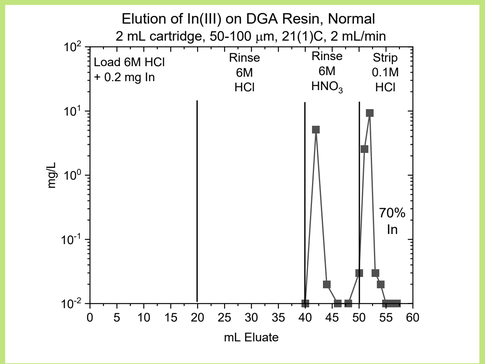
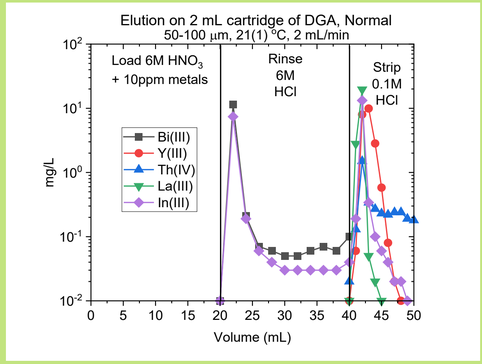
Extraction of Bismuth and Indium by Diglycolamides

Daniel McAlister[1], Ed Rush[1], Ferris Bissen[2], Madeleine Eddy[1]
[1]Eichrom Technologies, LLC [2]Michigan State University

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Abstract Diglycolamide (DGA) extractants have been utilized in solvent extraction (SX) and extraction chromatography (EXC) for the separation of actinides[1], rare earths[2], strontium[3], and transition metals[4]. Previous work in our laboratory has shown interesting behavior for the extraction of metal ions by DGA utilizing anionic metal chlorides as the counter ion[5]. In addition, selected metal ions (In and Bi), which can be extracted by DGA utilizing nitrate and chloride counter ions, have been shown to be poorly extracted from any combination of nitrate and chloride in the mobile phase, while actinides (III, IV, and VI) and rare earths (III) are efficiently extracted from nitrate, chloride, and combinations of nitrate and chloride. Solvent extraction, FTIR, stoichiometric analysis, column elutions, and batch extraction studies have been used in an attempt to elucidate the mechanism of In(III) and Bi(III) extraction disruption from the mixed HCl/HNO_3 systems.

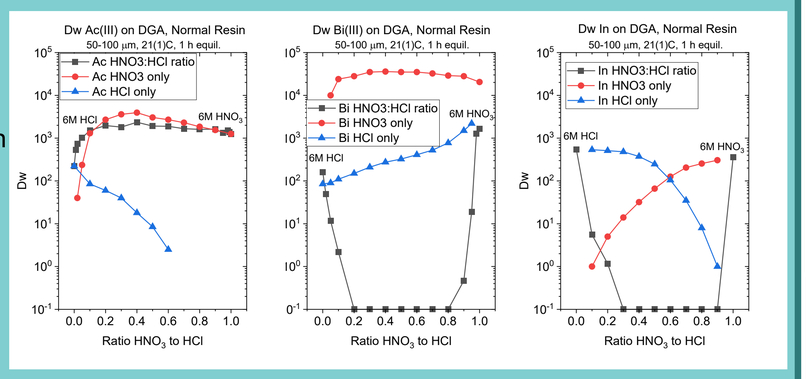




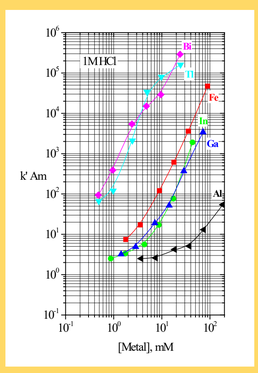
In column separation Elution of In(III) on DGA resin columns produce an interesting phenomenon, where a significant portion of In(III) is lost when transitioning from HNO_3 to HCl or HCl to HNO_3, despite In(IIII) being retained strongly from both media. Similar behavior is observed on DGA resin for Bi(III), but not for La(III), Ac(III), Th(IV), or U(VI).

HCl-HNO_3 Ratios Batch Extraction

From mixtures of HCl and HNO_3, the extraction of In(III) and Bi(III) on DGA, normal resin exhibit a strong antagonistic effect. The In and Bi Dws decrease more significantly for any mixture of HNO_3 and HCl than predicted from the dilution of HNO_3 or HCl. The extraction of Ac(III) and Th(IV) by DGA resin does not exhibit the antagonistic behavior from HCl-HNO_3 mixtures, with the retention dominated by the HNO_3 concentration. U(VI) retention on the DGA resin from the HCl-HNO_3 mixtures reflects a combination of what would be expected from pure HNO_3 or HCl. Fe(III) is not retained on the DGA resin from HNO3, but its behavior from mixtures of HCl and HNO_3 is nearly identical to the behavior from HCl alone.



Metal chlorides as counterions

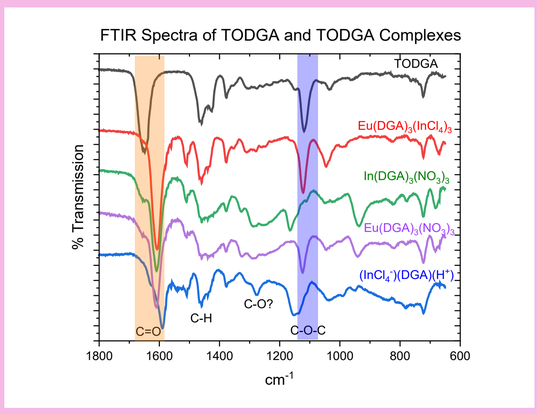


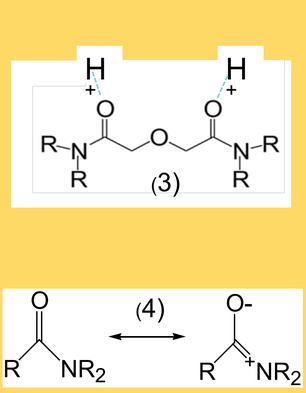
In addition to being extracted by DGA resin as anionic metal chlorides, Bi(III), In(III), Fe(III), Ga(III), and Tl(III) can serve as the counterion for the extraction of trivalent lanthanides and actinides, and Th(IV) by DGA resin. The enhancement in extraction in the presence of these metal chlorides, MCl_4^-, is much higher than expected from the excess chloride, as illustrated by the extraction of Am(III) in the presence of the anionic metal chlorides and the neutral $AlCl_3$.

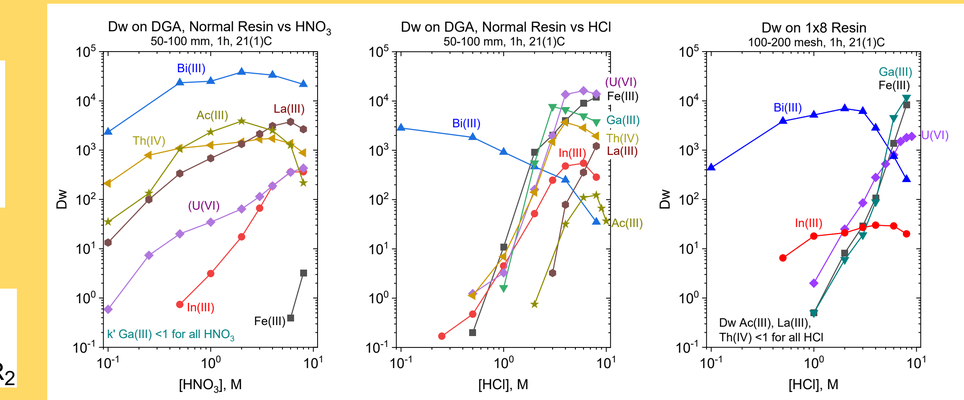
X-ray absorption fine structure (XAFS) experiments on powder sources of the isolated $Eu(DGA)_3(BiCl_4)_3$ compounds showed the Eu-O interactions between the amide and ether oxygens of the DGA extractant, but no Bi interactions with the DGA coordination environment.[6]

FTIR of TODGA complexes

Fourier Tranform Infrared Spectra (FTIR) were measured for TODGA and solid compounds of DGA with Eu and In from HCl and HNO_3 using a single pass Attenuated Total Reflectance (ATR) interface. The spectra exhibit characteristic C=O peaks near 1650 cm^{-1} for TODGA, which shifts to lower energy upon complexation with the metal ions. The shift of the C=O band is nearly identical for Eu extracted from HNO_3, In extracted from HNO_3 and Eu extracted using $[InCl_4]^-$ as the counterion. For In extracted from HCl, the shift in the C=O stretch is much more significant, suggesting a difference from the other complexes. Similar behavior is observed in the C-O-C stretching region, 1120 cm^{-1} for the neat TODGA. In this case, the band shifts to slightly higher energy upon complexation with Eu and more significantly for the $In(NO_3)_3$ complex. For the extraction of In from HCl, the C-O-C band is broader than in the other complexes.







$$M^{n+} + nNO_3^- + xDGA \leftrightarrow M(DGA)_x(NO_3)_n \quad (1)$$

$$M^{n+} + (n+1)Cl^- + xDGA + H^+ \leftrightarrow [MCl_n]^- \cdots [H(DGA)_x]^+ \quad (2)$$

DGA Batch Extraction Diglycolamide (DGA) extractants form extractable complexes with a wide variety of metal ions from HNO_3 and HCl. From HNO_3, metal ions such as La(III), Ac(III), Bi(III), In(III), Th(IV), and U(VI) are primarily extracted via a solvating mechanism with DGA, with nitrate coextracted to form neutral species (1).

From HCl, Ac(III), La(III), and Th(IV) are likely extracted via the same solvating mechanism (1). However, Bi(III), Fe(III), Ga(III), In(III), and U(VI) may also be extracted via an ion exchange mechanism (2). The anion exchange mechanism may involve protonated (3) or tautomerized DGA (4). The tetrachloro anionic species of Fe(III), In(III), Bi(III) and Ga(III) are also moderately chaotropic or water structure disrupting, so it is also possible that the tetrachloro anion species are rejected from the aqueous phase into the resin phase without direct complexation to the DGA extractant via a hydrophobic interaction chromatographic extraction mechanism.

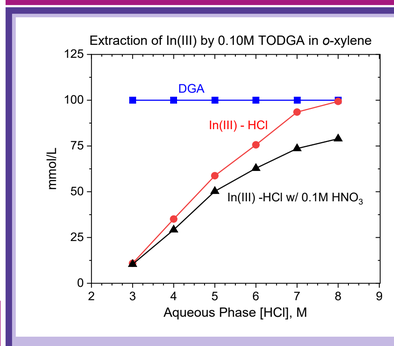
In addition to the cations, anions and extractant molecules represented in the extraction mechanisms (1) and (2), the presence of water solvating the metal ions and anions in the aqueous phase play an important role in the thermodynamics of metal ion extraction. In systems where metal ions are extracted by the solvating mechanism (1) and the metal ions and anions are dehydrated upon complexation and extraction into the resin phase, one would expect significant decrease in the magnitude of extraction when changing the anion from nitrate to chloride, due to the higher free energy of dehydration for the chloride ion relative to nitrate. For DGA resins, the difference in extraction between nitrate and chloride systems is not as great as expected due to the significant co-extraction of water molecules into the resin phase.

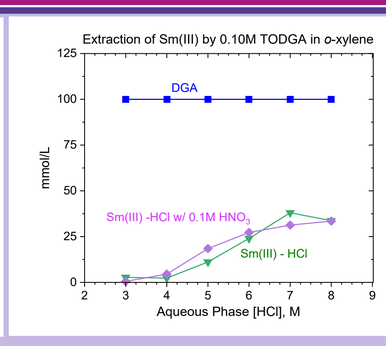
Solvent extraction (TODGA/Fe/Eu/HCl) When saturated by contact with high aqueous HCl concentrations, the 0.1M TODGA in *o*-xylene extracts nearly 2 HCl molecules per DGA extractant (5). When Fe(III) and HCl are present, nearly equal amounts of Fe(III), HCl and DGA are present in the organic phase, supporting $[FeCl_4]^-$ extraction via the protonated DGA (6). In the Eu(III), Fe(III), HCl system, the extracted HCl is almost fully replaced by Eu(III), suggesting the $Eu(DGA)_3(FeCl4)_3$ stoichiometry (7).

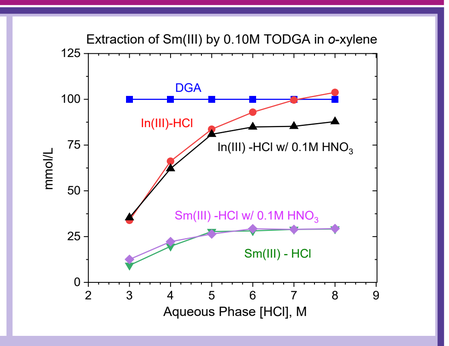
$$TODGA + xHCl \leftrightarrow TODGA(HCl)_x \quad (5)$$

$$TODGA + H^+ + FeCl_4^- \leftrightarrow TODGA(HFeCl_4) \quad (6)$$

$$3TODGA + Eu^{3+} + 3FeCl_4^- \leftrightarrow Eu(TODGA)_3(FeCl_4)_3 \quad (7)$$







Solvent Extraction (TODGA/In/Sm/HCl) The TODGA, Sm(III), In(III), HCl system exhibits similar trends to the DGA/Eu/Fe/HCl system. When only In and HCl are present, the In(III) reaches a saturated value of 1:1 with DGA, likely extracted as the $[InCl_4^-]$ via the protonated DGA extractant. The full saturation of the TODGA phase with In(III) occurs only at the highest HCl concentration, 8M HCl, whereas with Fe, the saturation occurred from 4-8M HCl. This suggests that the Fe(III) forms stronger complexes with the Cl^- anion than In(III). Addition of 0.1M HNO_3 to the aqueous phase decreases the amount of In extracted into the organic phase, possilbly through the disruption of the $[InCl_4^-]$ anion.

When only Sm(III) and HCl are present in the aqueous phase, Sm(III) reaches a saturation value of 1:3 Sm:DGA. When 0.1M HNO_3 is added to the organic phase, the Sm(III) extraction remains essentially unchanged. One difference, however, is that when only HCl is present, a third phase forms from 5-8M HCl upon extraction of Sm(III), whereas no third phase forms when the 0.1M HNO_3 is present. The small amount of HNO_3 seems to prevent aggregation of the the extracted Sm-DGA complexes.

When In(III), Sm(III), and HCl are present in the aqueous phase, the saturated organic phase stoichiometry is $Sm(DGA)_3(InCl_4)_3$, and the In(III) saturation occurs at lower HCl concentrations than in the In/HCl only system. Upon addition of 0.1M HNO_3 to the aqueous phase, the Sm(III) content remains the same, but the In(III) decreases by about 20-25%, likely replaced by NO_3^- as the counterion for neutralization of the extracted Sm(III)-DGA complex. The inclusion of nitrate is supported by the appearance of nitrate bands in the ~300 nm region of the UV-VIS spectra of the back-extracted TODGA organic phases.

Conclusions and Future Work

The extraction of various metal ions by DGA was studied by various techniques in an attempt to explain the anomalous behavior of In(III) and Bi(III) from mixed HNO_3-HCl systems. Analysis of the extracted species suggest that In(III) and Bi(III) are extracted from HNO_3 via a neutral solvating mechanism, forming the species $M(DGA)_3(NO_3)_3$ as previously determined for REE(III) and Actinide(III) complexes of DGA from HNO_3 and HCl. From HCl, In(III) and Bi(III) are extracted by DGA as anionic chlorides, MCl_4^-, likely via a weak anion exchange mechanism by the H^+ adduct of the DGA extractant. The poor extraction of In(III) and Bi(III) by DGA when HCl and HNO_3 are both present in the aqueous phase may be due to issues transitioning from the solvating extraction mechanism in HNO_3 to the anion exchange mechanism from HCl, where the presence of HNO3 disrupts the formation of the MCl_4^- anion. Methods for the analysis of the aqueous speciation of Bi(III) and In(III) from mixed HNO_3-HCl matrices may provide additional insight.

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