Metal Extractions by Diglycolamide-Type Tridentate Ligands

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Three tridentate extractants including soft and hard donor has been developed and examined. The extractants are termed as *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA), methylimino-*N,N'*-dioctylacetamide (MIDOA) and *N,N,N',N'*-tetraoctyl-thiodiglycolamide (TDGA). The results of the present study indicate that TODGA can extract mainly hard acid metals, MIDOA can extract soft acid metals and oxyanions, and TDGA can extract soft acid metals. We can compare the distribution ratios of these metals obtained by TODGA, MIDOA, and TDGA. These results can be supported by some spectrometric studies, i.e., IR, and NMR and calculations of metal complexes.

1. Introduction

Recently, the tridentate diamide compounds were developed and their extraction performances were investigated worldwide [1-4] because of the strong extractability with not only actinide (An) and lanthanides (Ln) but also noble metals. The most famous tridentate diamide is TODGA (*N,N,N',N'*-tetraoctyl-diglycolamide), which shows very high distribution ratio (*D*) of An from nitric acid and is very useful to recover An and Ln from high level radioactive waste. This compound has three oxygen donors (two carbonyl oxygen and an ether oxygen atoms), and shows very strong complexation with hard acid metals. Referring to the structure of TODGA, N and S donor extractants can be synthesized by substitution of their atoms to ether O atom in TODGA, N-compound is MIDOA (methylimino-*N,N'*-dioctylacetamide) and S-compound is TDGA (*N,N,N',N'*-tetraoctyl-thiodiglycolamide), the structures of these extractants are described in Figure 1. Three compounds have their own extraction properties, O donor favors the complexation with hard acid metals and S and N donor favor the complexation with soft acid metals. Probably, S donor extractant may have difference with its extraction ability from that of N donor. In this work, we would like to see the difference among three extractants using extraction results, spectrophotometry and calculation.

2. Experimental

The extraction procedure was following that each extractant was dissolved in *n*-dodecane at room temperature. Each metal in the standard solution was evaporated and the residue was dissolved by the appropriate concentration of acids (HNO$_3$). The organic and aqueous phase were mixed and mechanically shaken at 1500 strokes/min for 30 min at 25 ± 0.1 °C. After centrifugation, the metal concentrations in the aliquots taken from the aqueous phases were measured by ICP-OES (SPS3100, Seiko Instruments Inc.). The metal concentrations in the organic phases were obtained by subtracting the aqueous concentration from the initial one. The *D* value is defined as the ratio of [M] in the organic phase to [M] in the aqueous phase.
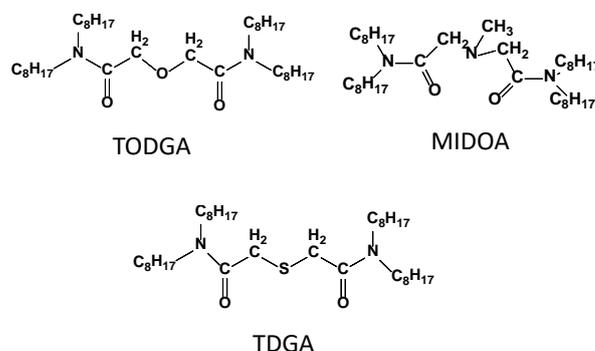
Figure 1 The structures of TODGA, MIDOA and TDGA

The sample preparation method for IR and NMR analysis was as follows: The extraction conditions at near-loading capacity were applied in order to reduce the concentration of free extractant in the organic phase. Here, the organic solvents, chloroform and carbon tetrachloride, are employed for NMR and IR measurements. After extraction and centrifugation, the organic phases containing metal complexes were used as the samples for IR (FT/IR4100, JASCO) and ^{1}H-NMR (JNM-ECA600, JEOL) studies.

All models of extractants, metal complexes and anions, were calculated *in vacuo* by using the Density Functional Theory (DFT) at the B3LYP/6-31g** level with the Gaussian03 series program, and the heats of formation of the metal complex, metal ion, extractant, and anion ($H_{f,\text{metal complex}}$, $H_{f,\text{metal}}$, $H_{f,L}$, $H_{f,\text{anion}}$) were obtained.

3. Results and Discussion

3.1 Matal extraction by three extractants

Results on metal extractions using TODGA and MIDOA are reported elsewhere [2,4]. In this work, we compare the results by three extractants and summarize the extractability trends from group 2 to group 16, the results are shown in Table 1. Columns in Table 1 show the kinds of metal, group No. stable valence of metals, HNO$_3$ concentration faced in extraction and extractability trends for three extractants. Concerning with this, from our experience, extraction behavior of fourth period (potassium-krypton line) is different from fifth (rubidium-xenon line) and sixth (cesium-radon line) period at the same group. So we should choose the metals in Table 1 from fifth and sixth periods.

From group 2 to 4, because of the hard acid metals, TODGA has very high *D* values, whose compound includes hard oxygen donor in the ether position of the structure. Lanthanides and actinides are included in these groups. Tetravalent Pu show high extraction ability with MIDOA as well as TODGA.

From group 5 to 10, MIDOA shows the highest extractability of all. Some metals at these groups form the oxonium anions (i.e., MoO_4^{2-} and TcO_4^{-}) and others are soft acid metals. Based on HSAB principle, these metals show the high preference by soft donor, like N and S donors. Nevertheless, TDGA including S donor show the low extractability for Tc, Ir, and Pt extractions than TODGA. Most of oxonium anions from this work are favorable to MIDOA rather than TDGA.

Table 1 Extractability trends for each metals among three extractants

Metals	group	valence	HNO$_3$ conc.	Extractability trend
Sr	2	2	3 M	TODGA >> MIDOA, TDGA
Nd	3	3	3 M	TODGA >> MIDOA, TDGA
Pu	3	4	3 M	TODGA ~ MIDOA > TDGA
Zr	4	4	3 M	TODGA > TDGA > MIDOA
Ta	5	5	0.2 M	MIDOA > TDGA > TODGA
Mo	6	6	0.2 M	MIDOA > TDGA > TODGA
Tc	7	7	0.2 M	MIDOA > TODGA > TDGA
Ru	8	3	0.2 M	MIDOA > TDGA > TODGA
Ir	9	3	3 M	MIDOA > TODGA > TDGA
Pd	10	2	0.2 M	MIDOA > TDGA > TODGA
Pt	10	4	3 M	MIDOA > TODGA > TDGA
Ag	11	1	3 M	TDGA >> TODGA, MIDOA
Au	11	3	3 M	TDGA > TODGA, MIDOA
Hg	12	2	0.2 M	TDGA > TODGA, MIDOA
In	13	3	3 M	TODGA > MIDOA, TDGA
Pb	14	2	3 M	TODGA > TDGA > MIDOA
Bi	15	3	3 M	TODGA > MIDOA > TDGA
Te	16	4	0.2 M	MIDOA > TODGA > TDGA

From group 11 to 12, TDGA shows the highest extractability of all. In addition, TDGA shows high *D* values for Pd in group 10, analog performance to MIDOA. Especially, TDGA has very high *D* value for Ag, other extractants show the negligibly small *D*(Ag). TDGA is an excellent extractant to recover Ag into organic phase from HNO$_3$.

From group 13 to 16, some metals are extractable by TODGA. Te in group 16 forms the oxonium anion, so N-donor extractants may indicate the high extractability.

Comparing the metal-extraction behavior of TODGA, MIDOA and TDGA, extraction by MIDOA indicates the decrease of *D* with HNO$_3$ concentration [3]. The reason that is the protonation of N donor in MIDOA, it comes up with competition reaction between protons and metal to N donor at high acid condition. This extraction behavior is different feature from those of other O and S donor-type ligands.

3.2 Spectrometric results by three extractants

We obtained the results for IR and NMR of three extractants, some of the results for TODGA and MIDOA are reported already [5-6]. The results of NMR study are shown in Figure 2. The chemical shifts for concerning protons can be seen in this figure. The columns, TDGA, TODGA and MIDOA, indicate the peak

positions for extractant alone and those with metals. From this figure, the spectrum ④ for TDGA and TODGA showing the large shift (0.19 ppm for TDGA and 0.267 ppm for TODGA to low magnetic field) suggest the metal complexation with S and O donors at the ether position in TDGA and TODGA. In addition, spectra ② and ④ for MIDOA sample shows the large shift before and after metal extractions (for spectrum ②, 0.572 and 0.615 ppm shift of Pd and Re extractions, and for spectrum ④, 0.861 and 0.965 ppm shift of Pd and Re extractions), which indicates N-donor in ether position may show the strong bond to Pd and Re. Saeki pointed out [6] that MIDOA may form H^+MIDOA (protonation to N donor in MIDOA) prior to solvent extraction. Not only protonation but also complexation of metal with N donor give large shift with appearance of MIDOA measurements.

We have also the results of IR for these samples. One of the representative peak of extractant is C=O stretching at 1600-1700 cm^{-1}. This peak is easy to identify and widely use for chemical shift between complexed and non-complexed samples. The results of chemical shifts are shown, TODGA: 1653 cm^{-1}, TODGA+La: 1624 cm^{-1}, MIDOA: 1646 cm^{-1}, MIDOA+Re: 1653 cm^{-1}, and TDGA: 1646 cm^{-1}, TDGA+Pd: 1644 cm^{-1}. From these results, TODGA sample has high difference (to red shift) between two samples. Because La is hard acid metal and may bond with carbonyl oxygen atom, then show the large shift.

Chemical shift of NMR spectrum ③ and ④ for TDGA samples

	Spectra (③)	Spectra (④)
TDGA	3.3 ppm	3.49 ppm
+ Pd	3.38	3.68
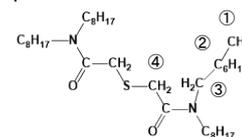
Chemical shift of NMR spectrum ③ and ④ for TODGA samples

	Spectra (③)	Spectra (④)
TODGA	3.153, 3.268 ppm	4.288 ppm
+ La	3.128, 3.284	4.555
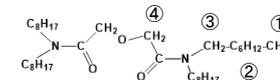
Chemical shift of NMR spectrum ③ and ④ for MIDOA samples

	Spectra (②)	Spectra (③)	Spectra (④)
MIDOA	2.545 ppm	3.235 ppm	3.555 ppm
+ Pd	3.117	3.282	4.416
+ Re	3.16	3.15	4.52
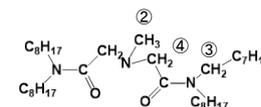
Figure 2 Peak positions of samples before and after metal extraction by ^{1}H-NMR

Other metals, Pd and Re, are soft acid metal or oxonium anion bond to S and N donor atoms, then show the weak bonding with carbonyl oxygen.

3.3 Calculation results by three extractants

In this work, the results of calculation for the complexes of TODGA, MIDOA and TDGA with Au, Pd, Zr and Tc are shown. Assuming that Au(III), Pd(II), Zr(IV), and Tc(VII) ions react with one to three molecules of extractant (see Table 2), the difference of the heat of formation during complex formation $[\Delta H_f/(kJ/mol)]$ can be calculated by

$$\Delta H_f = H_{f,\text{metal complex}} - (H_{f,\text{metal}} + nH_{f,L} + mH_{f,\text{anion}}).\qquad(1)$$

where H_{fi} (i = metal complex, metal, L (TODGA, MIDOA, TDGA), and anion (NO_3^-)) are the relevant heat of formation of the species obtained by DFT calculations, and n and m are the stoichiometric coefficients of extractant and anion in metal complex. The $H_{f,L}$ (L: TODGA, MIDOA, TDGA) and $H_{f,\text{anion}}$ values for NO_3^- were calculated to be 20.5, 24.88, 13.95 and 4.58 kJ/mol, respectively, and the values were introduced into equation (1). The results of calculations are shown in Table 2. The apparent extraction constant, Int. y, can be inferred from the values of log y from the slope analysis of log D vs log [extractant]. The trend of ΔH_f decreasing with log y values can be referred from the previous paper [7]. The present results may be in agreement with the former studies that

Table 2 Relationship between Int. y and ΔHf among three extractants

	Extractant	No. of ligands	Int y	ΔHf
Au(III)	TODGA	1	0.964	322.26
	MIDOA	1	1.09	306.98
	TDGA	1	2.55	294.41
Pd(II)	TODGA	2	1.89	415.74
	MIDOA	2	5.05	341.28
	TDGA	1	3.71	287.99
Zr(IV)	TODGA	3	8.59	337.06
	MIDOA	2	3.81	352.1
	TDGA	2	1.5	377.06
Tc(VII)	TODGA	2	1.96	461.3
	MIDOA	1	2.71	251.42
	TDGA	1	1.8	314.95

indicates a negative relationship between ΔH_f and $\log K_{ex}$ [7]. The small difference obtained in this work from the previous paper might be the difference of No. of extractant associated in metal-complexes.

4. Summary

Three extractants, TODGA, MIDOA and TDGA, are compared to see the difference of extractabilities. From the present work, it is clear that metals of group 2-4 and 13-16 can be easily extracted by TODGA, metals of group 5-10 are for MIDOA and 11-12 are for TDGA. NMR and IR give the information on bonding of metals with donor atoms. The results of calculation for the heat of formation during complex formation give the reverse-correlation between ΔH_f and $\log K_{ex}$.

References

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