

# REVERSED-PHASE PARTITION CHROMATOGRAPHY OF THE RARE EARTHS USING METHYLENEBIS[DI(2-ETHYLHEXYL)-PHOSPHINE OXIDE] AS THE STATIONARY PHASE\*

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## INTRODUCTION

The separation of the rare-earth elements by reversed-phase partition chromatography using the neutral, bifunctional compound, methylenebis(di-*n*-hexylphosphine oxide) (MHDPO), was recently reported<sup>1</sup>. In view of the rather large effects which variations in the organic groups of monoacidic esters of phosphoric and phosphonic acids have on the partition coefficients and separation factors in the extraction of several trivalent lanthanide and actinide cations<sup>2</sup>, it seemed of interest to investigate the use of bifunctional phosphine oxides analogous to MDHPO, but with branched alkyl side chains, as stationary phases for the partition chromatography of the rare-earth cations. The extraction of samarium, thorium and uranium(VI) by methylenebis[di(2-ethylhexyl)phosphine oxide], (2-ethylhexyl)<sub>2</sub>P(O)CH<sub>2</sub>P(O)(2-ethylhexyl)<sub>2</sub> (MEHDPO), and methylenebis[di(2-ethylbutyl)phosphine oxide] (MEBDPO) had been previously studied by PARKER AND BANKS<sup>3</sup> and it was concluded that: (a) methylenebis(dialkylphosphine oxide) extractants with straight chain alkyl groups were better extractants than compounds with branched side chains; (b) the compounds with branched alkyl side chains were relatively better extractants for uranium(VI) than for thorium, and the converse was true for compounds with unbranched alkyl groups; (c) the partition coefficient of samarium nitrate was much smaller than for thorium or uranium(VI) nitrate.

The possibility that the partition coefficients of the rare earths into MEHDPO might vary more rapidly with ionic radius than they would with less sterically hindered extractants, such as MHDPO, seemed likely; and the movement of the rare-earth nitrates, chlorides and perchlorates on paper treated with MEHDPO was studied. The partition behavior of the rare earth salts into MEHDPO is considerably different from that reported for MHDPO and significantly larger separation factors are obtained in some cases.

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## EXPERIMENTAL

Methylenebis[di(2-ethylbutyl)phosphine oxide] (MEBDPO) and methylenebis[di(2-ethylhexyl)phosphine oxide] (MEHDPO) were synthesized by a procedure previously reported<sup>4</sup>. Some cleavage of the compounds, presumably at the methylene bridge, invariably resulted during the distillation step (215°/0.1 mm Hg, and 225°/1 mm Hg for the ethylbutyl and ethylhexyl compounds, respectively). After the distillation step, any acidic compounds were removed by extraction with a 5 % aqueous solution of potassium hydroxide. Unlike MHDPO, it was not possible to recrystallize either MEBDPO or MEHDPO from diethyl ether, quite possibly because the introduction of the ethyl group in the side chain results in an asymmetric carbon and, hence, a number of stereoisomers are possible.

Paper chromatography of the distilled product (after extraction of acidic impurities) indicated substantial amounts of some neutral impurity. The paper was developed with a 40 % ethanol solution and then sprayed with a titanium-thiocyanate reagent<sup>5</sup>. Two bright yellow bands appeared, one near the solvent front and the other near the origin. It was assumed that the more water-soluble band (near the solvent front) was caused by a monofunctional impurity, possibly methyldialkylphosphine oxide. The ethylhexyl compound, MEHDPO, was further purified by column chromatography on cellulose columns, again using 40 % ethanol, to remove the more water-soluble impurity. The final product showed only one band when chromatographed on paper. It was recently observed that the chromatographic procedure was not necessary if a molecular distillation step at  $10^{-4}$  mm/Hg was used for the initial purification rather than normal distillation procedure.

The papers were treated and developed in exactly the same manner as with MHDPO<sup>1,6</sup>. Because of the apparently greater solubility of the ethylbutyl compound in water and the very similar behavior of the rare earths on papers treated with MEBDPO and MEHDPO in some preliminary studies with these compounds, only the latter, MEHDPO, was purified and studied in the present work.

## RESULTS AND DISCUSSION

$R_F$  values for the movement of the rare-earth nitrates on paper impregnated with MEHDPO are given in Table I. The paper was soaked in a 0.2 *M* solution of MEHDPO in carbon tetrachloride and the latter allowed to evaporate at room temperature. Plots of  $1/R_F - 1$  for several of the rare-earth nitrates as a function of the nitric acid concentration are shown in Fig. 1. Minimum values for  $1/R_F - 1$  were obtained with 9 *M* nitric acid as the mobile phase. This is also the acid concentration at which maximum values for the separation factor,  $\beta$ , were obtained for most rare-earth couples ( $\beta$  is here defined as the ratio of the two  $1/R_F - 1$  values).

Plots of  $\log(1/R_F - 1)$  as a function of the log of the concentration of MEHDPO on the paper are shown in Fig. 2 for three rare earths at both 3 *M* and 9 *M* nitric acid. The solid lines are drawn with a slope of unity and fit the data fairly well, except at low values of  $1/R_F - 1$  ( $R_F$  values over 0.8). This indicates a value of one for the solvation number<sup>1,7</sup>.

$R_F$  values for the rare-earth chlorides on paper treated with 0.2 *M* MEHDPO were 1.0 (moved with solvent front) at all acid concentrations of the mobile phase

TABLE I

 $R_F$  VALUES FOR RARE-EARTH NITRATES ON MEHDPO-TREATED PAPER

Element	Nitric acid concentration						
	0.1 M	1.0 M	3.0 M	6.0 M	9.0 M	12.0 M	16.0 M
La	0.25	0.61	0.88	0.93	0.99	1.0	1.0
Ce	0.13	0.25	—	—	—	—	—
Pr	0.14	0.27	0.70	0.80	0.96	0.95	1.0
Nd	0.13	0.26	0.67	0.75	0.93	0.91	1.0
Sm	0.10	0.17	0.44	0.58	0.82	0.73	0.87
Eu	0.10	0.16	0.37	0.50	0.76	0.64	0.78
Gd	0.12	0.15	0.36	0.49	0.75	0.62	0.74
Tb	0.07	0.08	0.18	0.30	0.47	0.36	0.48
Dy	0.06	0.06	0.13	0.23	0.37	0.27	0.33
Ho	0.05	0.05	0.09	0.17	0.29	0.19	0.21
Er	0.05	0.04	0.06	0.11	0.18	0.13	0.13
Tm	0.03	0.03	0.05	0.08	0.12	0.07	0.09
Yb	0.03	0.03	0.04	0.06	0.08	0.05	0.06
Lu	0.03	0.03	0.04	0.06	0.07	0.06	0.05
Y	0.08	0.08	0.12	0.20	0.29	0.19	0.24

except 9.0 *M* and 12.0 *M*. In this case the heavy rare earths were slightly retained with an  $R_F$  value for lutetium of approximately 0.80.

$R_F$  values for the rare-earth perchlorates on MEHDPO-treated paper are given in Table II for 0.5 *M*, 1 *M*, and 3 *M* perchloric acid. The  $R_F$  values appear to be relatively insensitive to the acid concentration of the mobile phase or the amount of MEHDPO on the paper (compare  $R_F$  values for 0.2 *M* HClO<sub>4</sub> and 0.5 *M* HClO<sub>4</sub>). Furthermore, there is little change in  $R_F$  with atomic number.

Log ( $1/R_F - 1$ ) values for the rare-earth chlorides, nitrates and perchlorates on papers treated with 0.2 *M* MHDPO, MEHDPO and TOPO (tri-*n*-octylphosphine oxide) are plotted as a function of atomic number in Fig. 3. The  $R_F$  data for MHDPO were taken from an earlier paper<sup>1</sup>. Several differences in the partition behavior of the rare-earth salts into these three extractants are clearly evident.

Fig. 3 and previously published liquid-liquid extraction data<sup>8</sup> show that the partition coefficients for the rare-earths salts into MHDPO from dilute acid decrease in the order perchlorates > nitrates > chlorides. The order in the case of MEHDPO is nitrates > perchlorates > chlorides. The decrease in log ( $1/R_F - 1$ ) as a function of decreasing atomic number in 9 *M* nitric is also considerably greater with MEHDPO than with MHDPO. Except in the case of MHDPO when dilute nitric or hydrochloric acids are used as the mobile phases, which results in an inversion of the usual order<sup>6</sup>, the partition coefficients increase with atomic number. Certain characteristic variations from a linear increase are clearly evident, however. The most striking of these are the similarity in the partition behavior of europium and gadolinium and the sudden increase in the partition coefficient from gadolinium to terbium.

The log ( $1/R_F - 1$ ) values (if the assumptions previously discussed concerning the linear relationship of the overall equilibrium constant,  $K$ , and  $1/R_F - 1$  hold) are linear functions of the overall change in free energy for the extraction process. The latter can be viewed as the sum of a number of partial changes corresponding to the solvation (or complex formation) energies of both cation and anion in the

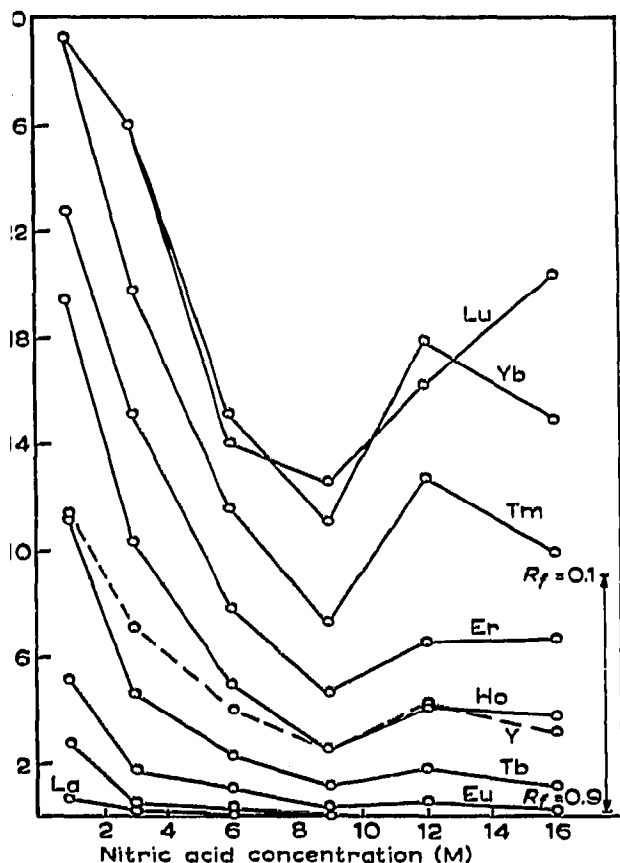


Fig. 1.  $1/R_f - 1$  values for the rare earth nitrates on MEHDPO-treated paper. Mobile phase: nitric acid.

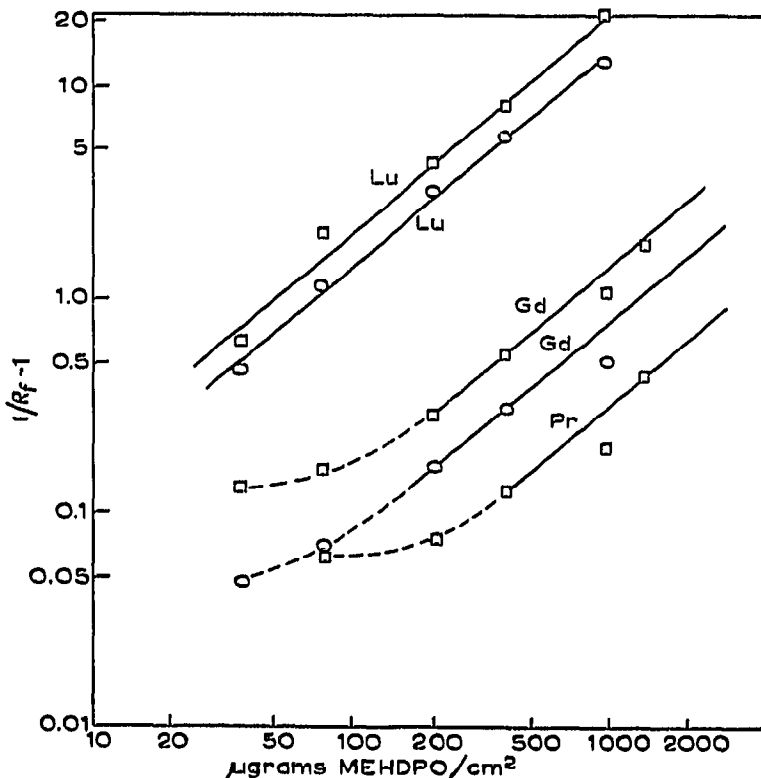


Fig. 2.  $\log (1/R_f - 1)$  values for several rare earth nitrates as a function of MEHDPO-concentration on paper. (O), 9 M  $\text{HNO}_3$ ; (□), 3 M  $\text{HNO}_3$ .

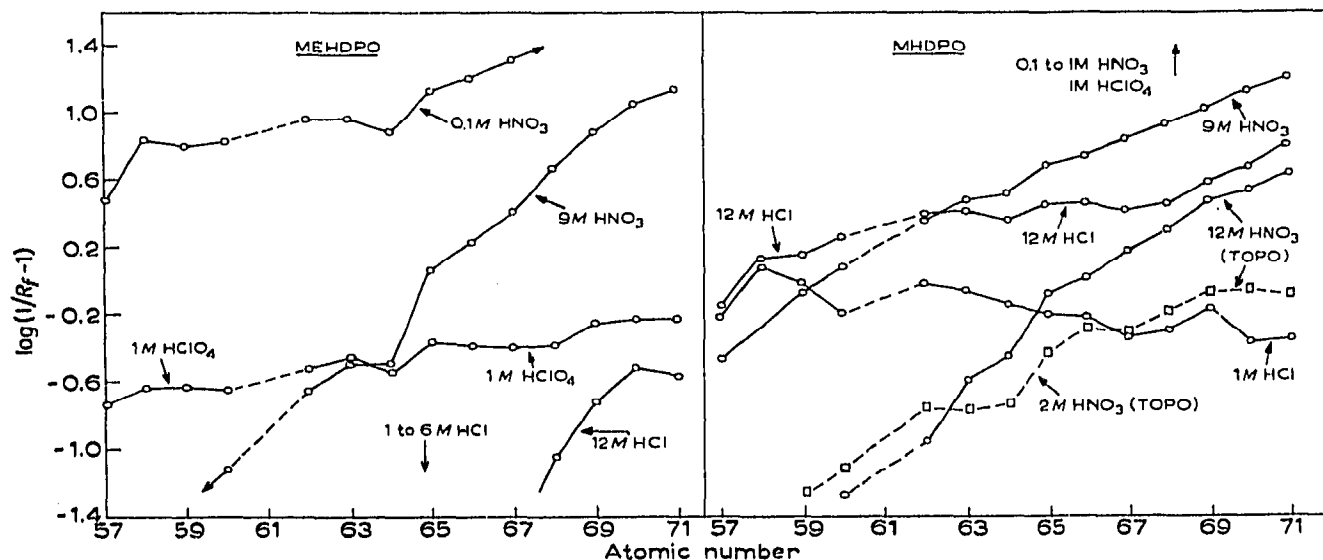


Fig. 3.  $\log (1/R_f - 1)$  data for the rare earths in nitric, hydrochloric and perchloric acid media on paper treated with TOPO, MHDPO and MEHDPO.

TABLE II

 $R_F$  VALUES FOR RARE-EARTH PERCHLORATES ON MEHDPO-TREATED PAPER\*

Element	Perchloric acid concentration			
	0.2 M	0.5 M	1.0 M	3.0 M
La	0.87	0.85	0.85	0.89
Ce	0.80	0.82	0.81	0.86
Pr	0.75	0.81	0.81	0.84
Nb	0.79	0.81	0.82	0.85
Sm	0.67	0.76	0.77	0.83
Eu	0.69	0.75	0.75	0.81
Gd	0.78	0.75	0.78	0.84
Tb	0.79	0.71	0.70	0.82
Dy	0.78	0.72	0.71	0.77
Ho	0.79	0.73	0.72	0.78
Er	0.76	0.72	0.71	0.79
Tm	0.75	0.71	0.65	0.74
Yb	0.71	0.70	0.63	0.74
Lu	0.72	0.70	0.63	0.75
Y	0.80	0.73	0.76	0.80

\* Paper treated with 0.1 M solution of MEHDPO in carbon tetrachloride except in the case of data for 0.2 M acid where paper was treated with 0.2 M MEHDPO in carbon tetrachloride.

aqueous and the organic phases<sup>9, 10</sup>. Because the change in free energy of each partial process is relatively large and the overall change is given by the difference of the sums of these partial processes in the two phases, it would be difficult to predict the magnitude of the partition coefficient even if reasonably accurate data for the partial processes were available. Conversely, it is rather risky to attribute differences in extraction behavior to any one of the partial processes involved in the overall extraction mechanism. It does seem probable, however, that the decreasing extraction order of the rare-earth salts into MHDPO in the order perchlorates > nitrates > chlorides is related to the solvation energy terms for these three anions<sup>1</sup>.

The much poorer extraction of the rare-earth perchlorates into MEHDPO in comparison to their extraction into MHDPO can be rationalized on the basis that MHDPO can more effectively solvate the rare-earth cation in the organic phase than can the more sterically hindered MEHDPO. This steric effect in the two extractants should be most evident in the extraction of metal perchlorates; because the perchlorate ion would not be expected to coordinate very well, if at all, with the cation. The coordination positions of the cation would then have to be filled either by the phosphoryl oxygens of the extractant or water molecules. The former would be consistent with high partition coefficients into the organic phase but would seem to require a solvation number (number of extractant molecules for each cation) of two or more.

The very low or high  $R_F$  values for the rare-earth perchlorates on paper treated with MHDPO or MEHDPO, respectively, prevented the determination of the solvation number by paper techniques. Although partition data using liquid-liquid extraction techniques should give this information, no such data are available at the present time for the above two extractants. It seems likely, however, that the solvation number of the rare-earth perchlorates is two or more with MHDPO in view

of their relatively good extraction. Both MHDPO and MEHDPO form 1:1 adducts with the rare earths in nitric acid media (Fig. 2 and ref. 1) and apparently act as bidentate donors. The latter assumption is based on the much better extraction of rare-earth nitrates into MHDPO and MEHDPO than into TOPO, and the fact that MHDPO acts as a bidentate donor with the uranyl ion<sup>8,11</sup>. The relatively poor extraction of the perchlorates into MEHDPO can then hardly be attributed to the inability of MEHDPO to act as a bidentate donor. The more likely alternative is that there is a steric problem in fitting more than one molecule of MEHDPO around the rare-earth cation so that the phosphoryl oxygens can effectively fill the coordination positions.

The extraction of the rare-earth nitrates appears to follow the same mechanism with both MHDPO and MEHDPO. It is believed the relatively good extraction of the 1:1 adduct of the rare-earth nitrates with both MHDPO and MEHDPO occurs because nitrate ions are capable of filling the remaining coordination positions of the cation in the organic phase. The inverted order for the extraction of the rare-earth nitrates previously reported for extraction from very dilute nitric acid into MHDPO<sup>1,6</sup> could well reflect a tendency in this case toward a higher solvation number. This inversion at low acid concentrations was not observed in the case of MEHDPO.

The sharper rate of decrease in  $1/R_F - 1$  with decreasing atomic number with MEHDPO as compared with MHDPO at the same acid concentration (9 *M* nitric) is likely to be caused by steric factors. The lighter rare earths with larger ionic radii presumably form less stable adducts with the bulky MEHDPO than with MHDPO.

The increase in  $1/R_F - 1$  for the heavier rare earths at nitric acid concentrations greater than 9 *M* and the smaller separation factors were not expected on the basis of the MHDPO data<sup>1</sup>. With the latter extractant, the  $1/R_F - 1$  values continued to decrease and the separation factors to increase up to 16 *M* nitric. Some recent work<sup>12</sup> on the solubilities of these extractants in nitric acid indicates that there is considerable chemical attack on MEHDPO at acid concentrations higher than 9 *M*. The possible formation of acidic degradation products could explain the higher  $1/R_F - 1$  values and lower separation factors observed with MEHDPO at high acid concentrations of the mobile phase. Although the solubility of MHDPO increased at high acid concentrations, there was no evidence of chemical attack.

The poor extraction of the rare-earth chlorides from dilute hydrochloric acid would be expected on the basis of the unfavorable electrostatic term for the extraction of three chloride ions into the organic phase. This would also be true for the extraction of the rare-earth nitrates from dilute nitric acid, but the nitrate ion, which could act as a bidentate donor, might be more effective in solvating the rare-earth cation in the organic phase than the chloride ion.

The small individual variations in partition behavior with atomic number, such as the generally sharp increase with partition coefficients from lanthanum to cerium and from gadolinium to terbium, might reflect splitting of the 4 *f* energy levels. YATSIMIRSKII AND KOSTROMINA<sup>13</sup> discuss the "extrastabilization energy" caused by the ligand field effect for rare earths with different symmetries. The gross deviations from linearity in the plots shown in Fig. 3, such as the similarity in the partition coefficients of europium and gadolinium and the rather large difference between gadolinium and terbium, seem consistent with this type of reasoning. The

agreement is not too good in many other cases, which, in view of the complexity of the system, is not too surprising. Other factors such as the possibility of a sudden change in coordination number might well be more important and could either obscure or account for these effects ascribed to ligand field splitting of energy levels<sup>14</sup>.

#### SUMMARY

$R_F$  values are given for the rare-earth nitrates, chlorides, and perchlorates on paper impregnated with methylenebis[di(2-ethylhexyl)phosphine oxide] (MEHDPO). The much lower  $1/R_F - 1$  values for the rare-earth perchlorates on MEHDPO-treated paper than on paper treated with the analogous extractant without the ethyl groups in the 2-position (MHDPO) are rationalized on the basis of steric factors. The greater separation factors for the rare earths observed in the nitric acid system with MEHDPO are explained on the same basis.

#### REFERENCES

- 1 J. W. O'LAUGHLIN, G. J. KAMIN AND C. V. BANKS, *J. Chromatog.*, 21 (1966) 460.
- 2 D. F. PEPPARD, G. W. MASON AND I. HUCHER, *J. Inorg. Nucl. Chem.*, 18 (1961) 245.
- 3 J. R. PARKER AND C. V. BANKS, *U.S. At. Energy Comm. Rep.*, IS-942, 1964.
- 4 J. J. RICHARD, K. E. BURKE, J. W. O'LAUGHLIN AND C. V. BANKS, *J. Am. Chem. Soc.*, 83 (1961) 224.
- 5 J. W. O'LAUGHLIN, F. W. SEALOCK AND C. V. BANKS, *Anal. Chem.*, 36 (1964) 224.
- 6 J. W. O'LAUGHLIN AND C. V. BANKS, *Anal. Chem.*, 36 (1964) 1222.
- 7 E. CERRAI AND C. TETA, *J. Chromatog.*, 8 (1962) 232.
- 8 J. E. MROCHEK AND C. V. BANKS, *U.S. At. Energy Comm. Rep.*, IS-827, 1964.
- 9 S. SIEKIERSKI, *J. Inorg. Nucl. Chem.*, 12 (1959) 129.
- 10 S. SIEKIERSKI, *Nukleonika*, 9 (1964) 601.
- 11 J. E. MROCHEK, J. W. O'LAUGHLIN AND C. V. BANKS, *J. Inorg. Nucl. Chem.*, 27 (1965) 603.
- 12 G. J. KAMIN, J. W. O'LAUGHLIN AND C. V. BANKS, to be published, 1966.
- 13 K. B. YATSIMIRSKII AND N. A. KOSTROMINA, *Russ. J. Inorg. Chem.*, 9 (1964) 971.
- 14 P. KRUMHOLZ, in L. EYRING (Editor), *Progress in the Science and Technology of the Rare Earths*, Vol. 1, Macmillan, New York, 1964, pp. 110-138.

*J. Chromatog.*, 24 (1966) 376-382