

Highly Selective Extraction of TcO_4^- , ReO_4^- , and MoO_4^{2-} by the New Ligand, 2,2'-(Methylimino)bis(*N,N*-Dioctylacetamide) (MIDOA)

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Highly selective extraction of oxonium anions can be achieved by the new ligand, 2,2'-(methylimino)bis(*N,N*-dioctylacetamide) (MIDOA). MIDOA has a high solubility in *n*-dodecane, any types of diluents can be employed for the solvent extraction. The extraction using MIDOA was performed under the condition, HNO_3 and *n*-dodecane, considering the chemical process of high-level radioactive liquid waste. It was obvious that the oxonium anions, like TcO_4^- , ReO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , and WO_4^{2-} , are extracted, and the distribution ratios (*D*) decrease with increase of HNO_3 concentration.

The separation methods for the long-lived radioactive metals, the heat source and the noble metals from high-level radioactive liquid waste (HLW) has been developing over 5 decades. Not only actinides but also Sr, Cs, Tc, Pd, Rh, Ru, and Mo are the aimed elements in this partitioning process, the chemical separation method to recover Tc, which has a long half life decaying, a catalytic and a medical use, has been studied intensively.¹⁻⁵ Among these metals, Tc and Mo behave as an oxonium acid in the aqueous solution, the specific chemical forms have some difficulties to extract these metals by the existing neutral and the acidic extractants. The analytical information up to now suggested that the extraction conditions to exhibit the high *D*(Tc) values are out of HNO_3 -dodecane.⁶⁻¹⁰ Some monoamides can extract Tc from HNO_3 to hydrocarbons but with *D* of approximate or lower than 0.1.^{11,12} The solvent extraction by CMPO and TBP, whose condition has been used in PUREX and TRUOX processes, can give *D*(Tc) as 1.48 and 2.36,¹³ these results indicate that the multi-step extraction is necessary to achieve the quantitative extraction of Tc. Some reports suggested that *D*(Tc) increases according to the concentration of co-extracted metal,^{11,14} in this case the calculation for its recovery become difficult. Therefore, the development of the neutral extractant, which has a high solubility in *n*-dodecane and shows a high performance on Tc extraction from nitric acid, is still-required.

The novel extractant, 2,2'-(methylimino)bis(*N,N*-dioctylacetamide) (MIDOA, see Figure 1), has three donors of two carbonyl oxygen and one nitrogen in the ether position. MIDOA, composed of carbon, nitrogen, hydrogen, and oxygen atoms, is expected to have the strong extractability by tridentation, as an

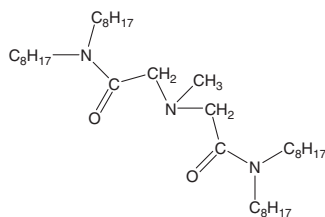


Figure 1. Structure of MIDOA.

analogue of diglycolamide or thiadiglycolamide.¹⁵ A preliminary investigation using MIDOA for the extraction of Tc, Re, and Mo is reported in this paper.

The reagents used for the organic synthesis and the solvent extraction were commercially available. The synthetic method of MIDOA was followed by the ordinary way of the diamide synthesis;¹⁵ methyliminodiacetic acid and thionyl chloride were reacted to produce methyliminodiacetic chloride. The organic chloride is then reacted with di-*n*-octylamine in the presence of triethylamine under the freezing point. After synthesis, the products were washed by water, sodium hydroxide and hydrochloride solutions, and purified repeatedly by passing the solutions through silica-gel columns. Its purity was determined to be 97% by liquid chromatography. The ¹H NMR signals for MIDOA were found (CDCl_3): δ 0.9 (t, $-\text{CH}_3$), 1.2–1.6 ($-\text{C}_6\text{H}_{12}-$), 2.5 (s, $-\text{CH}_3$), 3.3 (t, $-\text{CH}_2-$), and 3.5 (s, $-\text{CH}_2-$). The solvent extraction was performed as the following method, two cm^3 of the pre-equilibrated organic phase was taken and mixed with the same volume of the aqueous phase, spiked with Tc-99 solution or the non-radioactive metal solution. The mixture was shaken mechanically for 2 h at 25 ± 0.1 °C. After centrifugation and separation of the phases, duplicate 0.50 cm^3 aliquots for both aqueous and organic phases were measured by a liquid scintillation counter (Tri-Carb 1600 TR, Packard Instrument Company) for the beta activities of ⁹⁹Tc in 5 cm^3 of the scintillation cocktail. The amounts of the non-radioactive metal ions in the sample solutions prepared from the aqueous and the organic phases were measured by an ICP-AES (SPS 3100, Seiko Instruments Inc) or an ICP-MS (SPQ 9000, Seiko-EG&G) spectrometers.

The solubility of MIDOA into *n*-dodecane was examined by observation, the clear solution of 1.66 g/cm^3 can be obtained. This solubility corresponds to approximate 1.1 M ($=\text{mol/dm}^3$) of MIDOA in *n*-dodecane. The C/O ratio of MIDOA is 18.5, which considers the very high lipophilic property compared to other extractants,^{16,17} this extractant is applicable to HNO_3 -*n*-dodecane extraction system.

Extraction of oxonium anions, TcO_4^- , ReO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , and WO_4^{2-} , was performed and Figure 2 indicates the relation between HNO_3 concentration and *D*(M). Here, other oxonium ions and some metal cations were hardly extracted. As shown in Figure 2, *D* for these metals depend on the HNO_3 concentration and Tc and Re have remarkably high *D* values from 0.1 M HNO_3 to *n*-dodecane. The publications for Tc coordination have introduced the soft donor ligands,^{18,19} MIDOA has one N donor in the center of backbone, which suggests N or S coordination is important for the Tc extraction. Concerning with this, TODGA (*N,N,N',N'*-tetraoctyldiglycolamide), whose ether oxygen is positioned at N donor of MIDOA, has low *D*(Tc) ($=2$).²⁰ Hard donor coordination may decrease *D*(Tc). As shown in Figure 2, *D* decreases with increase of the HNO_3 concentra-

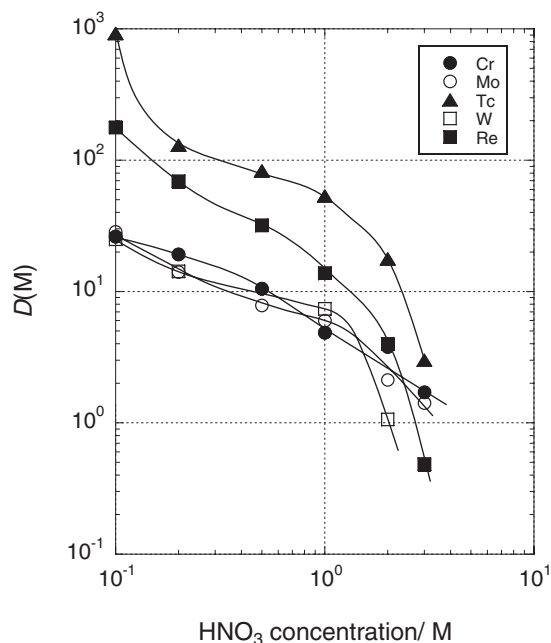


Figure 2. Dependence of $D(\text{Tc})$ on HNO_3 concentration. MIDOA concentration: 0.1 M/dodecane.

tion. The references generally support this behavior, the extractant concentration may be reduced by the complex formation with NO_3^- .⁹

The D values of Tc and Re at less than 1 M HNO_3 concentration are over 50 and 10, which are very high values from HNO_3 to n -dodecane. The order of D is $\text{Tc} > \text{Re} > \text{W} > \text{Mo} > \text{Cr}$ trend from 1 M HNO_3 . The various metal extraction using quaternary amine was performed and this extractant has high D values not only Tc but also Cr, W, and Re, suggesting that MIDOA has strongly complexing ability with the same metals as those for this amine.⁶ MIDOA is a neutral donor and Tc is an oxo-acid, it is important to investigate the extraction behavior and the reaction. The relations of $\log D$ vs. $\log[\text{MIDOA}]$ was shown in Figure 3. Assuming that the activity coefficient is constant, these slope values in Figure 3 are related to the number of MIDOA in the extraction reactions. The $\log D - \log[\text{MIDOA}]$ relation shows the first-order dependence, which suggests one molecule of MIDOA contributes to the extraction reaction. Neutralization of complex in the organic phase is performed by the aid of protons. MIDOA is a tridentate ligand, three coordination site in Tc are occupied by this ligand. Referred with other reports, TBP needs three, CMPO for two, monoamide for two or three molecules in Tc extraction,^{13,21,22} which suggests 2–4 sites of Tc can be coordinated by the organic ligands.

The extraction behavior of Tc, Re, and Mo by MIDOA was reported preliminarily. Tc and Mo are aimed elements among fission products in HLW and difficult to recover due to their chemical forms in the aqueous solution. It is clear from the present work that more than 95% Tc and 90% Mo can be extracted by 0.1 M MIDOA/ n -dodecane from lower concentration than 0.5 M HNO_3 and the multi-step extraction is necessary to achieve the quantitative recovery of both metals from 3 M HNO_3 , as a condition of HLW.

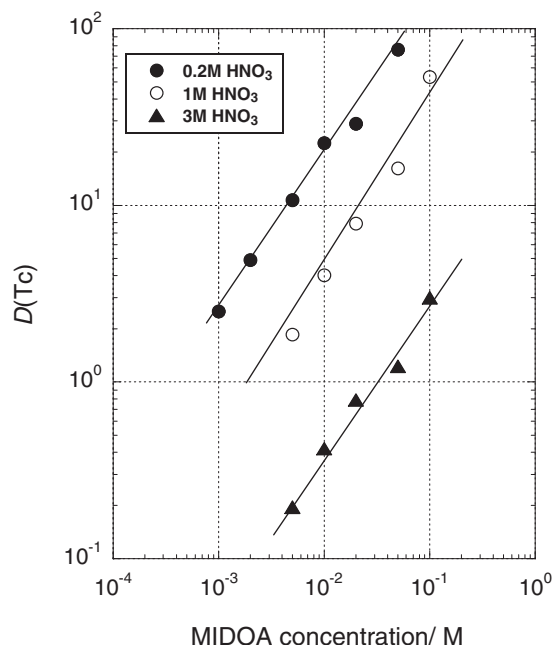


Figure 3. Dependence of $D(\text{Tc})$ on MIDOA concentration. HNO_3 concentration: 0.2, 1, and 3 M. Slope values calculated are: 0.853 ± 0.04 (0.2 M), 1.06 ± 0.08 (1 M), 0.853 ± 0.07 (3 M).

Present study includes the result of “Development of separation technology of transuranium elements and fission products by using new extractants and adsorbents” entrusted to “Japan Atomic Energy Agency” by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

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