Extractions and Spectroscopic Studies of Various Metals with Diglycolamide-Type Tridentate Ligands

Yuji SASAKI1*, Morihisa SAEKI2 and Kazuharu YOSHIZUKA3
1Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan; 2National Institutes for Quantum and Radiological Science and Technology, Tokai, Ibaraki 319-1106, Japan; 3The University of Kitakyushu, Hibikino 1-1, Kitakyushu 808-0135, Japan
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Three tridentate extractants and three masking reagents including O, N, and S donors have been developed and their properties are compared and discussed. The extractants are $N,N,N',N''$-tetraoctyl-diglycolamide (TODGA), methylimino-$N,N'$-dioctylacetamide (MIDOA) and $N,N,N',N''$-tetraoctyl-thiodiglycolamide (TDGA(C8)) together with masking agents having the same central frame but with short alkyl chains. The results of the present study indicate that TODGA can extract mainly hard acid metals belonging to groups 2-4,13-15 in the periodic table. MIDOA can extract soft acid metals and oxyanions (groups 5-10, 16), and TDGA can extract soft acid metals (groups 10-11). Some spectrophotometric studies (UV-vis., IR, and NMR) indicate the stoichiometry and the effect of donor atoms for metal-complexation. The $\Delta H_f$ values, the heat generation during complex formation, obtained by chemical calculation by DFT theory show a reverse-correlation with their extraction ability.

1. Introduction

Recently, tridentate extractants and ligands have been developed and studied worldwide [1-6]. Tridentate ligands can complex effectively with metals with 6 and 9 coordination sites with 1 : 2 and 1 : 3 metal-ligand complex stochiometries, rather than monodentate and bidentate extractants. The strong extractabilities and high complexation abilities for metals by tridentate ligands have been reported in many papers[1,4,6]. One of the most important tridentate extractant is TODGA ($N,N,N',N''$-tetraoctyl-diglycolamide) [5]. This compound has three oxygen donors (two carbonyl oxygen donors and an ether oxygen atom) attached with diamide groups outside of the central frame. Based on the HSAB principle [7], oxygen donors are preferred for hard acid metals, metals belonging groups 2-4 in the periodic table. TODGA can dissolve in $n$-dodecane and shows a very high distribution ratio ($D$) for actinides (An) and lanthanides (Ln) from nitric acid. Therefore, TODGA is a useful extractant for metal separation from high level radioactive liquid waste [8-12]. TODGA is composed of C, H, O, N atoms and complete gasification takes place on combustion, thus producing less secondary waste.

N and S donor extractants, which are similar to TODGA, can be produced by substitution of the O atom at the ether position in TODGA. The N-compound with a methyl group attached is termed as MIDOA (methylimino-$N,N'$-dioctylacetamide) and the S-compound is TDGA ($N,N,N',N''$-tetraoctyl-thiodiglycolamide) [6, 13-16]. These extractants can be synthesized by changing the initial materials to methylimino-diacetatic acid or thiodiacetic acid from the diglycol acid of TODGA. Both N and S donors are soft donors and complexing well with soft acid metals.
based on the HSAB principle. Some papers reported that these extractants have strong extraction abilities for Mo, Tc, Re and Pd (MIDOA), and Pd, Ag, Au and Hg (TDGA) [13-16]. These extractants have the same central frame but with different donor atoms, however less work has been reported on the investigation of the role of O, N and S donors and comparison with their extractabilities.

In this work, using these extractants, the feature of metal-extraction on the periodic table by different donor atoms is investigated. These donor atoms are situated just at the center position of the extractants, thus allowing strong involvement in metal-complexation. The UV-vis., IR, and NMR spectrometry using not only the extractants but also their water-soluble ligands (see Figure 1) was recorded in order to see the effects due to the donor atoms and functional groups in their structures [17-22]. Chemical calculation by density functional theory (DFT) gives the binding energy concerning the guest-host system of the metal complex [23-24]. The heat value, $H$, calculated at each state using DFT is employed to obtain $\Delta H$ for the metal-complexation reaction. These values and apparent extraction constants, $\text{Int. y value}$ (Int. y value is $\log D$ when $\log \text{[extractant]} = 0$, using the linear relation of $\log D$ vs $\log \text{[extractant]}$) can be used as an indication of the stability and strength of the metal-complex before and after the extraction reaction [25-26]. From the present work, we try to evaluate the extractable metals for each donor atom, the role of the donor and the functional group in the extractants, and the correlation between heat of formation and Int. y values.

![Figure 1. Structures of extractants and masking agents.](image)

### 2. Experimental

#### 2.1 Reagents

The extractants, TODGA, MIDOA, and TDGA(C8) and the masking agents, TEDGA, MIDEA and TDGA(C2) were purchased from Wako Pure Chemical Industries. Extractants with more than 98% purity were used for solvent extraction without further purification. Standard solutions of 1000 ppm concentration of metals (Wako Pure Chemical Industries) were used for solvent extraction, and approximate ppt levels of Pu-238 and sub-ppb levels of Tc-99 are dissolved in 5 M HNO$_3$ and 0.01 M HNO$_3$ and used as the working solutions. Other reagents, e.g., organic solvents and nitric acid, were of analytical grade.

#### 2.2 Solvent extraction method

The extraction procedure was as follows: each extractant was dissolved in $n$-dodecane at ambient temperature. The standard solution of each metal was evaporated and the residue was dissolved by the appropriate concentration of acids (HNO$_3$). The organic and aqueous phases 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.) or ICP-MS (SPQ 9000, Seiko-EG&G). The metal concentrations in the organic phases were obtained by subtracting the aqueous concentration from the initial concentration. The beta activity of Tc and alpha activity of Pu-238 were measured by a liquid scintillation counter (LSC, Tri-Carb 1600 TR, Packard Instrument Company). Aliquots from both aqueous and organic phases are mixed with a PICO-AQUA cocktail, 3 mL, and subsequently sent for LSC measurements. The \( D \) value is defined as the ratio of \([M]\) in the organic phase to \([M]\) in the aqueous phase.

2.3 Spectrometry of UV-vis., IR, and NMR

The metals in the sample solutions for UV-vis. spectrometry are selected as Nd and Pd because they have relatively strong absorptions. These metals are well-extracted and expected to complex strongly with TEDGA (for Nd), and MIDEA (Pd) and TDGA(C2) (Pd). The sample solution of the metal (M) in 1 M HNO\(_3\) is taken and mixed with a water-soluble ligand (L) in the same HNO\(_3\) concentration in order to prepare different molar ratios of M/L. The UV-vis. spectrum of Nd and Pd is obtained using JASCO V-570, and the peaks of spectrum at 796 – 801 nm for Nd, and 322 – 327 nm and 380 – 382 nm for Pd have been studied.

The sample preparation method for IR and NMR spectrometry was as follows: the solvent extraction method is used for IR samples. The extraction conditions at near-loading capacity were used in order to reduce the concentration of the free extractant in the organic phase. Here, the diluents, D\(_2\)O and carbon tetrachloride, are employed for the NMR and IR measurements. After extraction and centrifugation, the organic phases with and without metal complexes were subject to IR (FT/IR4100, JASCO) and \(^1\)H-NMR (JNM-ECA600, JEOL) studies in order to determine the degree of the chemical shift values.

2.4 Chemical calculation

All structures of extractants, metal complexes, and anions were calculated \textit{in vacuo} using DFT at Becke’s three parameters (B3) exchange functional along with the Lee-Yang-Parr (LYP) non-local correlation functional (B3LYP) level [27]. Split valence basis set 6-31G** with extra polarization [28] and diffuse [29] functions were used in all calculations. Input coordinates were obtained from X-ray crystal structure data available from the Cambridge Crystallographic Data Centre (CCDC). These calculations were terminated when the forces are smaller than the cutoff value over several cycles even though the displacement was larger than the cutoff value. The DFT calculations were performed using the Gaussian03 program package. The heats of formations of the metal complexes, metal ions, extractants, and anions (\(H_{f,\text{metal complex}}\), \(H_{f,\text{metal}}\), \(H_{f,\text{TDGA}}\), and \(H_{f,\text{anion}}\)) were obtained from these calculations. The \(\Delta H_f\) values were obtained by subtracting the sum of \(H_{f,\text{metal}}, H_{f,\text{TDGA}},\) and \(H_{f,\text{anion}}\) from \(H_{f,\text{metal complex}}\) and were compared with the information obtained from the solvent extraction experiments (i.e., the apparent extraction constants).

3. Results and Discussion

3.1 Metal extraction by three extractants

Results on metal extraction using TODGA, MIDOA and TDGA are reported elsewhere [26, 30-31]. In this work, the extraction data are reconfirmed, obtained under the same conditions, new data added and plotted in Figure 2(a)-(f). In these figures, the results by the three extractants are compared. Figure 2(a) shows the results for Sr, Nd,
Figure 2. Relationship between $D(M)$ and the extractant concentration, referring from papers, 26, 30 and 31. (a): Sr, Nd, Pu (3 M HNO$_3$), (b): Zr (3 M HNO$_3$), Ta, Mo (0.2 M HNO$_3$), (c): Tc, Ru (0.2 M HNO$_3$), Ir (3 M HNO$_3$), (d): Pd (0.2 M HNO$_3$), Ag, Au (3 M HNO$_3$), (e): Hg (0.2 M HNO$_3$), In, Pb (3 M HNO$_3$), (f): Bi(3 M HNO$_3$), Te (0.2 M HNO$_3$).
and Pu, 2(b) for Zr, Ta and Mo, 2(c) for Tc, Ru and Ir, 2(d) for Pd, Ag, and Au, 2(e) for Hg, In, Pb, and 2(f) for Bi and Te. These metal ions are selected from 2-16 groups in the periodic table. From these figures, the order of extractability of the three extractants can be determined and the results are summarized in Table 1. Table 1 shows the metals, their periodic table groups, oxidation states, nitric acid concentrations, and their extractability trends.

Table 1. Extractability trend for each metal among three extractants.

<table>
<thead>
<tr>
<th>Metals</th>
<th>group</th>
<th>valence</th>
<th>HNO₃ conc.</th>
<th>Extractability trend</th>
</tr>
</thead>
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<tr>
<td>Sr</td>
<td>2</td>
<td>2</td>
<td>3 M</td>
<td>TODGA &gt;&gt; MIDOA, TDGA</td>
</tr>
<tr>
<td>Nd</td>
<td>3</td>
<td>3</td>
<td>3 M</td>
<td>TODGA &gt;&gt; MIDOA, TDGA</td>
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<tr>
<td>Pu</td>
<td>3</td>
<td>4</td>
<td>3 M</td>
<td>TODGA ~ MIDOA &gt; TDGA</td>
</tr>
<tr>
<td>Zr</td>
<td>4</td>
<td>4</td>
<td>3 M</td>
<td>TODGA &gt; TDGA &gt; MIDOA</td>
</tr>
<tr>
<td>Ta</td>
<td>5</td>
<td>5</td>
<td>0.2 M</td>
<td>MIDOA &gt; TDGA &gt; TODGA</td>
</tr>
<tr>
<td>Mo</td>
<td>6</td>
<td>6</td>
<td>0.2 M</td>
<td>MIDOA &gt; TDGA &gt; TODGA</td>
</tr>
<tr>
<td>Tc</td>
<td>7</td>
<td>7</td>
<td>0.2 M</td>
<td>MIDOA &gt; TDGA &gt; TODGA</td>
</tr>
<tr>
<td>Ru</td>
<td>8</td>
<td>3</td>
<td>0.2 M</td>
<td>MIDOA &gt; TDGA &gt; TODGA</td>
</tr>
<tr>
<td>Ir</td>
<td>9</td>
<td>3</td>
<td>3 M</td>
<td>MIDOA &gt; TODGA &gt; TDGA</td>
</tr>
<tr>
<td>Pd</td>
<td>10</td>
<td>2</td>
<td>0.2 M</td>
<td>MIDOA &gt; TDGA &gt; TODGA</td>
</tr>
<tr>
<td>Ag</td>
<td>11</td>
<td>1</td>
<td>3 M</td>
<td>TDGA &gt;&gt; TODGA, MIDOA</td>
</tr>
<tr>
<td>Au</td>
<td>11</td>
<td>3</td>
<td>3 M</td>
<td>TDGA &gt; MIDOA &gt; TODGA</td>
</tr>
<tr>
<td>Hg</td>
<td>12</td>
<td>2</td>
<td>0.2 M</td>
<td>TDGA &gt; TODGA, MIDOA</td>
</tr>
<tr>
<td>In</td>
<td>13</td>
<td>3</td>
<td>3 M</td>
<td>TDGA &gt; MIDOA, TDGA</td>
</tr>
<tr>
<td>Pb</td>
<td>14</td>
<td>2</td>
<td>3 M</td>
<td>TDGA &gt; TDGA &gt; MIDOA</td>
</tr>
<tr>
<td>Bi</td>
<td>15</td>
<td>3</td>
<td>3 M</td>
<td>TDGA &gt; MIDOA &gt; TDGA</td>
</tr>
<tr>
<td>Te</td>
<td>16</td>
<td>4</td>
<td>0.2 M</td>
<td>MIDOA &gt; TODGA &gt; TDGA</td>
</tr>
</tbody>
</table>

From the results of the metal extractions for groups 2 to 4 and 13 to 15 used in this work, because of the hard acid metals TODGA has very high $D$ values, as TODGA has a hard oxygen donor in the ether position. Lanthanides and actinides are included in these groups. Tetravalent Pu shows high extractability with MIDOA as well as TGDGA. Metals in group 13-15 are also well-extracted by TODGA. These metals show a high complexation with hard donor, oxygen atoms. Generally speaking, alkali and alkali earth metals can be extracted by crown-ether compounds having 5 or greater numbers of oxygen atoms. Ln in group 3 can be extracted easily by TODGA, and Zr is extractable by TODGA and HDEHP [5-6, 32-34]. Earlier publications also supported the present results, concerning the easy extraction of In and Bi with the crown ether compound [35-37].

From group 5 to 10 and 16 in Table 1, MIDOA shows the highest extractability of all. Some metals in these groups form oxonium anions (i.e., MoO$_4^{2-}$, TcO$_4^{2-}$ and TeO$_3^{2-}$) and others are soft acid metals. Based on the HSAB principle, these metals show a high preference for soft donors, like N and S. Nevertheless, TDGA including an S donor atom show lower extractability for Tc, and Ir extraction than TODGA (see Figure 2(c)). Most of the oxonium anions in this work are more favorable to MIDOA than TDGA. It is noted that only MIDOA extraction shows a decrease of $D(M)$ with acid concentration due to the protonation of MIDOA [13-14]. For other extractants, $D(M)$
increases with HNO₃ concentration, based on ion-pair extraction. It was already reported that Mo and Tc are extractable by Aliquat 336, quaternary ammonium compounds, and soft acid metals, like the platinum metals group, can be easily extracted by N-donor extractants [38-40].

From group 11 to 12, TDGA shows the highest extractability. In addition, TDGA shows high $D$ values for Pd in group 10, similar to MIDOA. In particular, TDGA has very high $D$ values for Ag and Au, while other extractants show negligibly small $D$(Ag) values. TDGA is an excellent extractant for the recovery of Ag into the organic phase from HNO₃. The high extractions by TDGA are limited to Pd, Ag, Au, and Hg [26, 41-43]. The present results indicate that the N-donor shows a high affinity to more metals, including not only soft acid metals and but also the oxonium anion, than those obtained by the S-donor.

3.2 Spectrometric studies for three extractants and three water-soluble ligands

We obtained the results of UV-vis., IR, and NMR studies for the metal-complexes. Here, we use different conditions for each study. Thus, TEDGA-Nd, MIDEA-Pd and TDGA(C2)-Pd, in aqueous solutions (1 M HNO₃), were used for UV-vis. measurement, the organic phases of CCl₄ containing TODGA-La, MIDOA-Pd and TDGA(C8)-Pd were used for IR measurements, a D₂O aqueous phase with TEDGA-La, MIDEA-Pd, and TDGA(C2)-Pd were used for NMR measurements. The results of each study are shown below:

The results of UV-vis. spectrometry are shown in Figure 3. Figure 3(a)(b) shows the results for Nd-TEDGA, 3(c)(d) for Pd-MIDEA, and 3(e)(f) for Pd-TDGA(C2). These metal ions have distinct absorption spectra in the visible and ultra-violet region [22, 44-45]. We focus on the absorptions at 796 nm for Nd-TEDGA, 380 nm for Pd-MIDEA, and TDGA(C2)-Pd. The sample solutions measured having different molar ratios of [M]/[L], namely ratios of 0.5 – 4 for [TEDGA]/[Nd], and 0 – 3 for [MIDEA]/[Pd] and 0 – 3 for [TDGA(C2)]/[Pd] were used in this work. Figure 3(a)(c)(e) show the spectra and Figure 3(b)(d)(f) show the relation between the (highest) absorption and the molar ratio of [L]/[M]. Figure 3(a) shows the obvious difference, namely increased absorption and a significant red-shift, when different molar ratios of [L]/[M] are used. On the other hand, Figure 3(c)(e) shows little change. Here, the absorption by HNO₃ is greatly affected at less than 350 nm, so the spectrum in this region could not be evaluated. The red-shift caused by changing the molar ratio can be seen in other publications. This is due to the change in the nature of the meta l[22, 46-47]. Figures 3(b)(d) and (f) indicate a gradual increase of absorption with the [L]/[M] ratio, the plateau value at a molar ratio of 2.5 for [TEDGA]/[Nd], high values at 1.5-2 for [MIDEA]/[Pd], and a maximum value of 2 for [TDGA(C2)]/[Pd] can be observed. These results suggest the stoichiometry of the 1 : 2 – 3 complex of [Nd]/[TEDGA], the 1 : 2 complexes of [Pd]/[MIDEA] and [Pd]/[TDGA(C2)] formed in the aqueous phases. These results are in agreement with the extraction systems of Nd-TODGA, Pd-MIDOA, and Pd-TDGA(C8)[14,26,30-31].

The results of the IR spectrometry are shown in Figure 4, Figure 4(a) gives the result for La-TODGA, 4(b) for Pd-MIDOA, and 4(c) for Pd-TDGA(C8), and the results concerning the chemical shift values are summarized in Table 2. Here, although some of the IR studies for the M-DGA complexes were carried out [48-50], less IR work for M-MIDOA and TDGA has been performed up to now. We can assign easily the CO stretching at 1650 cm⁻¹. Although other peaks are difficult to assign because these are in the finger print region, the peaks are roughly assigned to be C-O-C stretching at 1123 cm⁻¹ for TODGA, C-N stretching at 1087 and 1437 cm⁻¹ for MIDOA, and
Figure 3. UV-vis. spectrum of metal and water-soluble ligands.

(a) and (b): Nd-TEDGA in 1 M HNO₃, (c) and (d): Pd-MIDEA in 1 M HNO₃, (e) and (f): Pd-TDGA(C₂) in 1M HNO₃. 

(b), (d), and (f): relationship between the (highest) absorbance and molar ratio of [L]/[M].

Condition: 50 mM Nd vs. 25-200 mM TEDGA in 1 M HNO₃.

Condition: 1 mM Pd vs. 0-3 mM MIDEA in 1 M HNO₃.

Condition: 1 mM Pd vs. 0-3 mM TDGA(C₂) in 1 M HNO₃.

(a) Highest absorbance at 796-801 nm
(b) Highest absorbance at 380-382 nm
(c) Absorption at 380 nm
(d) Absorption at 380 nm
(e) Absorption at 380 nm
(f) Absorption at 380 nm
C-S-C stretching at 1216 cm\(^{-1}\) for TDGA(C8). Therefore, the peaks around 1650 cm\(^{-1}\) are used for determination of the chemical shift with and without metals. Here, we use the condition of 100 mM La or 20 mM Pd in the aqueous phase and 0.1 M extractant concentrations (TODGA, MIDOA and TDGA(C8)) in CCl\(_4\) in order to reduce the free extractant in the organic phase and to see less IR peaks from CCl\(_4\). From Table 2, the chemical shift to low wavenumbers in TODGA-La sample can be seen, because the strong La bond to the carbonyl oxygen atom leads to the weak bonding of C=O. This result is agreement with Murakami et al [50]. Other samples show a somewhat high wavenumber or almost no shift. These samples of MIDOA-Pd and TDGA(C8)-Pd do not indicate a strong bond between C=O and Pd metal. From these results, it can be suggested that the La ion shows a strong bond to the carbonyl oxygen in TODGA but the Pd ion shows weak bonding with MIDOA or TDGA(C8).

Figure 4. IR spectrum of the extraction solvent including metal and extractant in CCl\(_4\).
(a): La-TODGA, (b): Pd-MIDOA, and (c): Pd-TDGA(C8).
The results of the NMR study are shown in Figure 5, Figure 5(a) show the results for La-TEDGA, 5(b) for Pd-MIDEA and 5(c) for Pd-TDGA(C2). The solvent used in this work is D2O. Here, less work on NMR studies for metal-complexation using these extractants was carried out, without authors' studies [20,22,26]. All the spectra of the samples could be assigned, as shown in these figures. The ligand and metal concentrations in the samples are as follows: 50 mM La + 100 mM TEDGA (Figure 5(a)), 20 mM Pd + 100 mM MIDEA (Figure 5(b)) and 20 mM + 100 mM TDGA(C2) (Figure 5(c)) in D2O in order to obtain less free ligand in the sample solution. The upper parts in these figures give the spectrum without metals while underneath the spectra with metals are given. Comparison of these figures show the chemical shifts to low magnetic field, especially from spectra in TEDGA and MIDEA. This is probably due to the low electron density by metal-ligand complexation. The chemical shift values are summarized in Table 3. Table 3 indicates the sample name, peak and their positions and chemical shift ($\delta$) values. From this table, relative large chemical shifts can be seen in 3 for TEDGA, and 2 and 4 for MIDEA, higher than the 0.1 ppm shift from the original ligand. The peak 3 in TEDGA corresponds to O-CH2*-CON, and peaks 2 and 4 in MIDEA correspond to N(CH3)-CH2*-CON and –CH2-N(CH3*)-CH2-, respectively. It can be considered that the large chemical shift of peak 3 in TEDGA reflects the complexation of La with both the ether oxygen and carbonyl oxygen atoms, and those in MIDEA give the complexation of Pd with the N donor atoms in the tertiary amine group. A smaller chemical shift is found in the TDGA sample, however, peak 3, which is adjacent to the S donor atoms, deformed completely after Pd-complexation. This might be the evidence of Pd-S complexation. Throughout the NMR studies, both carbonyl and ether oxygen atoms in TEDGA may bond with the La ion, N in the tertiary amine or S in the ether position may bond with the Pd ion. 13C-NMR is more informative concerning this study because the C atom bonds directly with the donor atoms (O, N, S). Murakami et al. report that the chemical shift of 13C-NMR shows stronger bonding to the carbonyl oxygen than ether oxygen donor [22].

### 3.3 Chemical calculation for metal-complexes with three extractants

The calculation on the complexes of TODGA, MIDOA and TDGA with the metals has been made. Assuming that metal ions react with one to three molecules of extractant from the slope analysis of the log-log plots (see Figure 2), the difference in the heat of formation during complex formation [$\Delta H_f / (kJ/mol)$] can be calculated by

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

where the relevant heat of formation of the metal complex, $H_{f,\text{metal complex}}$, that of the metal, $H_{f,\text{metal}}$, that of the ligand (L: TODGA, MIDOA or TDGA), $H_{f,L}$, and that of the anion (= NO3−), $H_{f,anion}$, can be obtained by DFT calculations, and $n$ and $m$ are the stoichiometric coefficients of the extractant and the anion in the metal complex. The $H_{f,L}$ and $H_{f,anion}$ values for NO3− were obtained as 20.5, 24.88, 13.95 and 4.58 kJ/mol, respectively. These values were introduced into equation (1). The results of $\Delta H_f$ are plotted against Int. y values in Figure 6. The apparent extraction constant, Int. y, can be obtained from the values of log $D$ at log [extractant] = 0. The Int. y values have been employed already in the previous papers [25,26]. Thus, the Int. y values for TODGA in Figure 6 are within the range 0.44 – 1.2 for Au, Re, Mo, W, Hg and Sb, and 1.5 – 3 for Zr, Pd, Pt and Tc. The Int. y values for MIDOA are 0.37-1.37 for

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$/ cm⁻¹</th>
<th>Chemical shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>TODGA</td>
<td>1653</td>
<td>- 29</td>
</tr>
<tr>
<td>+ La</td>
<td>1624</td>
<td></td>
</tr>
<tr>
<td>MIDOA</td>
<td>1646</td>
<td>7</td>
</tr>
<tr>
<td>+ Pd</td>
<td>1653</td>
<td></td>
</tr>
<tr>
<td>TDGA</td>
<td>1646</td>
<td>- 2</td>
</tr>
<tr>
<td>+ Pd</td>
<td>1644</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Summary of chemical shift of IR spectrum.
Figure 5. $^1$H-NMR spectrum of M-water soluble ligands in D$_2$O
(a): La-TEDGA, (b): Pd-TDGA(C2), (c): Pd-MIDEA.
Table 3. Results of NMR spectrometry for the TEDGA, MIDEA and TDGA(C2) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>peak</th>
<th>position/ ppm</th>
<th>chemical shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEDGA</td>
<td>②</td>
<td>3.282, 3.339</td>
<td>-0.014, 0.071</td>
</tr>
<tr>
<td>+ 50 mM La</td>
<td>②</td>
<td>3.268, 3.41</td>
<td></td>
</tr>
<tr>
<td>TEDGA</td>
<td>③</td>
<td>4.328</td>
<td>0.364</td>
</tr>
<tr>
<td>+ 50 mM La</td>
<td>③</td>
<td>4.692</td>
<td></td>
</tr>
<tr>
<td>TDGA (C2)</td>
<td>②</td>
<td>3.41, 3.54</td>
<td>-0.01, 0.03</td>
</tr>
<tr>
<td>+ 20 mM Pd</td>
<td>②</td>
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<td>TDGA (C2)</td>
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<td></td>
</tr>
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<tr>
<td>+ 20 mM Pd</td>
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<td>③</td>
<td>3.337, 3.367</td>
<td></td>
</tr>
<tr>
<td>MIDEA</td>
<td>④</td>
<td>3.397</td>
<td>0.237</td>
</tr>
<tr>
<td>+ 20 mM Pd</td>
<td>④</td>
<td>3.634</td>
<td></td>
</tr>
</tbody>
</table>

U, Au, Pt, Ru, Tc, Re, W, V, Ir, Hg and Sb, and 1.58 – 2.2 for Pu, Zr, Pd, Mo and Ta. The Int. y values for TDGA are 0.45 – 1.5 for Au, Pd, Mo, Tc, Re, Ru, Ir and Sb, and 1.6 – 3.5 for Ag, Zr, Hg, U, Pu and W. Here, Figure 6(a) shows the ΔH_f values for the 1 : 1 complex, obtained from the slope analysis of log [extractant] –log D(M) plots, and Figure 6(b) shows the sum of the results for 1 : 2 and higher orders of the molar ratio of the metal complexes (see Figure 2). The reasons to make such a distinction are (1) the high order of the molar ratio readily gives high Int. y values and (2) the same conditions should be chosen as much as possible for a proper comparison. From these figures, the trend of ΔH_f decreasing with increase of Int. y values can be seen, their linearities are 0.78 and 0.83 (1 : 1, and 1 : 2 and 1 : 3, TODGA), 0.72 and 0.77 (MIDOA), 0.85 and 0.87 (TDGA). This indicates that low heat values promote extraction. These results are in agreement with the former studies that indicated a negative relationship between ΔH_f and logK_{ex} [51-52].

4. Conclusion

Three extractants, TODGA, MIDOA and TDGA, developed in our group are used for comparison of their extractabilities. From the present work, it is clear that metals of group 2-4 and 13-15 used in this work can be easily extracted by TODGA, metals of group 5-10 and 16 are extractable by MIDOA and 11-12 are extractable by TDGA. Some spectrometries are employed for elucidation of the metal-ligand complexes. From the present work, the chemical shift values for UV-vis. gives the molar ratio of [M]/[L]. IR spectra indicate that the carbonyl oxygen atom works actively as the donor atom for the La-TODGA complexation, however less evidence can be seen in Pd-MIDOA and Pd-TDGA complexation. 1H-NMR indicates indirectly the activities of the ether position of donor atoms, O, N, and S, for TEDGA, MIDEA and TDGA(C2), respectively. The results of calculation for the heat of formation during complex formation give the reverse-correlation between ΔH_f and Int. y values, which indicates that low heat of formation promotes the extraction.
Figure 6. Relationship between $\Delta H_f$ and Int. $y$, values.
(a): data from 1:1 complex of M:L, (b) 1:2 and 1:3 complex.

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