
- [18] L. Nigondl, C. Musikasc, C. Cuillerdiere, *Solvent Extr. Ion Exch.* 12 (1994) 297.
- [19] V.E. Pretsch, D. Ammann, H.F. Osswald, *Helv. Chim. Acta* 63 (1980) 191.
- [20] A. Boualia, A. Mellah, A. Silem, *Hydrometallurgy* 24 (1990) 1.
- [21] J.A. Dean, in: J.F. Shang, S.J. Cao, W.M. Xin, Y.F. Zheng, (Eds.), *Lange's Handbook of Chemistry (in Chinese)*, Science Publishing Company, Beijing, 1991.
- [22] G.X. Xu, W.Q. Wang, J.G. Wu, H.C. Gao, N. Shi, *Principles of Extraction Chemistry*, Shanghai Science and Technology Press, Shanghai, 1984.
- [23] S.V. Mahamuni, S.S. Kolekar, P.P. Wadgaonkar, M.A. Anuse, *J. Iran. Chem. Soc.* 6 (2009) 200.

Archive of SID