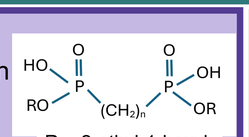
Extraction Chromatography Resins based on Diphosphonic Acid Extractants

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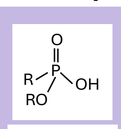
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Abstract Lipophilic diphosphonic acid extractants have been studied extensively in solvent extraction[1-5], but relatively little work with has been done to evaluate extraction chromatography (EXC) resins prepared from the diphosphonates[6]. Solvent extraction and EXC studies with the diphosphonates have focused primarily on the actinides, Fe(III), and alkaline earth cations. The diphosphonate H2DEH[MDP] (used in Actinide Resin) forms very strong complexes with tri, tetra and hexavalent metal ions, but recovery of extracted metal ions can be difficult, even with high concentrations of mineral acids or complexing agents. Aiming to retain the selectivity of the H2DEH[MDP] while easing the recovery metal ions, a series of di-2-ethyl-1-hexyl substituted diphosphonic acids have been synthesized with 1-4 carbons bridging the two phosphonic acid groups. EXC resins were prepared from the diphosphonates, and the extraction of a wide selection of metal ions was evaluated. The properties of the diphosphonate resins were also compared to LN2 resin containing the analogous monophosphonate, HEH[EHP].



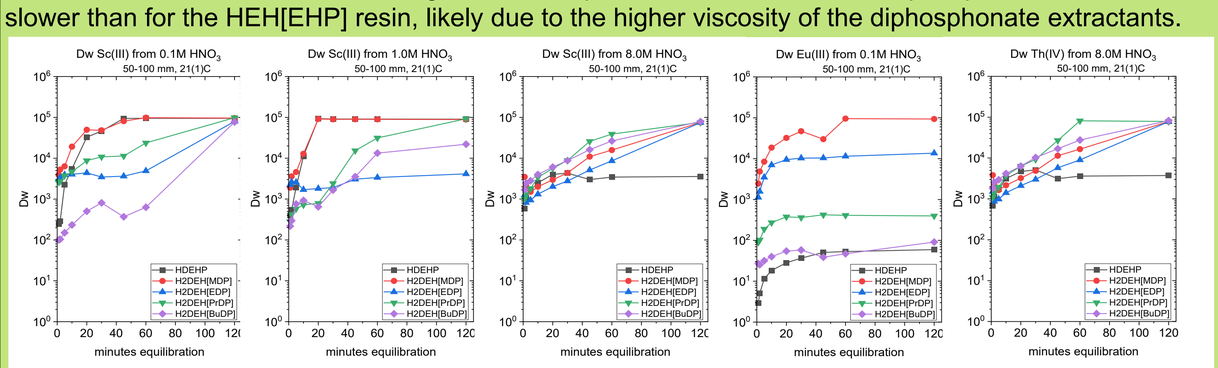
R = 2-ethyl-1-hexyl

Diphosphonates
n = 1 H2DEH[MDP]
n = 2 H2DEH[EDP]
n = 3 H2DEH[PrDP]
n = 4 H2DEH[BuDP]



HEH[EHP]

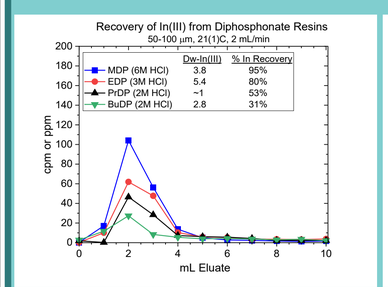
Kinetics/Capacity The kinetics of absorption of metal ions on the HEH[EHP] and diphosphonate EXC resins were studied using different metal ions and acid conditions to determine if different mechanisms of extraction occur at different rates. In general, the uptake of metal ions on the diphosphonate resins is slower than for the HEH[EHP] resin, likely due to the higher viscosity of the diphosphonate extractants.

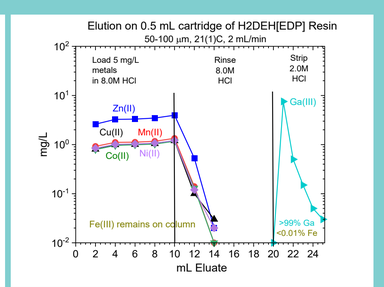


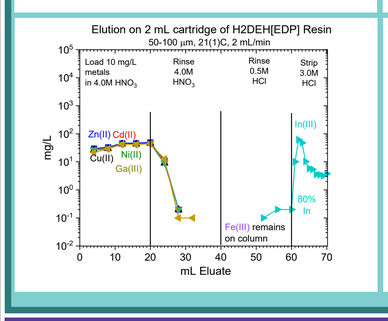
The capacities of the diphosphonate resins were also lower than expected for certain combinations of metal ion and matrix, such as Th from 1.0M HNO_3, likely due to kinetic issues arising from the viscosity of the hydrogen bonded diphosphonates.Reduction of the extractant loading in the H2DEH[MDP] resins and the addition of the isodecanol diluent improved the relative capacity. Additional work is being performed to study the impact of hydrogen bonding diluents on the metal extraction, kinetics, and extractant leaching properties of the diphosphonate resins.

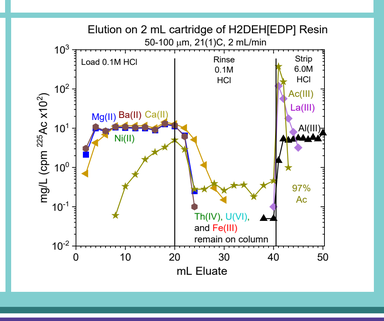
Capacity mg metal / gram resin						
Resin	Fe(III) 0.1M HCl	Fe(III) 6.0M HCl	Th(IV) 1.0M HCl	Th(IV) 6.0M HNO_3	U(VI) 1.0M HCl	U(VI) 6.0M HNO_3
LN2	5.7 ± 0.3	6.3 ± 0.2	28.4 ± 0.2	84 ± 8	45.7 ± 1.1	80 ± 11
H2DEH[MDP]	22.4 ± 1.0	25.0 ± 2.1	11.2 ± 0.5	30.2 ± 1.7	64.3 ± 3.3	83.4 ± 1.3
H2DEH[EDP]	18.6 ± 0.5	9.4 ± 0.3	22.9 ± 1.2	36.2 ± 1.6	82 ± 8	96 ± 14
H2DEH[PrDP]	18.5 ± 0.1	9.1 ± 0.3	39.2 ± 1.6	45.4 ± 1.3	79.9 ± 4.0	100 ± 17
H2DEH[BuDP]	20.4 ± 0.6	8.5 ± 0.2	38.3 ± 4.0	43.8 ± 2.2	69.4 ± 4.6	103 ± 18
1:1 MDP:isodecanol	15.4 ± 0.2	15.1 ± 0.6	28.4 ± 3.4	34.9 ± 2.4	45.4 ± 4.4	71.7 ± 1.6
3:1 MDP:isodecanol	21.3 ± 0.1	21.6 ± 1.2	21.3 ± 1.9	40.0 ± 1.1	48.4± 2.1	76.9 ± 0.4

Column Separations Increasing the number of carbons bridging the phosphonate groups in the diphosphonate extractants did achieve the primary goal of reducing the equilibrium Dw values of several metal ions suggesting potential improvements in the recovery of metal ions. However, in column tests, the EXC resins prepared from the extractants containing 3-4 bridging carbons exhibited very poor kinetics, leading to broad elution bands during stripping conditions, with In(III) recovery decreasing from 95% for n=1 to only 31% for n=4.Due to the poor column results for the PrDP and BuDP resins, the remaining column experiments focused on the MDP and EDP resins.









Ga(III) could not be recovered from the MDP resin with any concentration of HNO_3 or HCl but is efficiently recovered from the EDP resin in a small volume of 2-3M HCl and separated from Zn(II) and Fe(III).

In(III) ecovery from MDP resin requires 6M HCl, while the EDP resin releases In(III) in 3M HCl.

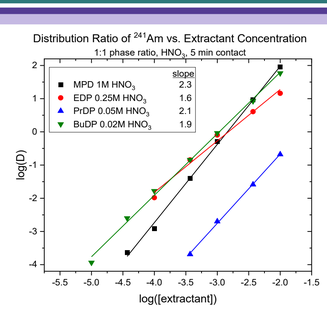
Ac(III) recovery from the MDP resin is poor from all HNO_3 and HCl, while Ac(III) can be recovered from the EDP resin with a small volume of 1-8M HCl.

All resins, regardless of the number of bridging carbons retain Fe(III) strongly from all HNO_3 and HCl concentrations, providing an effective tool for the removal of Fe(III) from nearly all other mono-, di-, and trivalent metal ions.

Extractant Leach The extractants are not covalently bound to the EXC resins but held in the pores of the inert methacrylate substrate via hydrophobic interactions, so small amounts of extractant can leach into the mobile phaseand impact subsequent separations. This behavior is seen for high specific activity radionuclides when a subsequent EXC resin with neutral/solvating extractants follow the phosphonic acid resins.

To assess the degree of extractant leach, mobile phases from eluted through columns were collected, back extracted with *o*-xylene to transfer the leached extractant into an organic solvent, and liquid-liquid distribution ratios (D) measured using ^{241}Am. The D_{Am} values were compared to calibration curves generated from known concentrations of the extractants in *o*-xylene to calculate the concentration of leached extractant.

The amount of leached extractant was similar for MDP and EDP, but decreased for the more hydrophobic PrDP and BuDP. Reducing the extractant loading of MDP reduced the extractant leach more than expected from the lower mass of extractant, and replacing the removed extractant with a corresponding mass of long-chain alcohol further reduced the extractant leach. Adding a cartridge of uncoated prefilter resin below the diphosphonate cartridge removed >75% of the leached extractant.



Extractant Leach from Diphosphonate Resins***

Sample	leach moles/L**	leach mg in 20 mL	% Extractant Loss	leach relative to MDP
MDP	2.45E-04	0.49	0.19	1.00
EDP	2.70E-04	0.54	0.21	1.10
PrDP	1.51E-04	0.30	0.12	0.62
BuDP	9.79E-05	0.20	0.075	0.40
75% MDP*	1.96E-04	0.39	0.15	0.80
50% MDP*	8.57E-05	0.17	0.066	0.35
75% MDP - 25% isodecanol*	1.39E-04	0.28	0.11	0.57
50% MDP - 50% isodecanol*	4.89E-05	0.10	0.038	0.20

*Relative loading to the 40% (m:m) extractant loading of the MDP resin
**Leach from 2 mL cartridge eluated with 20 mL of 2.0M HNO_3
***Measured in triplicate with error <10%

>75% of leached material removed by prefilter resin cartridge

Dry Weight Distribution Ratios Dry weight distribution ratios (Dw) for selected metal ions were measured by contacting an aqueous phase with a mass of dry resin and measuring the metal ion concentration or radioactivity before and after equilibration. Dw values were caculated using the following equation:

$$Dw = \frac{(Ao-Af)}{Af} \times \frac{mL}{g}$$

Where Ao = initial metal ion concentration or radioactivity, Af = metal ion concentration or radioactivity after equilibration with g grams of dry resin, and mL = the volume of aqueous phase in mL.

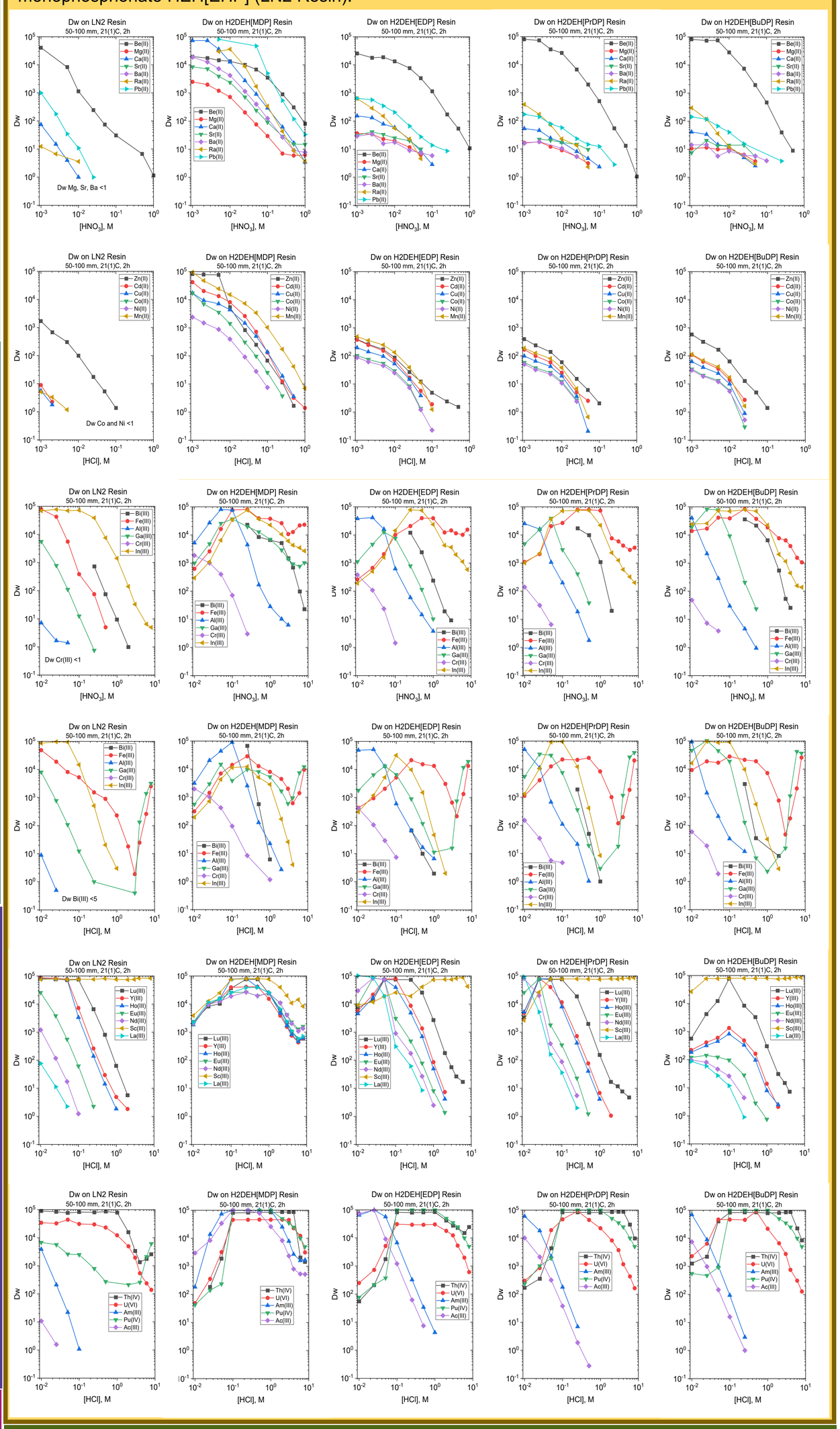
Metal ion extraction by the diphosphonate EXC resins mirror what has been previously observed in solvent extraction studies. Divalent alkaline earth and transition metal cations and trivalent lanthanides and actinides are primarily extracted through cation exchange mechanisms with an acidic proton of the extractant exchanged for each charge of the metal ion extracted. The Dw values for these metal ions from HNO_3 and HCl are essentially the same.

$$M^{2+} + \overline{2(H_2L)_2} \leftrightarrow \overline{M(HL\cdot H_2L)_2} + 2H^+$$

Selected trivalent transition metals which form neutral or anionic chloride and nitrate complexes exhibit different behavior from HNO_3 and HCl. Additionally, the acid dependent extraction curves may not decrease linearly with increasing acid concentration due to the contributions of several extraction mechanisms, including cation exchange, neutral solvation, and weak anion exchange mechanisms through the protonated extractant.

$$MCl_x + \overline{2(H_2L)_2} \leftrightarrow \overline{MCl_x[(H_2L)_2]_2\cdot(H^+)_{(x-3)}}$$

Extraction of metal ions with the H2DEH[MDP] resin exhibits very little selectivity for metals of the same charge, likely due to the strong chelation effect of the two phosphonate groups. As the distance between the phosphonates increases, the metal ion extraction decreases and matches more closely to that of the monophosphonate HEH[EHP] (LN2 Resin).



Conclusions and Future work The extraction of metal ions by EXC resins containing diphosphonate extractants mirror data previously obtained in solvent extraction studies. Increasing the number of carbons separating the phosphonate groups generally decreases the magnitude of metal ion extraction and changes the selectivity to more closely match the EXC resin containing the monophosphonate HEH[EHP]. The extraction kinetics also becomes slower as the number of bridging carbons increases, as the extractants become more viscous. Resins prepared from the neat extractants H2DEH[PrDP] and H2DEH[BuDP] exhibit very poor behavior in column elution tests due to their slow kinetics. Future work will focus on the effect of diluents, such as isodecanol, on the extraction kinetics, extractant leach, metal ion retention, radiation stability, and capacity of the monophosphonate and diphosphonate EXC resins, while also expanding this research to other EXC resins commonly used in nuclear medicine radionuclide production and EXC resins produced on alternative supports.

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