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Ion-Pair Extraction Studies of Zr, Hf, Nb, Ta, and Oxonium Anions Using Extractants Containing Amino N Atom from Various Acids

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Ion-pair reactions play a key role in the extraction of anionic metal ions –such as chlorinated, fluorinated, or sulfated ions, and oxonium anions– through the use of cationic extractants whose amino N atoms are protonated under acidic conditions. Focusing on these reactions, we investigated the extraction of Zr, Hf, Nb, and Ta anionic metal species present in sulfuric and hydrofluoric acids, and oxonium anions of group 6 and 7 elements, including Tc, Re, Cr, Mo, and W, under various conditions. The distribution ratio, *D*(M), for some anions exceeded 100. NTAamide (hexaalkyl-nitrilotriacetamide), having a tetradentate mode, exhibited the highest *D* values among all extractants tested. Monovalent oxonium anions, such as Tc and Re, showed higher *D* values than divalent anions, and these anions were efficiently extracted from acids containing affinitive anions, such as HF, HCl, and H_2SO_4, rather than from HNO_3 and $HClO_4$.

1. Introduction

Solvent extraction techniques are typically applied to metal cations through solvation or chelation, using β-diketones, neutral amides, and phosphorus compounds. In addition to these techniques, a novel extraction reaction has been reported that enables extractants containing amino N donors to extract oxonium anions and other metal anions, such as Rh(III), Nb(V), and Re(VII), with the assistance of H^+ [1-6]. These metal ions have long been considered difficult to extract. Rh(III) can form chlorinated metal anions, while Nb(V) and Ta(V) can form fluorinated metal anions at sufficiently high HCl and HF concentrations, respectively, based on their stability constants [7-10]. The amino N atom in the extractant becomes protonated under acidic conditions, forming a cationic extractant, while the anionic metal species, including chlorinated, fluorinated, and oxonium anions, are present under acidic HCl or HF conditions. Ion-pair extractions proceed through the interaction between the cationic extractant and the anionic metal ions (Figure 1). This reaction enables the recovery of metals that have previously been difficult to extract. Therefore, it is important to accumulate foundational data for these extraction reactions.

In this work, we measured the distribution ratio, *D*, of Zr(IV) and Hf(IV) in H_2SO_4; Zr(IV), Hf(IV), Nb(V), and Ta(V) in HF; and oxonium anions (Cr, Mo, W, Tc, and Re) in five acids (HNO_3, HCl, H_2SO_4, HF, and $HClO_4$) using five extractants dissolved in different diluents. These metal ions may form anions in these acids, and we studied their extraction behavior under various conditions. The extractants used are shown in Figure 2. They include monodentate (TOA, trioctylamine), bidentate (IDCA (*N,N,N',N'-*

tetraoctylimidodicarbonic diamide)), tridentate (IDOA (imino-bis-*N,N*-dioctylacetamide) and MIDOA (methylamino-bis-*N,N*-dioctylacetamide)), and tetradentate (hexaalkyl-*N,N,N',N',N'',N''*-nitrilotriacet(NTA)amide) ligands, all of which have an amino N atom in their structures and were developed at the Japan Atomic Energy Agency (JAEA), except TOA. The organic diluents employed include polar solvents (nitrobenzene (NB), 1,2-dichloroethane (DCE), 1-octanol (OC), and 2-decanone (DCN)), chloroform (CL), toluene (TL), and a nonpolar solvent (*n*-dodecane (DD)). Based on these results, we confirmed the performance of ion-pair extraction.

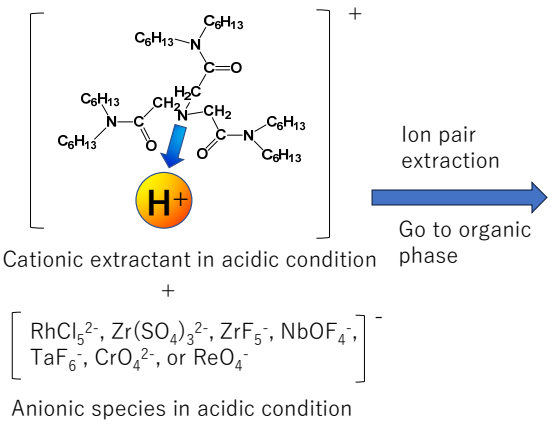

Figure 1. Ion-pair extraction considered.

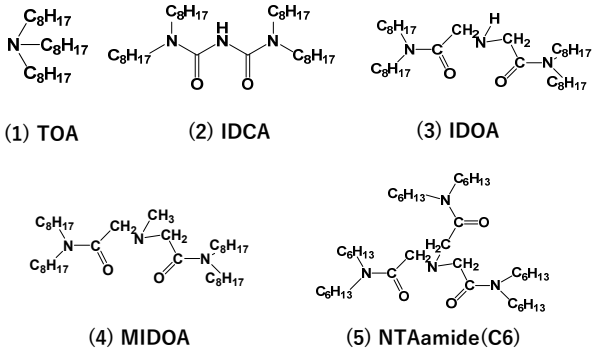

Figure 2. Extractants used in this work.

2. Experimental

2.1 Reagents

The extractants NTAamide, MIDOA, IDOA, IDCA, and TOA were purchased from Wako Pure Chemical. All other reagents, including acids and organic solvents, were of analytical grade. The metal solutions used for atomic absorption spectrometry (1,000 ppm) were also obtained from Wako Pure Chemical.

2.2 Solvent extraction

The organic phase was prepared by dissolving extractants in *n*-dodecane or other diluents. The aqueous phase was prepared by dissolving metal residues, obtained after careful evaporation of metal standard solutions to remove anions, in the target acid or HNO_3. This process was repeated at least twice. The metal concentration in the aqueous phase was approximately 200 ppm (~2 mM). Equal volumes (1:1) of the organic and aqueous phases containing the metal (1:1 volume ratio of organic and aqueous phases) were mixed and mechanically shaken at 1,500 – 2,000 rpm (SI-300C, As One) for 20 min at 25 ± 0.1 °C. After phase separation, aliquots of the aqueous phases were diluted to a maximum concentration of 10 ppm with 0.5 M HNO_3 prior to measurement by inductively coupled plasma (ICP) optical emission spectrometry (SPS3100, Seiko Instruments Inc.) and ICP-mass spectrometry (SPQ 9000, Seiko-EG&G). The metal concentration in the organic phase was determined by subtracting the metal concentration of the aqueous phase from the initial value. The distribution ratio, D, was calculated as the ratio of the metal concentrations in the organic ($[M]_{org}$) and aqueous ($[M]_{aq}$) phases: $D = [M]_{org}/[M]_{aq}$.

3. Results and Discussion

3.1 Extractions of Zr(IV) and Hf(IV) from H_2SO_4

Solvent extractions of Zr(IV) and Hf(IV) were performed from H_2SO_4 media using three of the extractants shown in Figure 2, and the results are presented in Figure 3. Under these conditions, the metals form anionic species such as $M(SO_4)_3^{2-}$ (M= Zr or Hf) in sulfuric acid [8,11,12]. Figure 3(a) shows the dependence of *D* on the H_2SO_4 concentration (○) and on the H_2SO_4 concentration at fixed 1 M SO_4^{2-} (□) using Na_2SO_4 solution. This figure shows a very high *D*(M), exceeding 100, at 0.1 M H_2SO_4 and a very low *D*(M) of less than 0.1 at 0.002 M H_2SO_4 and 0.998 M Na_2SO_4. Zr and Hf can be easily extracted and stripped under these conditions. Figure 3(b) shows the dependence of *D*(M) on the extractant concentration using the three extractants. Zr(IV) appears to be more extractable than Hf(IV), and the extractive trend for extractants is NTAamide (tetradentate) > MIDOA (tridentate) > TOA (monodentate). Figure 3(c) shows the dependence of *D*(Zr) on the NTAamide concentration using seven different diluents. After extraction, polar solvents can be used as electrolytic solutions, and platinum metals in the organic phase can be recovered as metal phases by electrolysis [13,14]. Taking ion-pair extraction into account, polar solvents should be effective for extracting these ions. However, *n*-dodecane shows the highest *D*(Zr), despite being a nonpolar solvent, while 1-octanol clearly exhibits a lower *D*(Zr) (Figure 3(c)).

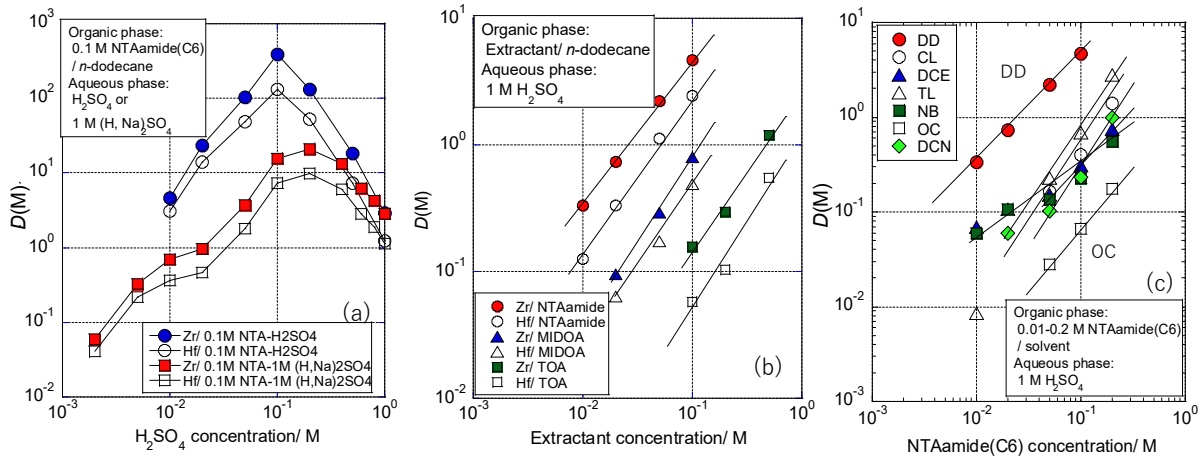

Figure 3. Extraction of Zr and Hf from H_2SO_4 media by extractants containing amino N atoms.
(a) Dependence of *D*(M) on H_2SO_4 using NTAamide, (b) dependence of *D*(M) on extractant concentration using NTAamide, MIDOA, and TOA from 1 M H_2SO_4, (c) dependence of *D*(Zr) on NTAamide concentration in different diluents from 1 M H_2SO_4.

3.2 Extractions of Zr(IV) and Hf(IV) from HF

Solvent extractions of Zr(IV) and Hf(IV) using NTAamide, MIDOA, and TOA were also performed from HF media, and the results are shown in Figure 4. Under these conditions, the metals primarily form anionic species such as MF_5^- in 1 M HF [8,15,16]. Figure 4(a) shows the dependence of *D*(M) on the HF concentration (○) and on the HF concentration at fixed 1 M F^- (□) using KF solution. This figure shows that *D*(M) increases then decreases from 1 M HF, with the highest *D* value exceeding 10. These *D* values are lower than those obtained with H_2SO_4 in Figure 3. The square symbols show sharply increasing *D* values

between HF concentrations of 0.2 and 1 M. As is well known, the dissociation constant of HF is low (approximately 0.001). Thus, a high concentration of fluoride ions may scavenge H^+ to form neutral HF, thereby suppressing ion-pair extraction under such conditions due to the low proton concentration. In other words, these conditions may be suitable for stripping Zr and Hf from the organic phase. Figure 4(b) shows the dependence of *D*(M) on the extractant concentration using the three extractants. Minimal differences in *D*(M) values and extraction behavior are observed among the extractants in this figure. Figure 4(c) shows the dependence of *D*(Zr) on the NTAamide concentration using seven different diluents. This figure also shows little difference among the diluents. Both polar and nonpolar solvents give relatively high *D*(M) values from 1 M HF when using 0.1 M NTAamide.

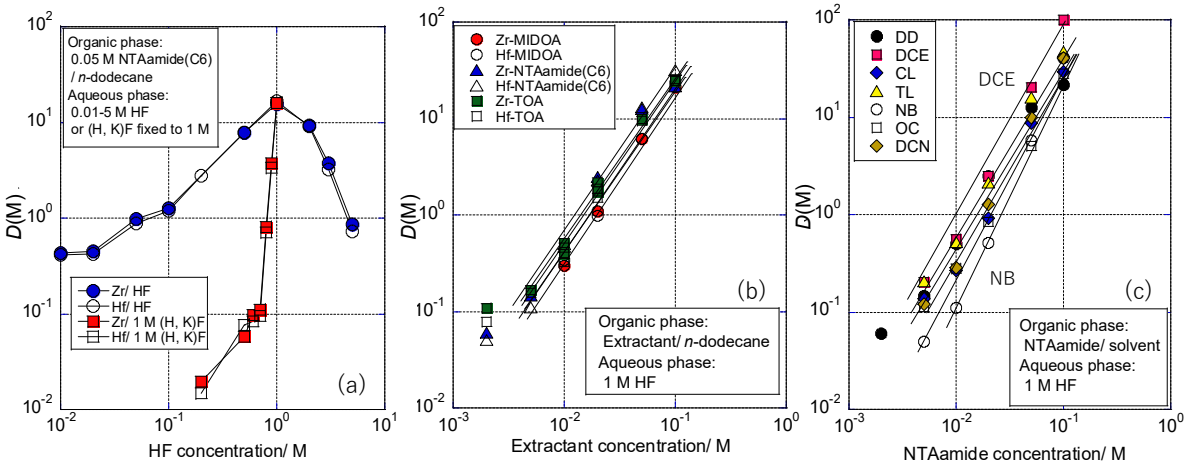

Figure 4. Extraction of Zr and Hf from HF media by extractants containing amino N atoms.
(a) Dependence of *D*(M) on HF concentration using NTAamide, (b) dependence of *D*(M) on extractant concentration using NTAamide, MIDOA, and TOA from 1 M HF, (c) dependence of *D*(Zr) on NTAamide concentration in different diluents from 1 M HF.

3.3 Extractions of Nb(V) and Ta(V) from HF

Niobium and tantalum exist as pentavalent cations and are difficult to prepare in most acids, except hydrofluoric acid. Fluoride complexes of Nb and Ta are stable in the aqueous phase, forming anionic complexes such as $NbOF_4^-$ and TaF_6^- [8,17,18]. Limited information is available on the solvent extraction of Nb(V) and Ta(V); therefore, recovery methods for Nb and Ta are generally employed for ion exchange. The results obtained using NTAamide, MIDOA, and TOA under conditions analogous to those in Figure 4 are shown in Figure 5. Similar results for extraction to those in Figure 4 can be observed, except that very high *D*(M) values of over 100 are recorded. From Figure 5(a), the extraction and stripping conditions of 1 M HF and 0.2 M HF + 0.8 M KF, respectively, can be identified. Figure 5(b) shows that Ta is more extractable than Nb, and Figure 5(c) demonstrates that Nb(V) can be effectively extracted into all diluents used in this study. These results indicate that Nb and Ta in HF can be easily extracted, with *D*(M) exceeding 100, via this ion-pair extraction method.

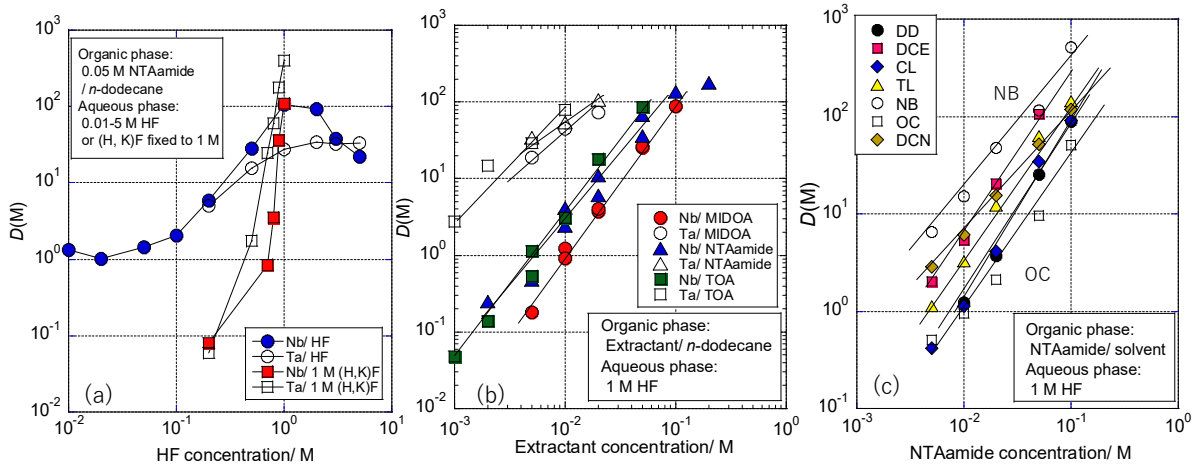

Figure 5. Extraction of Nb and Ta from HF media by extractants containing amino N atoms. (a) Dependence of D(M) on HF concentration using NTAamide, (b) dependence of D(M) on extractant concentration using NTAamide, MIDOA, and TOA from 1 M HF, (c) dependence of D(Nb) on NTAamide concentration in different diluents from 1 M HF.

3.4 Extractions of oxonium anions from several acids

Group 6 and 7 elements tend to be oxonium anions under ordinary conditions, except for Mn. Thus, Cr, Mo, and W typically form MO_4^{2-}, while Tc and Re form MO_4^-. Because these metal ions are stable in the aqueous phase and are difficult to extract via solvation or chelation methods, anion exchange is commonly used for their recovery. We investigated these metal extractions using the extractants in Figure 2. The dependence of D(M) on the HNO_3 concentration using the NTAamide extractant is shown in Figure 6(a). D(M) decreases with increasing HNO_3 concentration, indicating a competitive reaction between the oxonium anion and NO_3^- at higher HNO_3 concentrations. At the low HNO_3 concentration of 0.2 M, D(M) exceeds 10 for all anions, suggesting that these anions can be extracted by NTAamide.

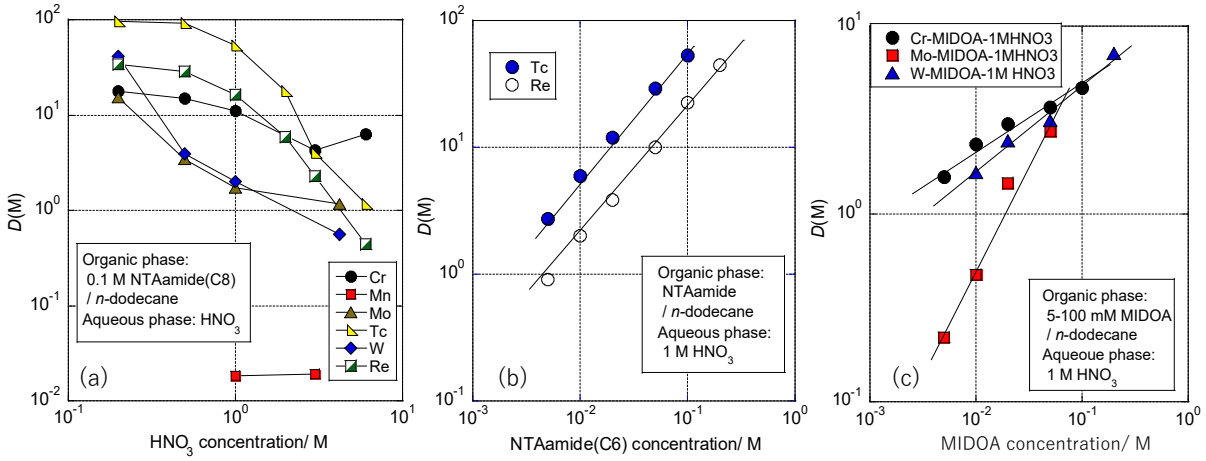

Figure 6. Extraction of oxonium anions from HNO_3 media by extractants containing amino N atoms. (a) Dependence of D(M) on HNO_3 concentration using NTAamide, (b) dependence of D(Tc,Re) on NTAamide concentration from 1 M HNO_3, (c) dependence of D(Cr,Mo,W) on MIDOA concentration from 1 M HNO_3.

D(M) for the monovalent anions Tc and Re appears to be higher than that for the divalent anions Cr, Mo, and W, suggesting that the neutralization of monovalent anions through ion-pair extraction proceeds more readily than for divalent anions. Figure 6(b) and (c) show a comparison of *D*(M) for metals in the same group; both figures indicate higher *D*(M) at lower atomic numbers. Here, Mn, another group 7 element, is stable as a divalent rather than heptavalent ion, while Cr, Mo, and W form several oxonium anions: MO_4^{2-}, $M_2O_7^{2-}$, $M_3O_{10}^{2-}$, and other multinuclear complexes. Therefore, a direct comparison of *D*(M) among these metals cannot be carried out. Overall, Figure 6(b) and (c) indicate that ion-pair extraction favors anions with high charge density.

We subsequently focus on Re, as a representative monovalent oxonium anion, for solvent extraction under various conditions. Figure 7(a) shows the dependence of *D*(Re) on the NTAamide concentration in various acids, (b) shows the dependence of *D*(Re) on the extractant concentrations, and (c) shows the dependence of *D*(Re) on the NTAamide concentration in four different diluents. From Figure 7(a), the trend of *D*(M) is HF ~ H_2SO_4 ~ HCl > HNO_3 > $HClO_4$, suggesting that acids with high affinity for metals exhibit high *D*(M) values. Ion-pair extraction is generally considered to be independent of the extractant structure; however, the extractability trend for the different extractants was found to be NTAamide > MIDOA > IDOA > IDCA (Figure 7(b)), which corresponds to the order of tetradentate > tridentate > bidentate ligands. Figure 7(c) indicates that Re can be extracted into both polar and nonpolar solvents, although this ion-pair extraction appears to have limited efficiency when using 1-octanol (Figure 3(c), 5(c), and 7(c)).

Finally, oxonium anions were extracted using divalent ions (Cr and Mo). Figure 8 was obtained under the same conditions as Figure 7. A similar trend of *D*(M) can be seen in the two figures. Regarding the back-extraction conditions for these oxonium anions, limited information is provided in the present work. As shown in Figure 6(a), *D*(M) decreases with HNO_3 concentration, due to the competitive reaction with nitrate ions. Thus, a high $HClO_4$ concentration (Figure 7(a) and 8(a)) is considered advantageous for stripping oxonium anions, based on the present work.

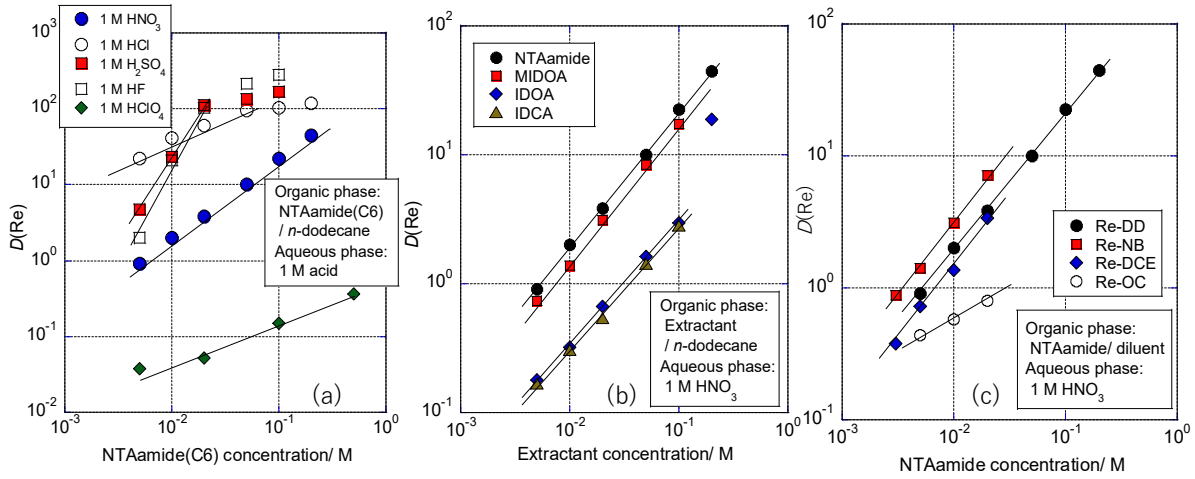

Figure 7. Extraction of Re by extractants containing amino N atoms under various conditions.
(a) Dependence of *D*(Re) on NTAamide concentration from various acids (1 M), (b) dependence of *D*(Re) on concentration of four extractants from 1 M HNO_3, (c) dependence of *D*(Re) on NTAamide concentration in four different diluents from 1 M HNO_3.

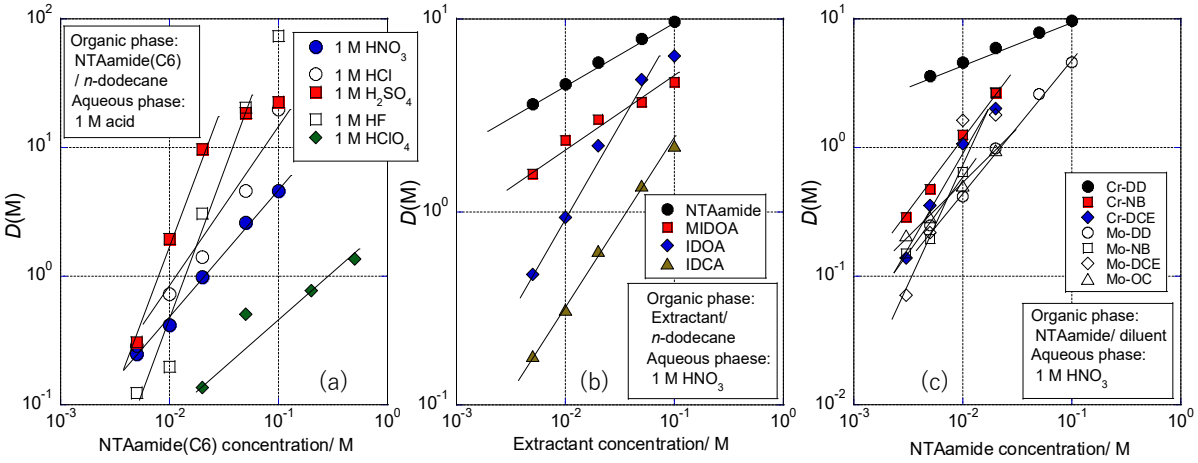

Figure 8. Extraction of Cr and Mo by extractants containing amino N atoms under various conditions. (a) Dependence of D(Mo) on NTAamide concentration from various acids (1 M), (b) dependence of D(Cr) on concentration of four different extractants from 1 M HNO_3, (c) dependence of D(M) on NTAamide concentration in different four diluents from 1 M HNO_3.

4. Conclusion

A new ion-pair extraction process was studied using novel extractants containing an amino N atom in their structure. These extractants are protonated under acidic conditions, enabling them to extract anionic species via ion-pair extraction. To investigate the characteristics of this extraction process, solvent extractions were performed using various anionic species under different conditions. Very high D(M) values ($D \geq 100$) were observed for Zr and Hf in H_2SO_4 and for Nb and Ta in HF. Conditions involving concentrated Na_2SO_4 and KF solutions resulted in low D(M) values ($D < 0.1$), indicating promising potential for stripping these metals from the organic phase. Even in ion-pair extraction, similar extraction behaviors and D(M) values were observed across *n*-dodecane and other polar solvents. The results of oxonium anion extractions indicate that monovalent anions are more readily extracted. Additionally, acids with high affinity for metals (HCl, HF, and H_2SO_4) tend to yield high D(M) values. Considering the minor effect of the extractant structure, the order of D(M) values followed the trend tetradentate > tridentate > bidentate (monodentate) ligands, implying strong extractability of these anions by multidentate ligands.

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Declaration

The authors declare that they have no conflicts of interest.

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