Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Horwitz, E. Philip , McAlister, Daniel R. and Dietz, Mark L.(2006) 'Extraction Chromatography Versus Solvent Extraction: How Similar are They?', Separation Science and Technology, 41: 10, 2163 — 2182
To link to this Article: DOI: 10.1080/01496390600742849
URL: http://dx.doi.org/10.1080/01496390600742849

Separation Science and Technology, 41: 2163–2182, 2006
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ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600742849

Extraction Chromatography Versus Solvent Extraction: How Similar are They?

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Abstract: Over the last decade, extraction chromatography (EXC) has emerged as a versatile and effective method for the separation and preconcentration of a number of metal ions. Frequently, EXC is described as a technique that combines the selectivity of solvent extraction (SX) with the ease of operation of chromatographic methods. Despite this, the extent to which EXC actually provides the selectivity of SX and to which solvent extraction data can be used for the quantitative prediction of the retention of metal ions on an EXC column has remained unclear. To address these questions, the extraction chromatographic and solvent extraction behavior of lanthanides using three different acidic organophosphorus extractants *bis*-(2-ethylhexyl) phosphoric acid (HDEHP), 2-ethylhexyl 2-ethylhexylphosphonic acid (HEH[EHP]), and *bis*-(2,4,4 trimethylpentyl)phosphinic acid (H[DTMPeP])) have been compared. Specifically, the rate and extent of uptake of selected lanthanides by the three extractants have been examined. In addition, the relationship between the volume distribution ratios obtained in the chromatographic and liquid–liquid extraction modes have been compared and their utility in predicting the chromatographic parameter, k′, the number of free column volumes to peak maximum determined.

Keywords: Solvent extraction, extraction chromatography, lanthanide separations

Received 23 October 2005, Accepted 16 March 2006

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INTRODUCTION

In recent years, extraction chromatography (EXC) has played an increasingly prominent role in radiochemical analysis, providing a facile means for the separation and preconcentration of any of a number of radionuclides, particularly actinides and selected fission products, from a wide variety of sample matrices for subsequent determination (1). Extraction chromatography has also found increasing use in the separation and purification of isotopes for use in nuclear medicine (e.g. ^{90}Y and ^{177}Lu) (2–4). Frequently, EXC is described as a technique that combines the selectivity of solvent extraction (SX) with the ease of operation of chromatographic methods. Although the general relationship between EXC and SX is well established (5), certain fundamental aspects of EXC and its relation to SX remain only incompletely understood. Among the more important of these are the extent to which the properties and behavior of an extractant dispersed on a solid support mimic those of the corresponding "free" extractant and the extent to which SX data can be used to predict quantitatively the retention of metal ions or anionic complexes on an EXC column.

Early studies, a number of which have been summarized by Akaza (6), would appear to have settled the latter question. Typical of these is the work of Pierce et al. (7, 8), in which the separation of lanthanides on a column comprising *bis*-(2-ethylhexyl) phosphoric acid (HDEHP) sorbed on a poly-(vinyl chloride/vinyl acetate) copolymer ("Corvic") was compared to their extraction from perchloric or hydrochloric acid into toluene. In all cases, metal ion retention on the column exhibited a near inverse third power acid dependency, consistent with results observed in the liquid–liquid system. In addition, separation factors for adjacent lanthanides on the HDEHP-loaded Corvic columns, while not identical to those observed in the liquid–liquid system, were (on average) in good agreement. Along these same lines, Akaza et al. (9), in an evaluation of the utility of polytrifluorochloroethylene-supported tri-*n*-butyl phosphate (TBP) in the separation of noble metals (i.e., gold, platinum (IV), and palladium) in hydrochloric acid, observed a strong similarity between the behavior of the metal ions in column and batch (liquid–liquid) extraction experiments. The dependence of D_{Pt} on the concentration of TBP in benzene, for example, was found to be virtually superimposable on the dependency obtained when the TBP-benzene solution was used as the chromatographic stationary phase. In related work, Sebesta (10) showed that the behavior of an extraction chromatographic column consisting of a carbon tetrachloride solution of dithizone sorbed on hydrophobized Celite was analogous to the corresponding SX system. The analogy was then applied to the separation of several pairs of cations (e.g., Zn-Cd, Ag-Hg, Cd-Ag) on a dithizone-Celite column (11).

Although such results suggest that the behavior of an extraction chromatographic system can be readily predicted from SX extraction data, more recent studies call this notion into question and in fact, suggest that the extent to which these data are predictive of EXC behavior will depend on the support chosen. For example, in an examination of the extraction of zinc, copper, and cadmium by HDEHP supported on the macroporous polymer Amberlite XAD-2, Cortina et al. (12) obtained distribution data (modeled using LETAGROP-DISTR) indicating that the extracted species are less solvated than in typical organic solvents and that a selectivity reversal between Cu and Cd occurs. Cortina proposed that it might be possible to systematically vary the separation factor(s) obtainable for a particular extractant by changing the nature of the support employed. Subsequent studies by Strikovsky et al. (13) of the extraction of Cu(II) from chloride media by the sulfur analog of HDEHP, *bis*-(2-ethylhexyl)dithiophosphoric acid (DEHTPA), have also revealed differences between extraction results obtained in solution and on a polymeric support (Amberlite XAD-2).

It is important to note here that over the last two decades, high surface-area macroporous polymers such as the Amberlite XAD-2 employed in these more recent studies have largely supplanted "classical" materials such as diatomaceous earth, silanized silica gel, and fluorocarbon polymers as supports for extraction chromatography (5). Thus, it is the relationship between SX data and the behavior of EXC materials employing these newer supports that is most relevant to the contemporary practice of extraction chromatography. With this in mind, we have undertaken a systematic examination of the behavior of lanthanide ions on a series of extraction chromatographic materials comprising three different acidic organophosphorus extractants *bis*-(2-ethylhexyl) phosphoric acid (HDEHP), 2-ethylhexyl 2-ethylhexylphosphonic acid (HEH[EHP]), and bis-(2,4,4-trimethylpentyl)-phosphinic acid (H[DTMPeP]) sorbed on Amberchrom CG-71, an aliphatic acrylic polymer. Of particular interest in our studies is the extent to which the results of SX experiments, employing either the undiluted extractants or their solutions in dodecane, are useful in understanding and predicting the performance of the EXC resins with respect to inter-lanthanide selectivity and the column retention parameters.

EXPERIMENTAL

Reagents

Nitric and sulfuric acid solutions were prepared from Trace Metal Grade acids (Fisher Scientific) using deionized water obtained from a Milli-Q2 water purification system. Metal ion solutions were prepared using single element atomic absorption standard solutions of 1,000 or 10,000 ppm metal ion in 2% (v:v) nitric acid (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc) (Fisher Scientific). ^{147}Pm was obtained from Isotope Product Laboratories. Dodecane (Reagent Plus, >99%), toluene (HPLC, >99.7%), diiodomethane (Reagent Plus, 99%) and methanol (HPLC, >99.9%) were obtained from Sigma-Aldrich.

Resin Preparation

The EXC materials were prepared from bis(2-ethyl-1-hexyl)phosphoric acid (HDEHP, Sigma-Aldrich), 2-ethylhexyl 2-ethylhexylphosphonic acid (HEH[EHP], Albright and Wilson) or bis(2,4,4-trimethyl-1-pentyl)phosphinic acid (H[DMTPeP], Cytec) on Amberchrom CG71 (25–53 μm, polymethacrylate, Eichrom Technologies, Inc.). The HDEHP, HEH[EHP] and H[DMTPeP] were purified by the third phase formation procedure (14) prior to production of the EXC materials. In a typical preparation, 10 grams of purified extractant were dissolved in 100 mL of methanol and mixed with 15 grams of substrate and then stirred for 1 h on a rotary evaporator. The methanol was removed by applying a vacuum and heating the mixture to 50°C using a water bath to yield a free flowing material comprising 40% (w:w) of extractant on the substrate.

Procedures

Determination of Weight Distribution Ratios (D_w) and Column Capacity Factors (k')

The uptake of metal ions by the EXC materials from acidic solutions was measured by contacting a known volume of solution (5.0 to 7.5 mL) with a known mass of resin (100–300 mg) in a borosilicate glass culture tube as described previously (15). Following equilibration with the resin, the aqueous phase was passed through a 0.45 μm PTFE filter to remove any resin particles. Metal ion concentrations were determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) on a Varian Liberty Series II sequential inductively coupled plasma atomic emission spectrometer using the parameters listed in Table 1. ^{147}Pm was determined using a Packard TriCarb 2550 TR/AB liquid scintillation Counter and Ultima Gold scintillation cocktail.

For the nitric acid dependencies of lanthanide uptake, five stock solutions were prepared containing 20 ppm each of 3–5 adjacent lanthanides (Table 1). Each stock solution contained a metal ion in common with the preceding and following solution, so that accurate separation factors could be measured for the entire series of lanthanides, yttrium and scandium. Duplicate measurements for the same metal ions in different stock solutions agreed within 10%, so no corrections were applied to the acid dependency data. An equilibration time of one hour was used in all determinations of weight distribution ratios, except for data generated on the kinetics of uptake by the EXC materials, where equilibration times were varied from 1–360 min.

Table 1. Metal ion determination by ICP-AES

Analyte	Peak (nm)	Window (nm)	Stock solution
La	333.749	0.060	1
Ce	413.380	0.060	1
Pr	422.533	0.060	1
Nd	401.225	0.060	1
Nd	401.225	0.080	2
Pm	N/A	N/A	2
Sm	359.262	0.080	2
Eu	381.967	0.080	2
Gd	342.247	0.080	2
Gd	342.247	0.080	3
Tb	350.917	0.080	3
Dy	353.170	0.080	3
Dy	353.170	0.080	4
Ho	345.600	0.080	4
Er	337.276	0.080	4
Y	371.030	0.080	4
Tm	313.126	0.040	4
Tm	313.126	0.060	5
Yb	328.937	0.060	5
Lu	261.542	0.060	5
Sc	361.384	0.060	5

Intefration time: 3.0 sec; Sample uptake delay: 30 sec; Replicates: 3; Pump rate: 15 rpm; Power: 1 kW; Instrument stabilization: 15 sec; Vieqing height: 10 mm; Rinse time: 30 sec.

Weight distribution ratios (D_w) were calculated using the following equation:

$$D_w = ((A_o - A_s)/w)/(A_s/V) \tag{1}$$

where A_o and A_s are the aqueous phase metal ion concentrations (ppm) before and after equilibration, w is the weight of the resin in grams and V is the volume of aqueous phase in milliliters. Duplicate experiments showed that the reproducibility of the D_w measurements is generally within 10%, although the uncertainty is somewhat higher for the highest D_w values ($>10^3$). The weight distribution ratios were converted to the number of free column volumes to peak maximum, k' (the resin capacity factor), by first calculating the volume distribution ratio, D_v, using the following equation:

$$D_v = D_w \cdot d_{extr}/0.4 \tag{2}$$

where d_{extr} is the density of the extractant and 0.4 is the extractant loading in grams of extractant per gram of resin. The D_v values were then converted to k'

Table 2. Physical constants of slurry-packed columns

	Amberchrom CG71			
	HDEHP	HEH[EHP]	H[DTMPeP]	Uncoated
Extractant density (g/mL)	0.96	0.91	0.89	N/A
Bed density (g/mL)	0.38	0.37	0.39	0.33
Resin density (g/mL)	1.15	1.13	1.13	1.28
v_s	0.16	0.16	0.18	N/A
v_m	0.67	0.67	0.66	0.74
v_s/v_m	0.24	0.24	0.27	N/A
D_v conversion factor $(C_1)^a$	0.239	2.27	2.22	N/A
k′ conversion factor$(C_2)^b$	0.57	0.55	0.60	N/A

[a] $D_v = D_w \times C_1$.
[b] $k' = D_w \times C_2$.

by using the following equation:

$$k' = D_v \cdot (v_s/v_m) \qquad (3)$$

where v_s and v_m are the volumes of stationary phase (extractant) and mobile phase, respectively, for slurry packed columns of the EXC materials. The physical constants necessary to convert D_w to k′ for slurry packed columns of the EXC materials are listed in Table 2. By combining equations (2) and (3) and using the values reported in Table 2 for d_{extr} and v_s/v_m, one obtains:

$$k' = D_w \cdot (d_{extr} \cdot v_s)/(0.4 \cdot v_m) \qquad (4)$$

The bed densities of the EXC materials were measured by slurry packing a known mass of resin into a graduated cylinder and dividing the mass of resin by the volume of the bed. The picnometric densities (resin densities) of the EXC materials were determined by achieving neutral buoyancy in solutions of known density. For densities between 0.95 and 1.00 g/mL, solutions of methanol in water were used. For densities between 1.00 and 1.30 g/mL, nitric acid solutions were used.

Determination of Liquid–Liquid Distribution Ratios (D)

Liquid–liquid distribution ratios were determined by contacting 0.50–1.0 mL of an organic phase containing HDEHP, HEH[EHP] or H[DTMPeP], either neat or 0.50 M in dodecane, with 5.0–7.5 mL of an aqueous phase containing the metal ion(s) of interest for ten minutes using a vortex mixer. Prior to use, the organic phases were twice preconditioned with aqueous phase without metals ions. Following equilibration, the phases were separated by centrifugation and aliquots taken for analysis by ICP-AES or liquid scintillation counting. The acid dependencies of the uptake of lanthanides, yttrium and scandium were determined using the same five stock solutions listed in Table 1.

Column Elution of Metal Ions

The column elution behavior of selected lanthanide ions was determined using the procedure and equipment detailed previously (4). The number of free column volumes to peak maximum, k′, was calculated by dividing the position of the peak maxima, in bed volumes, by the void volume (the volume of the mobile phase, v_m, Table 2) and subtracting one void volume (16).

RESULTS AND DISCUSSION

Kinetics of Lanthanide Uptake

Figure 1 depicts the time dependence of the uptake of various lanthanide ions from aqueous nitric acid by the three EXC resins. In an effort to keep all equilibrium k′ values in the range 100–200, different pairs of Ln(III) ions were used for each resin. The separation factor, α, is the ratio of k′s for the lanthanides. As can be seen, in all cases, sorption equilibrium is rapidly achieved, a result consistent with the behavior of a number of other EXC resins employing various other extractants (1, 15). The rapid attainment of equilibrium for 4*f* elements with most EXC systems may be explained by the rapid interfacial mass transfer of the metal ion across the aqueous/organic interface (17). Because metal ion extractants are interfacially active, the hydrophilic portion of the extractant is ideally positioned to complex metal ions that diffuse to the aqueous/organic interface. On the basis of these results, a 1 hour equilibration time was chosen for all subsequent measurements.

Nitric Acid Dependencies

Figure 2 depicts the nitric acid dependency of k′ for the entire lanthanide series and yttrium on the three EXC resins, while Figs. 3 and 4 show the analogous nitric acid dependencies of the liquid–liquid distribution ratios for 0.5 M solutions of the three extractants in dodecane and for the undiluted extractants, respectively. As can been seen, both the k′ and D values for the HDEHP systems are significantly (30×) higher than the corresponding values for the HEH[EHP] systems. The HEH[EHP] systems, in turn, exhibit k′ and D values three orders of magnitude higher than the corresponding values in the H[DTMPeP] systems. The added steric hindrance, as well as the reduced acidity of the phosphinic acid, are most likely responsible for this significant difference.

For the liquid–liquid systems, both HDEHP and HEH[EHP] show the expected inverse third power dependency (4, 18, 19). The k′ data for the

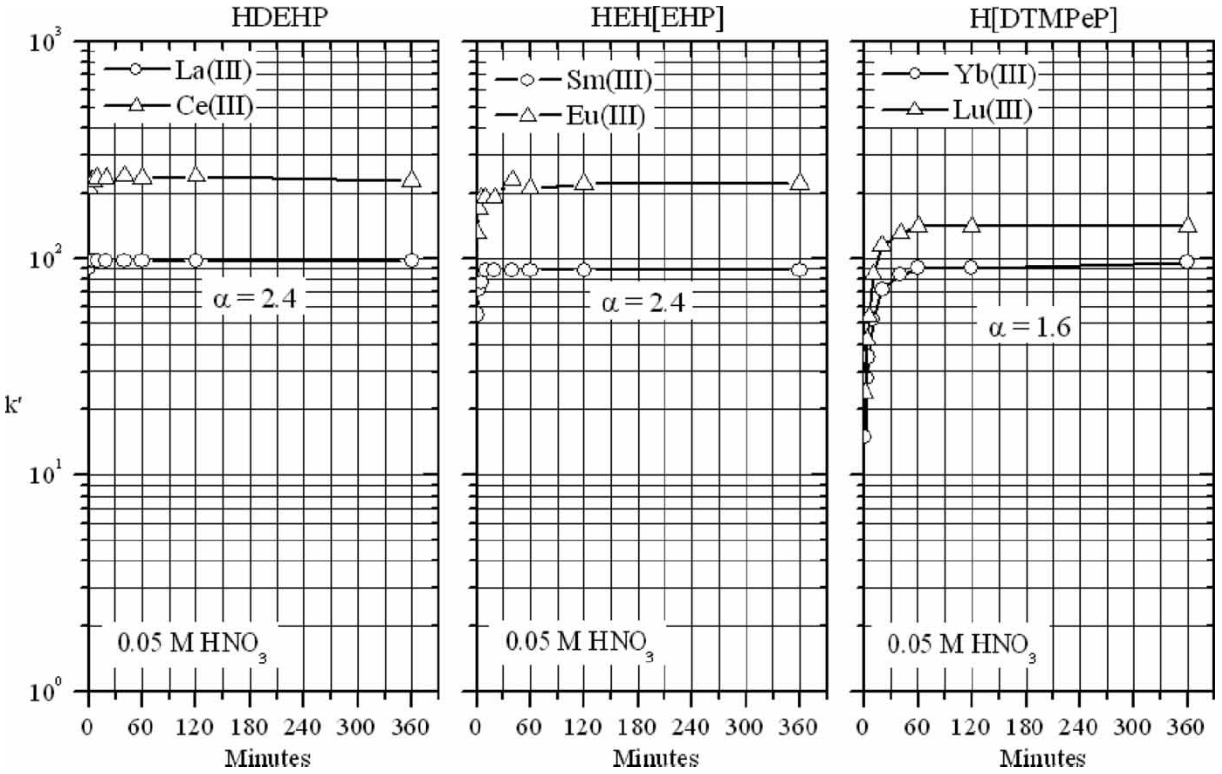

Figure 1. Comparison of the rate of uptake of La(III) and Ce(III), Sm(III) and Eu(III) or Yb(III) and Lu(III) from 0.05 M HNO_3 on HDEHP, HEH[EHP] and H[DTMPeP] EXC resins, respectively, 40% (w:w) extractant loading on Amberchrom CG-71, 25-53 μm, 22(1)°C.

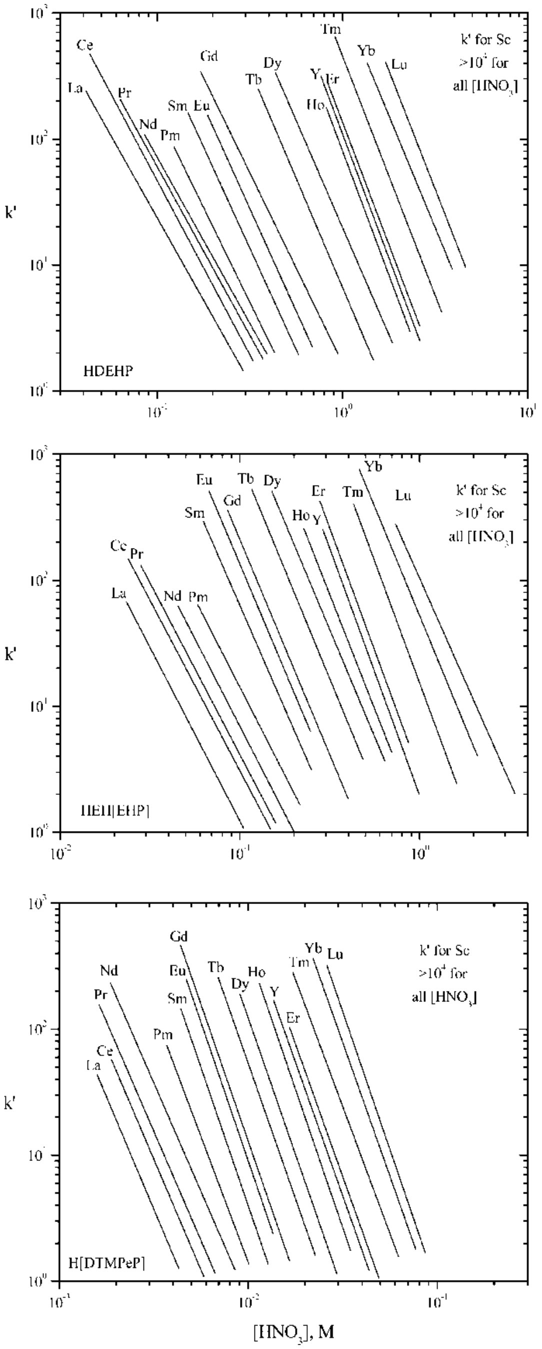

Figure 2. Nitric acid dependencies of k′ for trivalent lanthanides and yttrium on LN resin series.

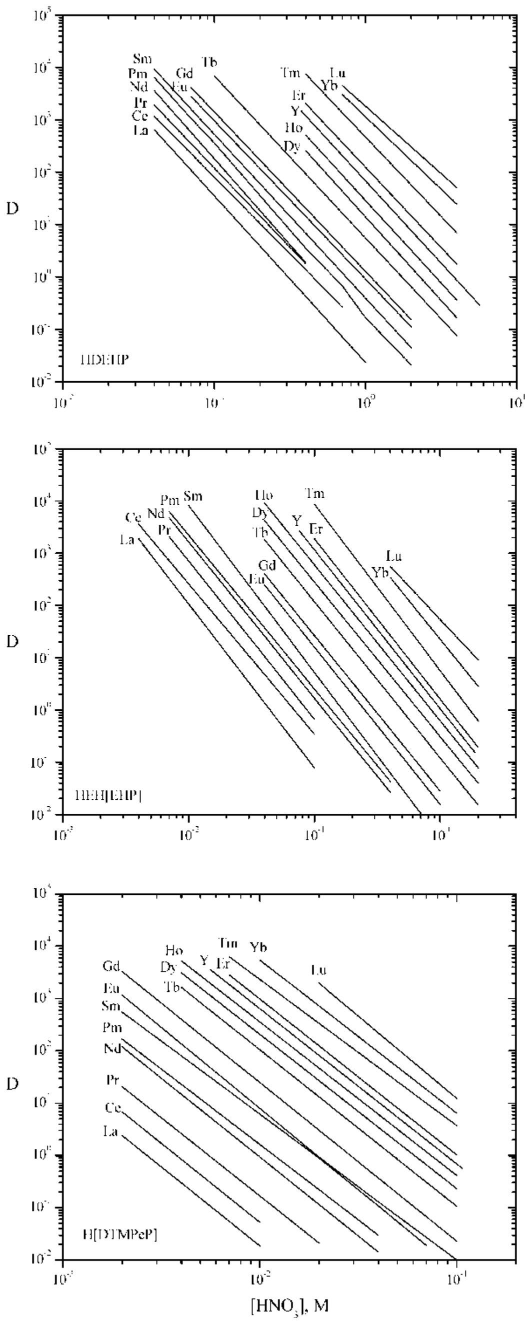

Figure 3. Nitric acid dependencies of the distribution ratios (D) of trivalent lanthanides and yttrium for 0.50 M solutions of HDEHP, HEH[EHP] and H[DTMPeP] in dodecane.

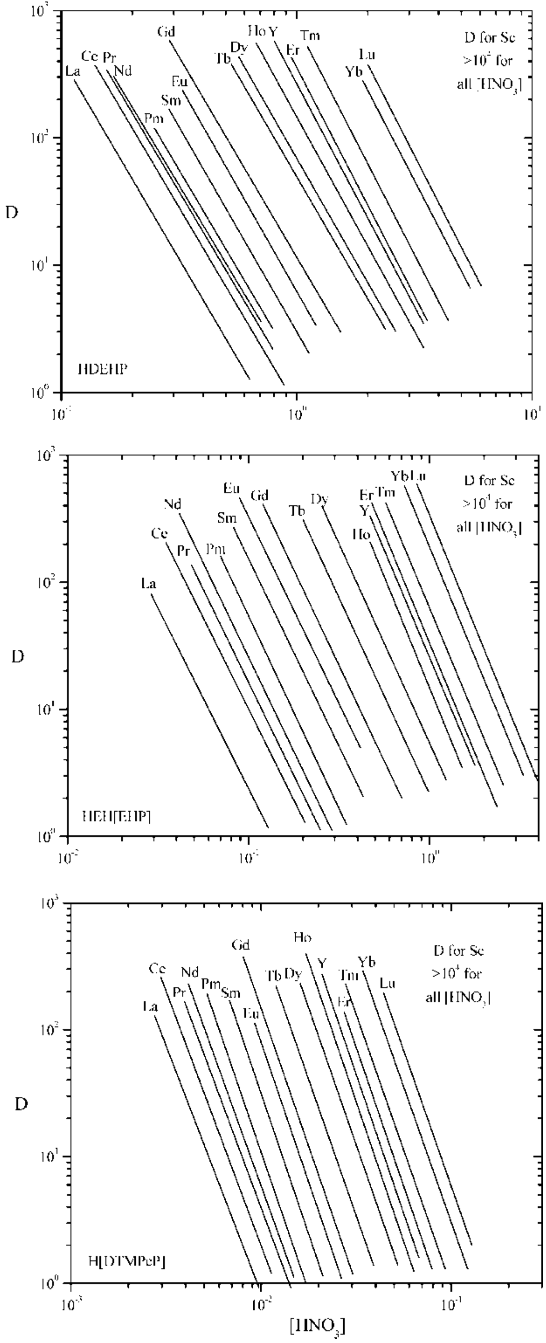

Figure 4. Nitric acid dependencies of the distribution ratios (D) of trivalent lanthanides and yttrium for neat HDEHP, HEH[EHP] and H[DTMPeP].

EXC resins prepared with these same extractants, however, exhibit increasingly negative slopes ranging from -2.7 to -3.5, as the atomic number of the lanthanide ion increases. The nitric acid dependency data for the H[DTMPeP] systems also show significant deviation from the expected negative third power dependency. Except in the case of the dodecane system, slopes of -4 are consistent throughout the lanthanide series for both the EXC and neat extractant systems. A partial explanation for these observations may be differences in the co-extraction of nitric acid. That is the phosphinic acid is a weaker acid and the basicity of the phosphoryl oxygen in the phosphinate extractant is higher than in the phosphate or phosphonate molecules. The H[DTMPeP] molecule would thus be expected to exhibit a greater tendency to behave as a neutral extractant, one more likely to extract nitric acid from the aqueous phase. This explanation cannot, of course, account for the differences observed between the EXC and SX data for HDEHP and HEH[EHP]. The origins of these differences, in fact, remain unclear at present.

Comparison of Selectivities of EXC and SX Systems

If EXC is essentially an SX system operated in a chromatographic mode, one would expect that the metal ion extraction/retention selectivities of the two systems to be very similar, if not identical. Figure 5 depicts the selectivities of the EXC resins and the two SX systems comprising each of the three extractants for the entire series of lanthanides. The data points were normalized to a value of one for La extraction with HEH[EHP]. (Data for Y are not shown because of crowding. However, Y lies between Ho and Er in all cases and agrees with the lanthanides with respect to the similarity of SX and EXC systems.) The data for HDEHP is consistent with that reported previously (8, and references therein). The similarity in selectivity for the three systems is noteworthy, particularly given the discrepancies between the acid dependencies in the EXC and SX systems noted above. Only in the case of the neat extractants with the heavy lanthanides is there significant deviation in selectivity between the EXC and SX systems. These results strongly support the notion that the coordination of the extractant in the first coordination sphere of the lanthanide is similar for the SX and EXC systems.

Comparison of k′ Calculated from D_w and Elution Curves

Equations 1–4 show the relationship between the dry weight distribution ratio, D_w, and the capacity factor, k′. These equations enable one to calculate the number of free column volumes to peak maximum, k′, by simply measuring D_w, v_s and v_m. All of these parameters are easily measured and, in principle, should enable one to accurately predict the optimum acidity of

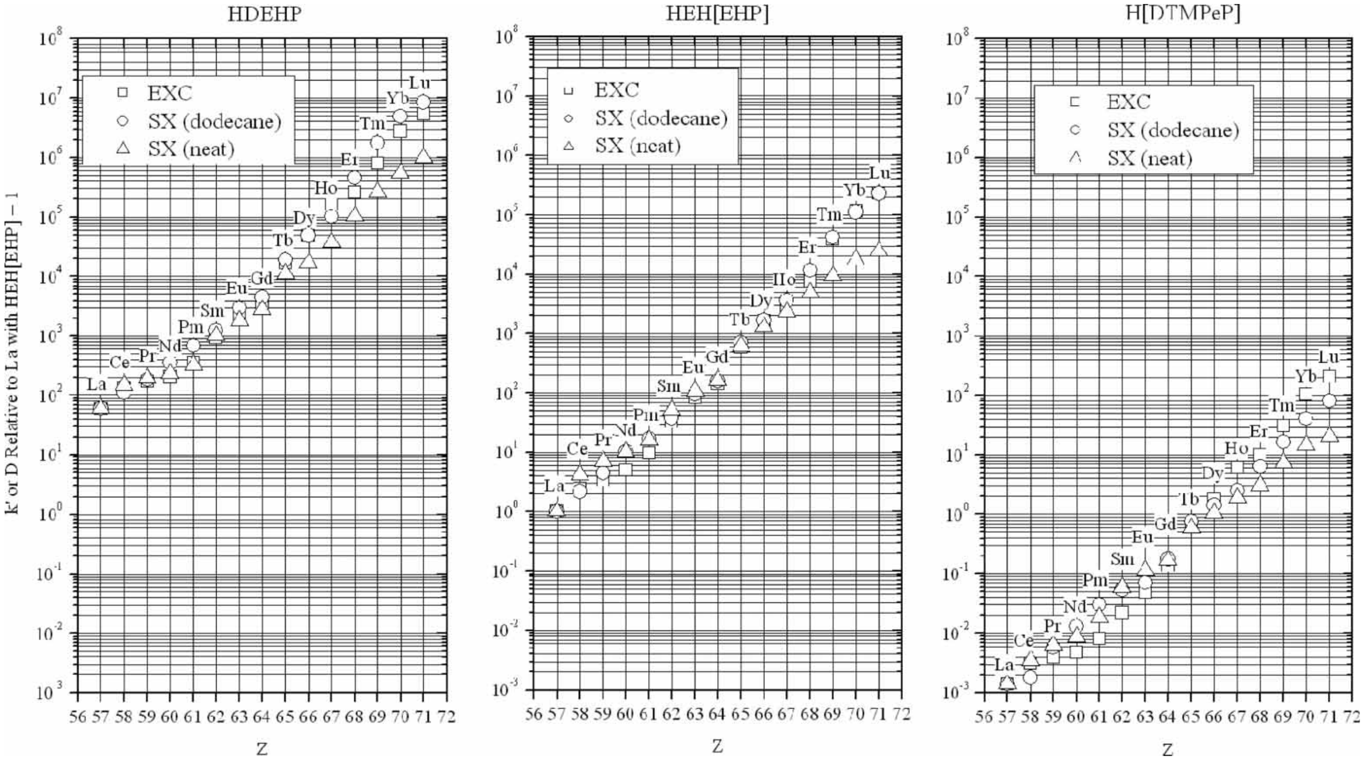

Figure 5. Comparison of the selectivities of HDEHP, HEH[EHP], and H[DTMPeP] for trivalent lanthanides and yttrium for EXC, SX with 0.5 M solutions in dodecane and SX with neat extractants.

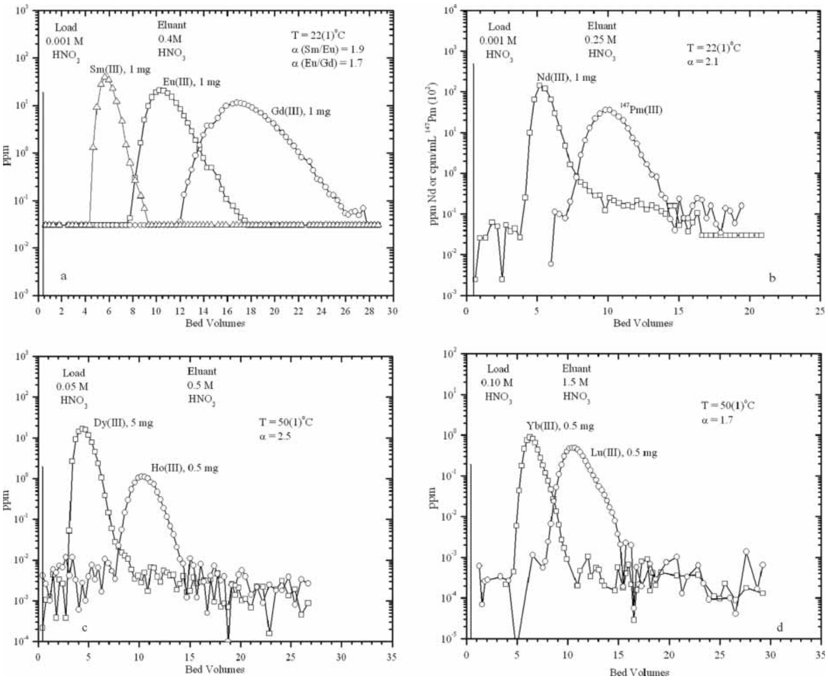

Figure 6. Elution curves for Nd(III) and Pm(III) and Sm(III), Eu(III) and Gd(III) on LN column, 22°C, and Dy(III) and Ho(III) and Yb(III) and Lu(III) on LN2 column, 50°C. Note that the abscissa is plotted in bed volumes. To convert to free column volume, divide by v_m (0.67). 20 mL column, 1.1 cm × 21.0 cm, 40% (w:w) HDEHP (LN) or HEH[EHP] (LN2) on 25–53 μm Amberchrom CG71, flow rate 5 mL/min.

the eluant for a chromatographic separation. How accurately, however, does the k′ calculated from D_w, v_s and v_m agree with the k′ obtained from an elution curve? This question was addressed by performing separations of four combinations of lanthanides using EXC resins prepared from HDEHP and HEH[EHP]. The elution curves are shown in Fig. 6. (Note that the Dy/Ho and Yb/Lu separations were carried out at 50°C, but the corresponding k′ values were corrected to room temperature using previously published data (4).) Table 3 compares the values of k′ calculated from D_w (see Fig. 2) and obtained from the elution curves. As can be seen, the agreement is quite good (often within experimental error), validating the relationships outlined in equations (1–4).

Comparison of D_v from EXC and SX Measurements

Although the data in Fig. 5 show that the *selectivities* achieved by EXC and the corresponding liquid–liquid systems agree, in most cases, to within

Table 3. Comparison of k′ calculated from Dw and k′ obtained from elution curves

Element	[HNO_3], M	k′ calculated from Dw	k′ from elution curve
Nd	0.25	6.5 ± 0.8	6.0 ± 0.3
Pm	0.25	11 ± 1	13 ± 0.7
Sm	0.40	7.0 ± 0.8	6.5 ± 0.3
Eu	0.40	13 ± 2	14 ± 0.7
Gd	0.40	25 ± 3	23 ± 1
Dy	0.50	8.0 ± 1.0	8.7 ± 0.4
Ho	0.50	18 ± 2	21 ± 1
Yb	1.5	11 ± 1	11 ± 0.6
Lu	1.5	20 ± 2	20 ± 1

experimental error (±10%), it still remains to be demonstrated that the volume distribution ratio, D_v, in equation (3) is the same as that obtained in the liquid–liquid extraction mode for the same extractant and acidity. To facilitate comparison of the D_v values obtained by EXC and SX for each of the lanthanides and Y, their ratio was calculated and plotted vs. atomic number for each of the three extractants (Fig. 7). (The error bars shown correspond to ±15% of the ratio in each case.) The abscissa of the plot also shows the HNO_3 concentration used to compare the two distribution ratios. Given that a ratio of one means that the values of D_v for the SX and EXC systems are identical, it can be readily seen that there is fair agreement between the values for a number of the lanthanides with the HDEHP and HEH[EHP] systems. In most cases, in fact, the D_v values differ by no more than a factor of 2–3. In the HDEHP system, a definite trend is evident, with the light lanthanides being more strongly extracted by the liquid–liquid system than they are retained in the EXC system. After Gd, the difference in retention is reversed. In the case of H[DTMPeP] system, the uptake of the lanthanides by the undiluted extractant is higher in every case than the corresponding EXC value by a factor of 2 to 4. Although this difference may seem rather large, it is important to keep in mind that an inverse fourth power hydrogen ion dependency makes comparison of the SX and EXC systems difficult because of the sensitivity to hydrogen ion concentration. It is noteworthy that the D_v ratio of SX to EXC for the last three lanthanides measured at the highest acidity is close to 1, whereas deviation from one for the light lanthanides, measured at the lowest acidity is the largest.

It is obvious from the data for the three extractants depicted in Fig. 7 that although the values of D_v obtained from SX and EXC are similar, they are not consistently similar enough for SX to be of practical value in predicting EXC behavior. This conclusion is supported by previous reports for other SX and

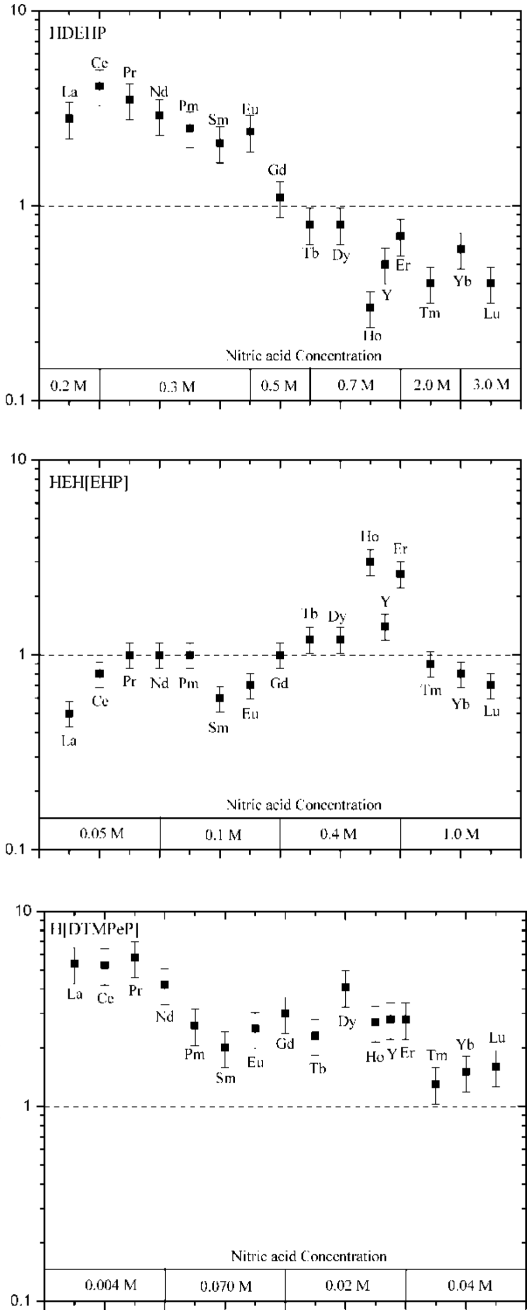

Figure 7. Comparison of the volume distribution ratio, Dv, calculated for the LN resin series and the distribution ratio measured by solvent extraction for the undiluted extractant.

EXC systems employing other extractants, diluents and support combinations that showed that the match between SX and EXC is inexact. Curiously, however, one of the authors' earlier studies showed a very close match between D_v values when the stationary phase was 1.5 M HDEHP in dodecane on a porous silica support (20). This suggests that the extent to which the values of D_v from SX and EXC agree is dependent upon the support. Further work is clearly needed to clarify this dependence.

Capacities of Resins vs. Solvents

Early studies by Peppard et al. (19) showed that acidic dialkyl organophosphorus extractants form very stable dimers (through hydrogen bonding) in hydrocarbon diluents. In addition, Peppard et al. observed that one tripositive lanthanide ion combines with six molecules of HDEHP, and that when the Ln(III) ion content of the organic phase exceeds the 1:6 metal-extractant ratio, a precipitate or gel forms. To determine if EXC systems exhibit unusual behavior when this Ln(III) to extractant concentration ratio is exceeded in the resin, EXC columns containing the three extractants were saturated with Eu(III) and the capacities of the three EXC resins measured (Table 4). One can see that in each case, the Eu(III) loading exceeds that expected on the basis of a 1:6 metal:extractant mole ratio. Also, a noticeable reduction in the flow rate through the column was observed as the column neared saturation with Eu. It is difficult to ascertain whether a precipitate was actually forming in the stationary phase at high metal loading, but the observed behavior of the columns during the saturation experiments are consistent with stationary phase expansion. Whether this is due to an increase in the volume of the stationary phase, rather than precipitate formation, is unclear at present. What is clear, however, is that the capacities of all three EXC materials exceed what one could achieve by analogous SX systems, again demonstrating a difference between the two techniques.

Table 4. Resin capacity

Extractant	Support	Capacity mg Eu/g resin	Ratio L:M[a]	Flow at high metal loading[b]
HDEHP	CG71	50	3.9	Slows
HED[EHP]	CG71	39	5.1	Slows
H[DTMPeP]	CG71	41	5.1	Slows

[a] Ratio of moles extractant in 1 g of resin to moles Eu extracted in saturated column.

[b] Gravity flow in 1.5 cm i.d. column packed with 1 gram of resin loaded with 2.0 mg/mL Eu in 0.001 M HNO_3 to column saturation.

CONCLUSIONS

The results presented here clearly illustrate the most significant similarities and differences between EXC and SX systems. As has been shown, the selectivities for all of the lanthanides and yttrium are essentially the same for the two techniques for a given extractant. On the other hand, consistently predicting the volume distribution ratio and thus, the elution behavior for an individual ion, even to within a factor of two, from SX data is difficult. Although part of the explanation undoubtedly lies in the (for now inexplicable) differences in nitric acid dependency observed for the SX and EXC systems, the unavailability of a portion of the extractant in the micropores of the solid support may also be a contributing factor. (Approximately 30% of the pores in Amberchrom CG-71 are less than 100 Å in diameter (21).) Nolte et al. (22) have shown that the pore size of silica supports does have an effect on capacity and distribution ratio in the HDEHP-SiO_2-HCl system. The possibility that pore size effects underlie some of our observations will be the subject of further study.

Although our results do preclude the use of SX-derived D_v values for anything other than a qualitative picture of the expected elution behavior of a given ion, our work also reinforces the utility of dry weight distribution ratio values, D_w, of an EXC material in predicting the volume to peak maximum in a chromatographic run. Since D_w is easily measured under a variety of conditions (e.g. acidity and temperature), these measurements provide a facile means of obtaining accurate predictions of elution behavior, with which one can readily identify conditions appropriate for a desired chromatographic separation.

ACKNOWLEDGEMENT

A portion of this work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, United States Department of Energy, under Contract No. W-31-109-ENG-38.

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