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Trivalent Actinide and Lanthanide Separations by Dialkyl-Substituted Diphosphonic Acids

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Abstract: The dialkyl-substituted diphosphonic acids are powerful solvent extraction reagents for actinide separation and preconcentration from biological, environmental, and nuclear waste samples. In spite of the intensive scrutiny of the solvent extraction properties of these compounds, only the extraction of Eu(III) and Am(III), among the lanthanides and trivalent actinides, has been investigated thus far. In this work, we report the extraction of all members of the lanthanide series, plus lanthanum, yttrium, Am(III), Cm(III), and Cf(III), by two representative diphosphonic acids [i.e., P,P′-di(2-ethylhexyl) methylenediphosphonic acid (H_2DEH[MDP]) and the P,P′-di(2-ethylhexyl) ethylenediphosphonic acid (H_2DEH[EDP])].

H_2DEH[MDP] shows very efficient extraction of all ions investigated, but little selectivity, except for the heaviest lanthanides. H_2DEH[EDP], on the other hand, exhibits less efficient extraction, but much higher selectivity, with an average separation factor between contiguous elements of 1.8, and extraction equilibrium constants spanning about three orders of magnitude along the lanthanide series. The extraction data for H_2DEH[EDP] also exhibit a significant tetrad effect. The differences in

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affinity and selectivity for the lanthanides and trivalent actinides observed with the two extractants are discussed in terms of chelating ring size, monofunctional character, extractant aggregation, and metal extraction stoichiometries.

INTRODUCTION

The rare earth elements are becoming increasingly more important for the production of modern technological materials. In addition to their use as neutron poisons in the nuclear industry, they find application in superconductors, optoelectronic materials, special alloys, catalysts, and radiotherapeutic reagents (1). The high level of lanthanide purity required for many applications justifies the interest in efficient preconcentration and separation procedures both from an analytical and industrial point of view (2).

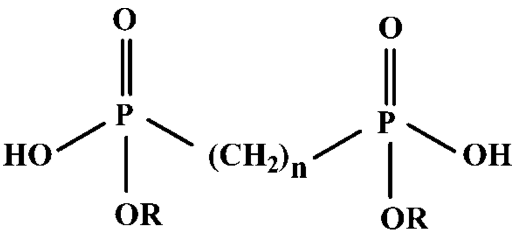
Various classes of extractants exhibit at least some utility in lanthanide separations [e.g., tertiary carboxylic acids (3), β-diketones (4), 4-acylpyrazolones (5, 6), quaternary alkylammonium salts (7), mono and bifunctional neutral organophosphorus compounds (7–9)]. Acidic organophosphorus extractants of the phosphoric, phosphonic, and phosphinic type, however, are predominantly used in solvent extraction procedures for rare earth separations (10–18). In these procedures, the separation factors for adjacent lanthanides are typically in the 1.5–2.5 range, and efficient separations of the various elements are achieved using multistage countercurrent systems (3). Di(2-ethyhexyl) phosphoric acid (HDEHP), with an average separation factor of 2.5 for adjacent members of the lanthanide series, is one of the most effective separation reagents for these elements (10, 11, 16).

In lanthanide separation studies using HDEHP and analogous acidic organophosphorus extractants, periodic variations across the lanthanide series have been reported (13–17). Typically, in a plot of the logarithm of the metal distribution ratio (or the extraction equilibrium constant) vs. Z, the lanthanide atomic number, the data points define four groups of four elements, with a pronounced minimum for gadolinium and two secondary minima in the 60–61 and 67–68 Z region. This periodic behavior is called the “tetrad effect” (19) or “double-double effect” (20). Possible explanations for this effect have been summarized by various authors (21–28). Nash and Jensen (3) have recently reported that, when the distribution ratios are plotted as a function of the reciprocal of the ionic radii of the lanthanides as determined by Shannon (29), the tetrad effect largely disappears. This confirms that the tetrad effect observed in lanthanide separations arises from tetradic variations in the radii of the lanthanides, which, in turn, arise from nephelauxetic effects and other related causes (21–28). The separation factors generated by the tetrad effect, however, are real and can be exploited to achieve intra-lanthanide separations.

Multifunctional acidic organophosphorus reagents have recently been investigated as solvent extraction reagents for intra-lanthanide separations. For example, the extractant *m*-xylenedi(phenylphosphinic) acid was reported to exhibit distribution ratios that increase by five orders of magnitude between lanthanum and lutetium with a pronounced tetrad effect (30).

In another study, the monoprotic reagent di(phenyl)phosphinylmethyl phenylphosphinic acid and the diprotic reagent P,P′-di(phenyl) methylenediphosphinic acid were investigated for their capability to extract lanthanides (31). Both extractants in 1,2-dichloromethane were much more efficient than HDEHP in the extraction of lanthanides at low aqueous phase acidity. However, the diprotic partial ester did not exhibit any selectivity along the lanthanides series, while the monoprotic reagent exhibited some selectivity only for the heaviest lanthanides. For both extractants, the plots of the distribution ratios vs. Z showed evidence for a limited tetrad effect.

In recent years, we have been investigating the solvent extraction behavior of P,P′-di(2-ethylhexyl) alkylenediphosphonic acid reagents with the general Structure I, where R is the 2-ethylhexyl group, and n is one or two for the P,P′-di(2-ethylhexyl) methylene- and ethylene-diphosphonic acids, (H_2DEH[MDP]) and (H_2DEH[EDP]), respectively (32–37).



Structure I

In the diesters of alkylenediphosphonic acids, the length of the alkylene bridge separating the phosphorus atoms determines the aggregation state of the extractants [e.g., H_2DEH[MDP] is dimeric (33, 36), while H_2DEH[EDP] forms hexameric spherical aggregates reminiscent of reverse micelles in aromatic diluents (34, 37)].

The type of extraction processes and metal-extractant complexes that are formed in the organic phase are different for the two extractants. Metal ion extraction by two H_2DEH[MDP] dimers results in the formation of a metal complex which contains a large number of chelate rings (four six-membered and three eight-membered rings) (32). In the case of H_2DEH[EDP], metal ions are transferred into the hydrophilic cavity of the hexameric aggregate, and coordination of the metal ion to the P=O and

POO^- groups of the extractant forms seven- and eight-membered rings which are considerably less stable than in the H_2DEH[MDP] case (35).

This behavior rationalizes why the alkaline earth cations are extracted much more efficiently by H_2DEH[MDP] than by H_2DEH[EDP] (32–35). However, while H_2DEH[MDP] does not exhibit selective extraction of any one alkaline earth cation over the series members (32), the reduction in extraction efficiency observed for H_2DEH[EDP] is accompanied by a strong preference for the smaller cation Ca^{2+} (35). In this respect, the behavior of H_2DEH[EDP] parallels that observed for monofunctional dialkyl phosphoric acid extractants [e.g., HDEHP (38)].

Given the growing interest in intra-lanthanide separations, we decided to evaluate the ability of H_2DEH[MDP] and H_2DEH[EDP] to effect separations across the lanthanide series. For this purpose, the extraction of yttrium, lanthanum, the members of the lanthanide series plus selected trivalent actinides (Am^{3+}, Cm^{3+}, and Cf^{3+}) by *o*-xylene solutions of H_2DEH[MDP] and H_2DEH[EDP] was measured under identical experimental conditions. The objective of this work was to determine whether the selectivity characteristics of alkaline earth extraction by H_2DEH[MDP] and H_2DEH[EDP] would be observed in the extraction of lanthanides, and the extent to which the intralanthanide separation capabilities exhibited by H_2DEH[MDP] and H_2DEH[EDP] would be compared to those of monofunctional analogues.

EXPERIMENTAL

Materials

H_2DEH[MDP] and H_2DEH[EDP] were prepared and purified following published procedures (32–35). Solutions of the two extractants in *o*-xylene or 1-decanol were used for the distribution experiments. Lanthanide oxides, except for Pm, were obtained from Argonne National Laboratory (ANL) stocks. Weighed amounts of the oxides were dissolved in HNO_3 to prepare the aqueous solutions for the extraction experiments. ^{147}Pm and $^{152/154}$Eu were obtained from Isotope Products Laboratories, Burbank, CA. ^{241}Am, ^{244}Cm, and ^{249}Cf (from the decay of ^{253}Bk) were from ANL stocks; and their purity was checked by alpha and gamma spectrometry. All other reagents were analytical grade and were used without further purification.

Measurements

Metal distribution ratios, D, calculated as the ratio of the metal concentration in the organic and aqueous phase, were obtained at 23 ± 1°C using the same techique described previously (32, 35). Counting of organic and aqueous radioactive samples was performed with a Packard Cobra Autogamma counter ($^{152/154}$Eu, ^{241}Am and ^{249}Cf) or via liquid scintillation on a Packard Model 2000 CA counter (^{147}Pm and ^{244}Cm). Aqueous samples of nonradioactive lanthanides were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP/AES) or, when needed, by mass spectroscopy (ICP/MS). In these cases, the metal concentration in the aqueous phase was obtained by difference. In a number of experiments, lanthanide mass balance was checked by stripping the lanthanides from the organic phase with 0.5 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) and analyzing the resultant aqueous solution by ICP/AES. Mass balance was generally within 5%. Duplicate experiments showed that the reproducibility of the D measurements was generally within 5%, although the uncertainty interval was higher for the highest D values ($D > 10^3$).

To reduce the number of experiments needed to characterize the behavior of yttrium, lanthanum, and the 14 lanthanides, the elements were divided in three groups. Each group contained a number of cations that could be analyzed simultaneously (ICP/AES). Pr, Sm, Eu, Er, Tm, and Y were in group I; Ce, Eu, Gd, Tb, Yb, and Lu were in group II; while La, Nd, Eu, Dy, and Ho were in group III. Eu was present in all groups so that its behavior could be used to monitor the internal consistency of the extraction data. Stock solutions for each group contained the relevant metal nitrates at concentrations chosen in such a way (in the 4- to 70-mM range) that the analytical sensitivity was approximately the same for all the elements. The total concentration of metal ions in each stock solution was about 0.15 M. Aliquots of the stock solutions were used to prepare aqueous phases for the extraction experiments having a total metal concentration between 1 and 2 mM at the required HNO_3 concentration. To test the accuracy of the distribution ratios calculated from the spectroscopic analyses for each group, the distribution of europium was also measured by spiking the aqueous solution with $^{152/154}$Eu. The results for the two cases were within experimental uncertainty, and their average is reported in the following sections. Extraction data for prometheum and actinides were obtained using group I solutions spiked with the radioisotopes ^{147}Pm, ^{241}Am, ^{244}Cm, and ^{249}Cf.

RESULTS AND DISCUSSIONS

Extraction Data

Acid dependencies at constant extractant concentration in *o*-xylene and extractant dependencies at constant aqueous acidity were measured for all cations keeping the ionic strength in the aqueous phase constant at 1 M NO_3^- concentration. Since in these experiments the total metal ion concentration was not much lower than that of the extractant, the logarithmic plots of the D values vs. the *initial* extractant or aqueous acid concentration (not shown for brevity) were nonlinear and generally uninformative. To obtain useful plots of the D values as a function of *equilibrium* concentrations of extractant and aqueous HNO_3, corrections to the analytical concentration data were required.

Extractant concentrations at equilibrium were obtained for each cation and set of experimental conditions by subtracting the concentration of extractant bound to the metal ions from the total extractant concentration. This correction implies knowledge of the extraction stoichiometry. The extraction reaction was identified for each system by selecting the stoichiometry that provided slopes for the acid dependency plots that best approximated the expected value of -3 (32, 35). The extraction stoichiometries that provided acid dependencies closest to -3 involve organic complexes where one metal atom is bound to two H_2DEH[MDP] dimers or to one H_2DEH[EDP] hexamer, respectively. These stoichiometries match those identified previously for Am^{3+} extraction (32, 35).

If the reaction stoichiometries are correct, it should be possible to directly compare distribution data obtained for a specific system at high metal ion concentrations with data obtained for the same system at trace metal concentration level. This has been attempted for the extraction of Eu^{3+}, Pm^{3+}, and Am^{3+} by H_2DEH[MDP] and H_2DEH[EDP] from 1 M NO_3^- aqueous solutions containing either only the radioisotopes or also all the group I lanthanides at a total metal nitrate concentration of 0.0022 M. The results are reported in Figs. 1 and 2.

Figure 1 (H_2DEH[MDP]) and Fig. 2 (H_2DEH[EDP]) show acid and extractant dependencies where the data obtained in the presence of 0.0022 M lanthanides are compared with those obtained at tracer concentration level of Eu^{3+}, Pm^{3+}, and Am^{3+} after introducing the correction described above. With few exceptions, the agreement between each pair of data sets (e.g., low- and high-metal concentration) is reasonably good, confirming the validity of the approach followed for the calculation of extractant and acid equilibrium concentrations. As expected, for both extractants, the acid dependency data exhibit slopes close to -3, while the extractant dependency slopes are close to 2 for H_2DEH[MDP] and 1 for H_2DEH[EDP], respectively.

Figures 3, 4, and 5 show the extractant and acid dependency plots for the extraction of Y^{3+}, La^{3+}, all lanthanides, and Am^{3+}, Cm^{3+}, and Cf^{3+} from 1 M NO_3^- aqueous solutions by H_2DEH[MDP] in *o*-xylene. For each D value, the extractant equilibrium concentration was obtained as described above.

The slope values for the acid and extractant dependency plots, obtained through linear regression analysis of the data in Figs. 3, 4, and 5, are reported in Table 1.

From Table 1, it appears that, while the slope of the acid dependency plots can be taken as -3 for all cations, the slopes of the extractant dependency plots are higher than the value of 2 implied by the extraction stoichiometry

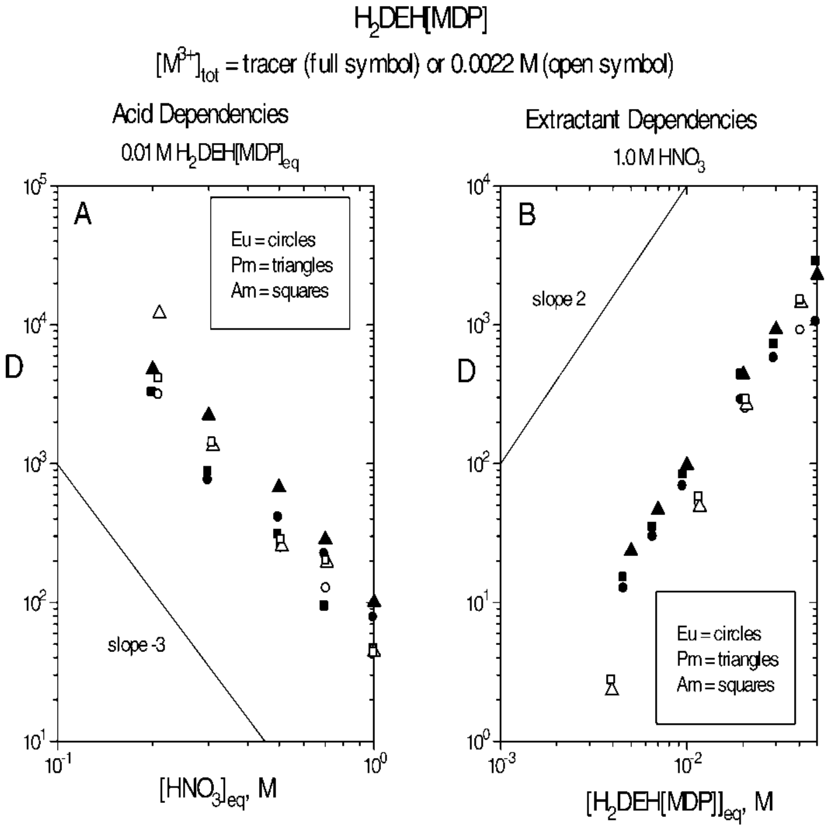


Figure 1. Extraction of Eu^{3+}, Pm^{3+}, and Am^{3+} by $H_2DEH[MDP]$ in *o*-xylene from 1 M NO_3^- aqueous solutions. Full symbols: tracer metal concentration level; empty symbols: 0.0022 M total lanthanide nitrate concentration. Panel A: Acid dependencies with D values normalized for 0.01 M $H_2DEH[MDP]$ equilibrium concentration. Panel B: Extractant dependencies at 1.0 M HNO_3.

used for plotting the D values vs. equilibrium extractant concentrations. The deviations from a slope 2 value are particularly high for the lighter lanthanides. A likely explanation for this behavior is that at relatively high concentrations of the metal in the organic phase, the concentration of unbound extractant becomes very low. Under these conditions, a significant portion of the free $H_2DEH[MDP]$ is monomeric. It has been previously shown that, when dissolved in the monomerizing diluent 1-decanol, three molecules of monomeric $H_2DEH[MDP]$ can react with Am^{3+} (39). In the lanthanide case, this reaction, which causes extractant dependency slope values higher than 2, is more important for the lighter lanthanides which can more easily accommodate three extractant monomers in their coordination sphere.

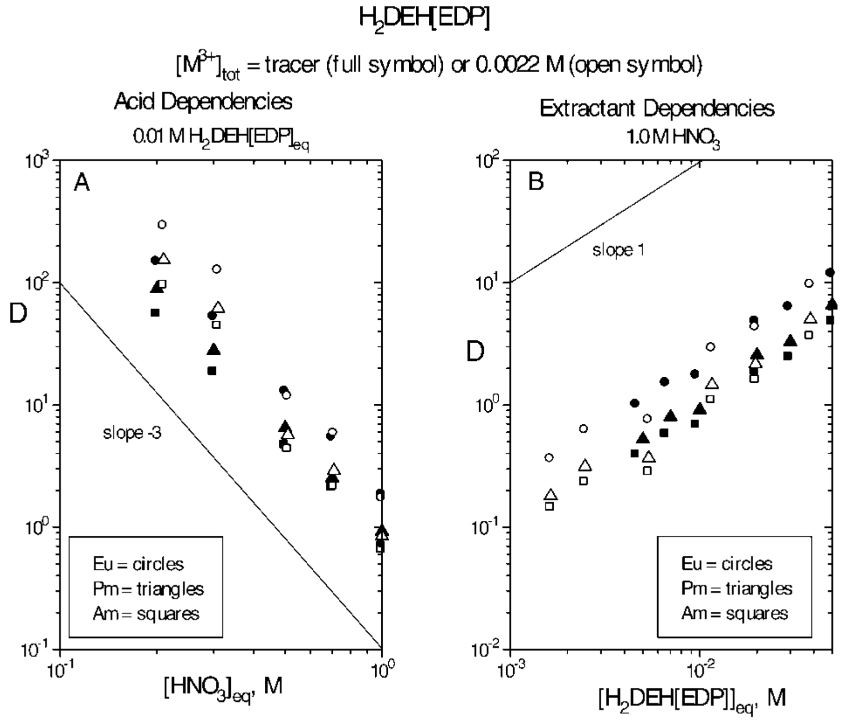


Figure 2. Extraction of Eu^{3+}, Pm^{3+}, and Am^{3+} by H_2DEH[EDP] in *o*-xylene from 1 M NO_3^- aqueous solutions. Full symbols: Tracer metal concentration level; empty symbols: 0.0022 M total lanthanide nitrate concentration. Panel A: Acid dependencies with D values normalized for 0.01 M H_2DEH[EDP] equilibrium concentration. Panel B: Extractant dependencies at 1.0 M HNO_3.

Figures 6, 7, and 8 show the extractant and acid dependency plots for H_2DEH[EDP] in *o*-xylene. The values of the slopes are also reported in Table 1.

For H_2DEH[EDP], the acid dependency slopes are −3, and the extractant dependency slopes are unequivocally equal to 1, confirming that for all cations extraction involves hexameric extractant aggregates.

Extraction Equilibrium Constants and Separation Factors

By considering, as an approximation, only the reaction of a cation with two H_2DEH[MDP] dimers, the extraction equilibrium can be written as

$$M^{3+} + 2\overline{(H_2A)}_2 \Longleftrightarrow \overline{M(HA)_3(H_2A)} + 3H^+ \qquad (1)$$

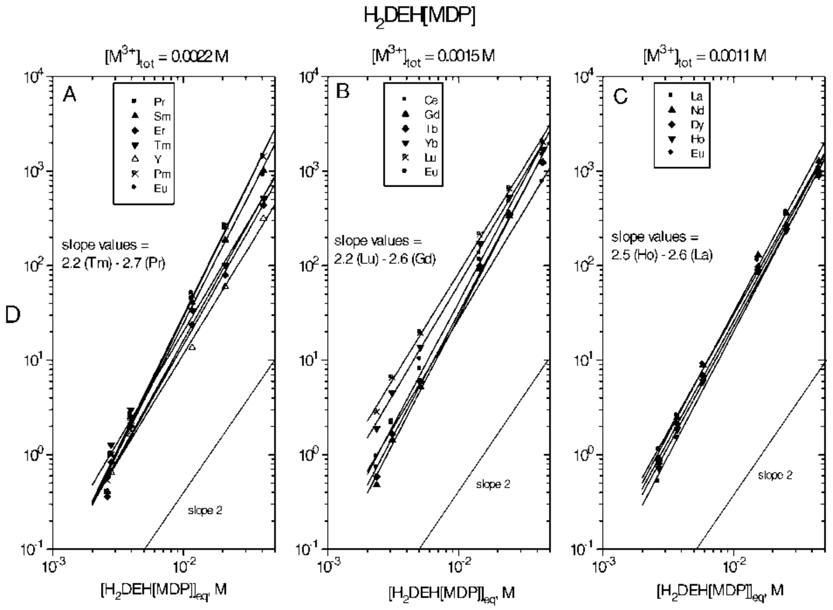


Figure 3. Extractant dependencies for lanthanide extraction by H_2DEH[MDP] in *o*-xylene at 1.0 M HNO_3 in the aqueous phase. Panels A, B, and C show data for lanthanides of groups I, II, and III, respectively.

(where the bar designates species in the organic phase, M^{3+} is a trivalent lanthanide or actinide ion, and H_2A represents H_2DEH[MDP]), with the equilibrium constant

$$K_{eq,MDP} = \frac{[\overline{M}]_{eq}[H^+]^3_{eq}}{[M^{3+}]_{eq}[(\overline{H_2A})_2]^2_{eq}} \qquad (2)$$

Ideal behavior is assumed for the species in the organic phase and the aqueous phase activity coefficients at constant ionic strength are included in the equilibrium constant.

Introducing in Eq. (2) the relations

$$[M]_{eq} = [M^{3+}]_{eq}(1 + \beta_1[NO_3^-]) \qquad (3)$$

$$D = \frac{[\overline{M}]_{eq}}{[M]_{eq}} \qquad (4)$$

$$D_0 = D(1 + \beta_1[NO_3^-]) \qquad (5)$$

where $[M]_{eq}$ represents the total aqueous metal concentration at equilibrium, $[M^{3+}]_{eq}$ is the concentration of the M^{3+} cation at equilibrium, D_0 is the

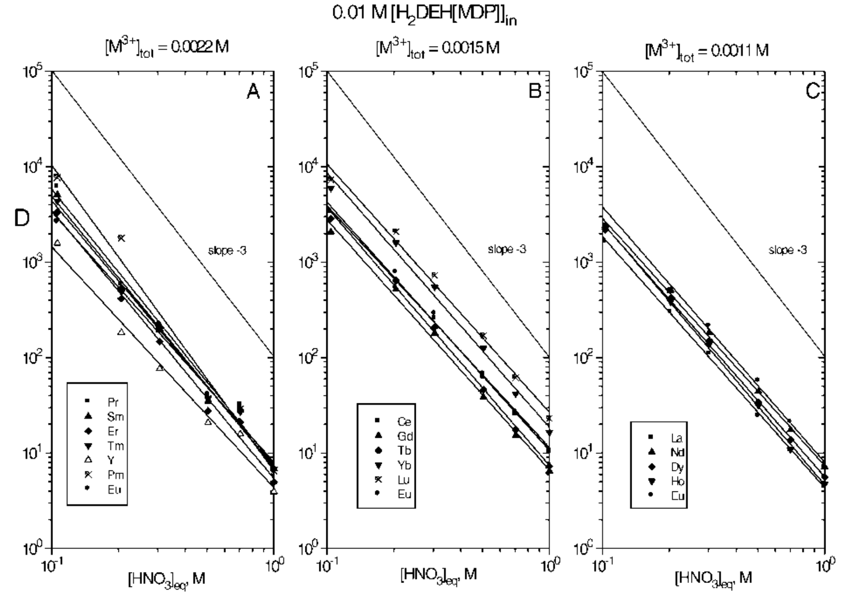


Figure 4. Acid dependencies for lanthanide extraction by 0.01-M $H_2DEH[MDP]$ in *o*-xylene from 1 M NO_3^- aqueous solutions. The D values were normalized for 0.005 M $H_2DEH[MDP]$ equilibrium concentration. Panels A, B, and C show data for lanthanides of groups I, II, and III, respectively.

distribution ratio corrected for the aqueous nitrate complexation, $[NO_3^-]$ is equal to one, and β_1 is the formation constant of aqueous phase nitrate complexes, one obtains

$$K_{eq,MDP} = D_0 \frac{[H^+]^3_{eq}}{[(\overline{H_2A})_2]^2_{eq}} \tag{6}$$

By further expressing the $H_2DEH[MDP]$ dimer concentration as $1/2C_{H_2A,eq}$, where $C_{H_2A,eq}$ is the $H_2DEH[MDP]$ equilibrium concentration, the expression for the equilibrium constant reduces to

$$K_{eq,MDP} = 4D_0 \frac{[H^+]^3_{eq}}{C^2_{H_2A,eq}} \tag{7}$$

Based on the slope analysis results, the extraction of trivalent lanthanides and actinides by $H_2DEH[EDP]$ can be written as

$$M^{3+} + (\overline{H_2A})_6 \Longleftrightarrow \overline{MH_9A_6} + 3H^+ \tag{8}$$

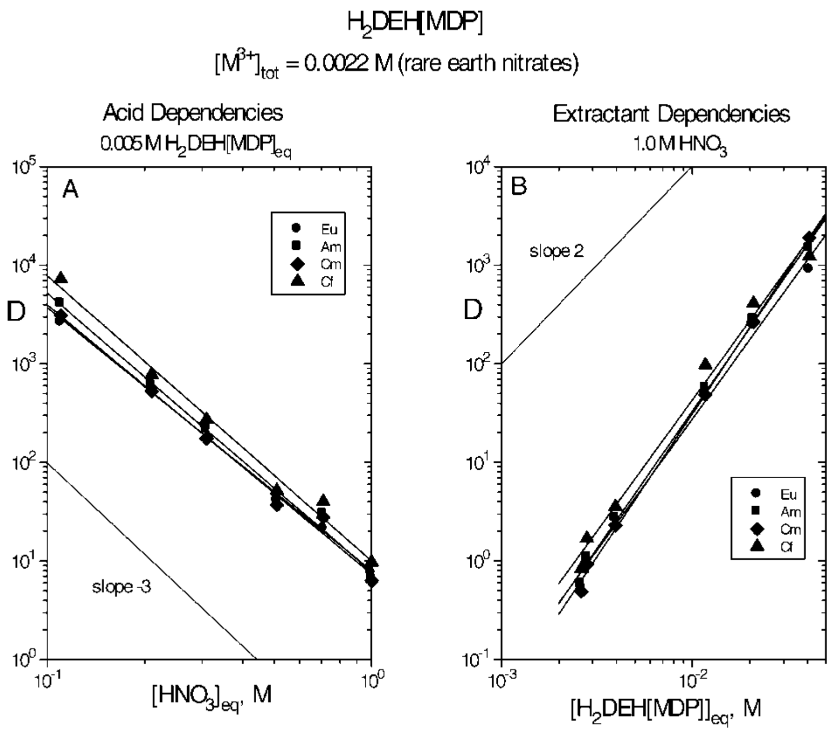


Figure 5. Acid and extractant dependencies for the extraction of Eu^{3+}, Am^{3+}, Cm^{3+}, and Cf^{3+} by H_2DEH[MDP] in *o*-xylene from 1 M NO_3^- aqueous solutions containing group I lanthanides at a total concentration of 0.0022 M. Panel A: Acid dependencies with D values normalized for 0.005 M H_2DEH[MDP] equilibrium concentration. Panel B: Extractant dependencies at 1.0 M HNO_3.

Following the reasoning used for H_2DEH[MDP], a similar expression for the equilibrium constant can be derived

$$K_{eq,EDP} = 6D_0 \frac{[H^+]^3_{eq}}{C_{H_2A,eq}} \tag{9}$$

where $C_{H_2\ A,eq}$ is the H_2DEH[EDP] equilibrium concentration.

The β_1 values for nitrate complexation of lanthanides and other cations used in Eqs. (7) and (9) were obtained from available sources (40). The values of the equilibrium constants calculated for *o*-xylene solutions of H_2DEH[MDP] and H_2DEH[EDP] are reported in Table 2.

Figure 9 shows a plot of the logarithm of $K_{eq,MDP}$ vs. the atomic number of the metal ions. In the figure, Y has been positioned at $Z = 68$, since the chemical properties of this cation most closely resemble those of holmium and erbium (2, 10).

Table 1. Acid and extractant dependencies for the extraction of lanthanides and trivalent actinides by H_2DEH[MDP] and H_2DEH[EDP] in *o*-xylene

Trivalent cation	H_2DEH[MDP] acid dependency	H_2DEH[MDP] extractant dependency	H_2DEH[EDP] acid dependency	H_2DEH[EDP] extractant dependency
La	-2.63 ± 0.04^{a}	2.63 ± 0.08	-2.71 ± 0.03	1.34 ± 0.05
Ce	-2.60 ± 0.06	2.51 ± 0.09	-2.78 ± 0.04	1.08 ± 0.10
Pr	-2.89 ± 0.18	2.72 ± 0.04	-3.08 ± 0.17	1.17 ± 0.12
Nd	-2.60 ± 0.05	2.58 ± 0.08	-2.71 ± 0.03	1.24 ± 0.05
Pm	-3.21 ± 0.24	2.75 ± 0.04	-3.30 ± 0.14	1.04 ± 0.10
Sm	-2.84 ± 0.16	2.65 ± 0.06	-3.13 ± 0.17	1.17 ± 0.12
Eu	-2.60 ± 0.09	2.36 ± 0.08	-3.15 ± 0.10	1.04 ± 0.04
Gd	-2.62 ± 0.09	2.58 ± 0.07	-2.79 ± 0.07	1.02 ± 0.07
Tb	-2.71 ± 0.07	2.53 ± 0.07	-2.71 ± 0.12	0.93 ± 0.07
Dy	-2.66 ± 0.04	2.53 ± 0.06	-2.50 ± 0.05	0.93 ± 0.05
Ho	-2.75 ± 0.05	2.53 ± 0.06	-2.73 ± 0.04	1.05 ± 0.05
Er	-2.81 ± 0.14	2.30 ± 0.03	-3.42 ± 0.16	0.91 ± 0.08
Tm	-2.79 ± 0.13	2.21 ± 0.04	-3.21 ± 0.24	0.94 ± 0.09
Yb	-2.67 ± 0.12	2.26 ± 0.07	-2.54 ± 0.09	0.90 ± 0.05
Lu	-2.60 ± 0.12	2.19 ± 0.07	-2.64 ± 0.07	0.95 ± 0.05
Y	-2.53 ± 0.15	2.26 ± 0.07	-3.45 ± 0.20	0.96 ± 0.09
Am	-2.82 ± 0.13	2.72 ± 0.04	-3.02 ± 0.18	1.02 ± 0.09
Cm	-2.73 ± 0.13	2.84 ± 0.03	-3.36 ± 0.15	1.03 ± 0.07
Cf	-2.89 ± 0.15	2.57 ± 0.13	-3.45 ± 0.15	0.95 ± 0.05

[a] Error interval provided by the linear fit of the distribution data (1σ).

The log $K_{eq,MDP}$ values in Fig. 9 have been tentatively grouped in four tetrads to emphasize that a tetrad effect may be present in the data, although obscured by the experimental uncertainties in the values of the equilibrium constants. However, the striking feature in Fig. 9 is the near complete lack of selectivity across the lanthanide series (and the limited actinide series) exhibited by H_2DEH[MDP]. This behavior is similar to that observed for the extraction of alkaline earth cations by H_2DEH[MDP] (32). For both series of trivalent and divalent cations, the highly stable complexes formed with the extractant are not sensitive to cation size.

Figure 10 shows a similar plot for H_2DEH[EDP]. This compound, although less efficient in extracting rare earths, exhibits a strong selectivity across the lanthanides with the selectivity being especially high for the heaviest members of the series.

The limited data available for the trivalent actinides are analogous to those for the lanthanides, with Cf^{3+} being significantly more extracted than Cm^{3+} and Am^{3+}. A tetrad effect is clearly visible in the data. The log $K_{eq,EDP}$ values in Fig. 10 span nearly three orders of magnitude. This makes

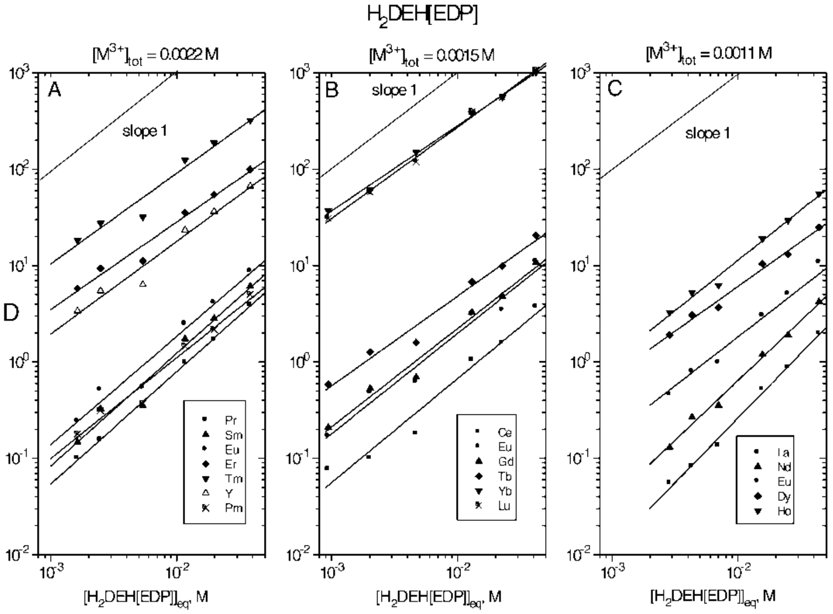


Figure 6. Extractant dependencies for lanthanide extraction by H_2DEH[EDP] in *o*-xylene at 1.0 M HNO_3 in the aqueous phase. Panels A, B, and C show data for lanthanides of groups I, II, and III, respectively.

H_2DEH[EDP] less intra-lanthanide selective than HDEHP, for which the equilibrium constants measured across the lanthanide series span about five orders of magnitude (16). However, the behavior of H_2DEH[EDP] is fully comparable to that of diprotic monofunctional organophosphorus acids, such as the 2-ethylhexyl phosphonic acid (H_2[EHP]) (15).

It is interesting to note that the behavior of H_2DEH[EDP] with lanthanides also parallels that observed with alkaline earth cations. In both cases, H_2DEH[EDP] exhibits a stronger affinity for cations with smaller ionic radii, consistent with the electrostatic nature of the metal-ligand interaction. The selectivity of H_2DEH[EDP] for Ca^{2+} over heavier alkaline earth cations was previously attributed to monofunctional behavior (35). The contrasting behavior of H_2DEH[EDP] and H_2DEH[MDP] with lanthanide cations gives further support to this hypothesis.

Because of the approximations involved in the calculations and the variation of nitrate complexation along the lanthanide series, the values of the equilibrium constants can only provide an estimate of the intralanthanide separation factors. In this respect, the actual values of the distribution ratios, experimentally measured under identical conditions, are more informative.

Figure 11 shows the experimental separation factor, defined as the ratio of the distribution ratio of a lanthanide ion to that of La^{3+} (D_Z/D_{La}) vs.

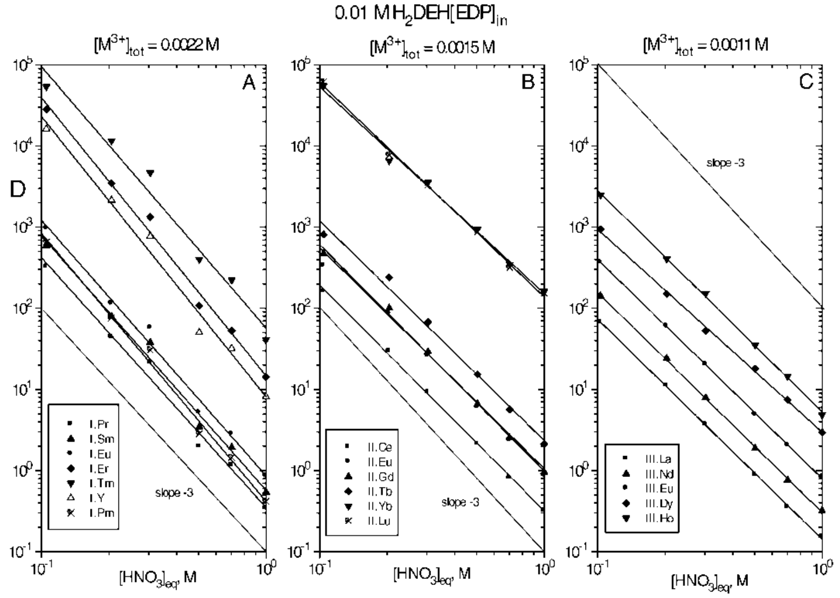


Figure 7. Acid dependencies for lanthanide extraction by 0.01 M $H_2DEH[EDP]$ in *o*-xylene from 1 M NO_3^- aqueous solutions. The D values were normalized for 0.005 M $H_2DEH[EDP]$ equilibrium concentration. Panels A, B, and C show data for lanthanides of groups I, II, and III, respectively.

lanthanide atomic number, for $H_2DEH[MDP]$ and $H_2DEH[EDP]$ under a particular set of experimental conditions.

From the figure, it appears that $H_2DEH[MDP]$ does not discriminate between lanthanides, with the exception of the heaviest members (Yb and Lu) over the lighter ones. Figure 11, on the other hand, shows that $H_2DEH[EDP]$ is much more selective. The selectivity of $H_2DEH[EDP]$ for the heavier over lighter lanthanides, for Y over light lanthanides, and for Cf over Am and Cm is remarkable. The average separation factor between adjacent lanthanides is 1.8. This value, although less than the value reported for HDEHP (10, 11, 16) is still more than adequate to make $H_2DEH[EDP]$ a plausible candidate for intralanthanide separations of practical importance.

Effect of Extractant Aggregation on Selectivity

Since $H_2DEH[MDP]$ and $H_2DEH[EDP]$ have different aggregation behaviors in *o*-xylene, the hypothesis could be formulated that the different extraction behaviors with lanthanides may be related to the aggregation state. To

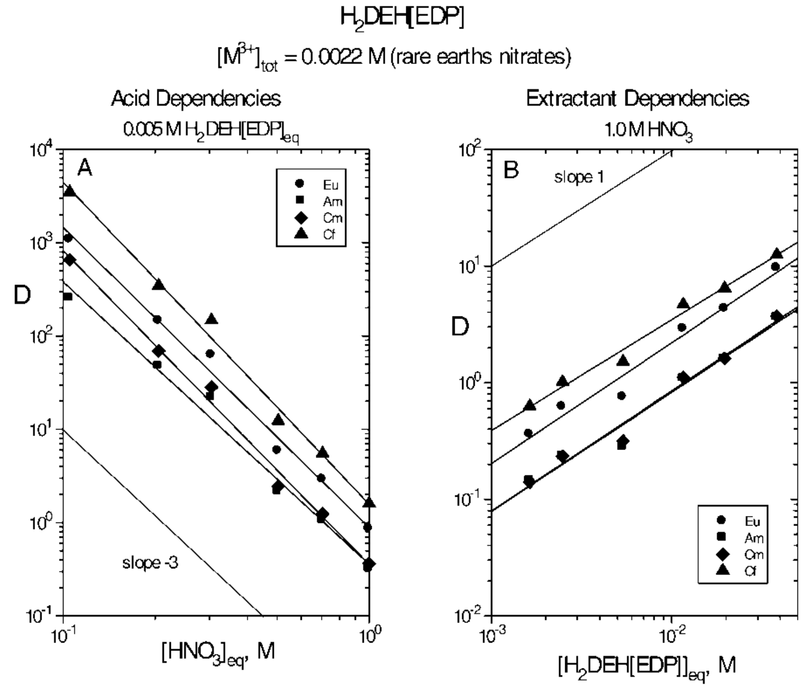


Figure 8. Acid and extractant dependencies for the extraction of Eu^{3+}, Am^{3+}, Cm^{3+}, and Cf^{3+} by $H_2DEH[EDP]$ in *o*-xylene from 1 M NO_3^- aqueous solutions containing group I lanthanides at a total concentration of 0.0022 M. Panel A: Acid dependencies with D values normalized for 0.005 M $H_2DEH[EDP]$ equilibrium concentration. Panel B: Extractant dependencies at 1.0 M HNO_3.

clarify this point, extraction experiments involving a selected number of lanthanides (those in Group I) were performed under conditions identical to those described above, with $H_2DEH[MDP]$ and $H_2DEH[EDP]$ dissolved in 1-decanol. As previously reported (41), both extractants are monomeric in this diluent. As expected, the acid and extraction dependencies obtained were -3 and 3, respectively (data not shown for brevity).

This indicates that the following alternative equilibria, previously identified for Am^{3+} extraction by $H_2DEH[MDP]$ and $H_2DEH[EDP]$ in 1-decanol (39), apply for the lanthanide cations as well

$$M^{3+} + 3\overline{H_2A} \Longleftrightarrow \overline{MA(HA)\cdot H_2A} + 3H^{+} \tag{10}$$

$$M^{3+} + 3\overline{H_2A} \Longleftrightarrow \overline{M(HA)_3} + 3H^{+} \tag{11}$$

where M^{3+} indicates a trivalent lanthanide cation, and H_2A represents the diphosphonic acid. Equilibria 10 and 11 are stoichiometrically identical but

Table 2. Equilibrium constants for the extraction of lanthanides and trivalent actinides by H_2DEH[MDP] and H_2DEH[EDP] in *o*-xylene

Trivalent cation	β_1 [40]	Log $K_{eq,MDP}$	Log $K_{eq,EDP}$
La	1.3	6.10 ± 0.20[a]	2.46 ± 0.14
Ce	1.6	6.41 ± 0.17	2.96 ± 0.13
Pr	1.6	6.34 ± 0.25	3.02 ± 0.19
Nd	2.0	6.37 ± 0.15	2.99 ± 0.14
Pm	2.0	6.30 ± 0.21	3.30 ± 0.12
Sm	2.0	6.33 ± 0.29	3.35 ± 0.14
Eu	2.0	6.43 ± 0.20	3.46 ± 0.10
Gd	1.0	6.24 ± 0.20	3.35 ± 0.11
Tb	1.1	6.32 ± 0.20	3.72 ± 0.14
Dy	0.50	6.20 ± 0.20	3.62 ± 0.18
Ho	0.63	6.10 ± 0.20	3.97 ± 0.11
Er	0.50	5.90 ± 0.19	4.51 ± 0.18
Tm	0.56	6.15 ± 0.15	5.03 ± 0.18
Yb	0.63	6.57 ± 0.16	5.38 ± 0.15
Lu	0.63	6.69 ± 0.15	5.36 ± 0.12
Y	0.63	5.81 ± 0.19	4.32 ± 0.18
Am	1.8	6.35 ± 0.20	3.12 ± 0.11
Cm	2.2	6.34 ± 0.20	3.25 ± 0.13
Cf	2.5	6.60 ± 0.29	3.94 ± 0.16

[a] Error interval given by the semidispersion of the log K_{eq} values calculated for each experimental point.

imply different structures for the metal species extracted into the organic phase (39).

It is easy to demonstrate, following a procedure similar to that used for Eqs. (7) and (9), that the equilibrium constant for equilibria 10 and 11 can be written as

$$K_{eq} = D_0 \frac{[H^+]^3_{eq}}{[\overline{H_2A}]^3_{eq}} \tag{12}$$

The logarithmic values of the equilibrium constants for the extraction of the Group I lanthanide cations by H_2DEH[MDP] and H_2DEH[EDP] in 1-decanol, calculated from the extraction data, are plotted vs. the atomic numbers in Fig. 12.

The data confirm the lack of selectivity for H_2DEH[MDP] and a strong selectivity for H_2DEH[EDP]. The similar behavior of the two extractants in *o*-xylene and 1-decanol unequivocally supports the conclusion that the intra-lanthanide selectivity exhibited by H_2DEH[EDP] is a result of the pronounced monofunctional behavior of this extractant and not a result of the different aggregation behavior of the two extractants in aromatic diluents.

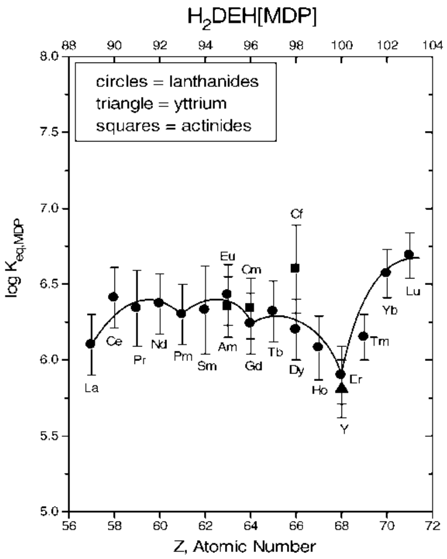


Figure 9. Logarithmic values of the equilibrium constants for the extraction of trivalent lanthanides and actinides by H_2DEH[MDP] in *o*-xylene plotted vs. the atomic number, Z.

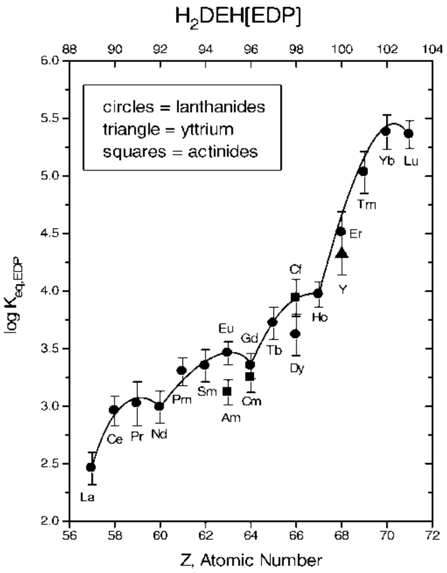


Figure 10. Logarithmic values of the equilibrium constants for the extraction of trivalent lanthanides and actinides by H_2DEH[EDP] in *o*-xylene plotted vs. the atomic number, Z.

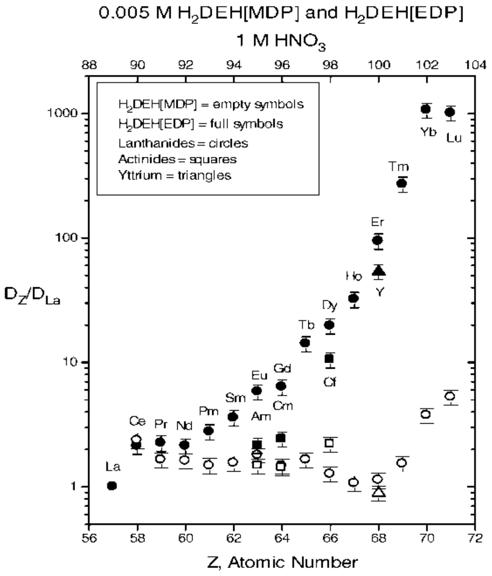


Figure 11. Separation factors, defined as D_Z/D_{La}, vs. the atomic number, Z, for the extraction of trivalent lanthanides and actinides at 0.005 M H_2DEH[MDP] and H_2DEH[EDP] in *o*-xylene from 1 M aqueous HNO_3.

CONCLUSIONS

In this work, the extraction of lanthanum, all members of the lanthanide series (plus yttrium), as well as Am(III), Cm(III), and Cf(III) by P,P′-di(2-ethylhexyl) methylenediphosphonic acid (H_2DEH[MDP]) and P,P′-di(2-ethylhexyl) ethylenediphosphonic acid (H_2DEH[EDP]) in *o*-xylene has been investigated. Extraction by H_2DEH[MDP] involves primarily the formation of organic phase complexes, where one trivalent cation is bound to two extractant dimers. At high metal loading, however, the formation of complexes where one cation is bound to three extractant monomers is also possible. Extraction of lanthanide cations by H_2DEH[EDP] involves the formation of organic phase complexes containing a single hexameric extractant aggregate.

H_2DEH[MDP] shows very efficient extraction of all ions investigated but little selectivity, except for the heaviest lanthanides. H_2DEH[EDP], in contrast, exhibits less efficient extraction but much higher selectivity, with an average separation factor between contiguous elements equal to 1.8, and extraction equilibrium constants spanning about three orders of magnitude along the lanthanide series. For H_2DEH[EDP], the extraction data also exhibit a significant tetrad effect.

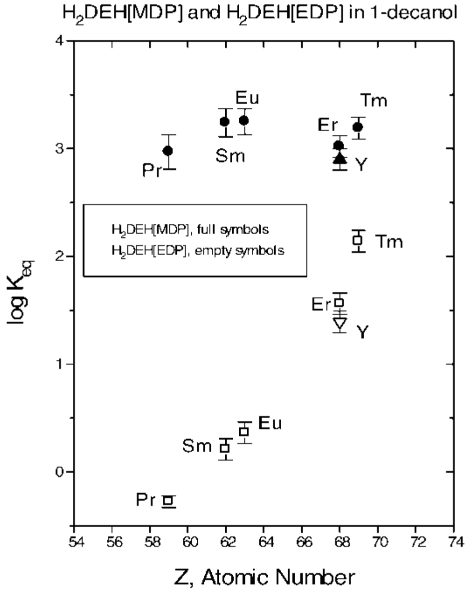


Figure 12. Logarithmic values of the equilibrium constants for the extraction of selected lanthanide cations by H_2DEH[MDP] and H_2DEH[EDP] in 1-decanol plotted vs. atomic number, Z.

Compared to H_2DEH[MDP], the decreased efficiency of H_2DEH[EDP] as a lanthanide extractant stems from the larger and considerably less stable rings formed by H_2DEH[EDP] upon metal coordination. The selectivity exhibited by H_2DEH[EDP] is a further manifestation of this phenomenon.

It is remarkable that the addition of a single methylene group in the alkylene bridge connecting the phosphorus atoms of H_2DEH[MDP] causes an abrupt transition from a powerful but unselective extractant to a less powerful but very selective one. Thus, H_2DEH[MDP] can be used as a general extractant when the separation of an entire class of metal ions, for example actinides or lanthanides, is desired. H_2DEH[EDP], on the other hand, is a better reagent for those cases where a selective separation is required.

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