

REVERSED-PHASE PAPER CHROMATOGRAPHY OF THE RARE EARTHS, THORIUM AND URANIUM USING METHYLENEBIS(DI-*n*-HEXYLPHOSPHINE OXIDE) AS THE STATIONARY PHASE*

JEROME W. O'LAUGHLIN, GEORGE J. KAMIN AND CHARLES V. BANKS

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa (U.S.A.)

(Received August 26th, 1965)

Bifunctional organophosphorus compounds such as methylenebis(dialkylphosphonates)¹, ethylenebis(dialkylphosphonates)^{2,3}, and methylenebis(dialkylphosphine oxides)⁴ have been shown to be powerful solvent extractants for the rare earth group. One of the latter compounds, methylenebis(di-*n*-hexylphosphine oxide) (MHDPO), was also shown to be quite suitable as a stationary phase for the reversed-phase partition chromatography of various metal salts including the rare earths⁵.

The present and more extensive study of the movement of the rare earths, uranium and thorium on papers impregnated with MHDPO was undertaken to determine the effect of the various experimentally variable parameters on the R_F values.

The effects of varying the type and concentration of acid in the mobile phase (from 1 to 12 *M* hydrochloric and 1 to 16 *M* nitric), the concentration of MHDPO on the paper, the rate of development, and the temperature of development were investigated. It was anticipated that with this information optimum conditions could be selected for the quantitative separation of the rare earths from each other and from other metal salts both by paper and column chromatography.

EXPERIMENTAL

Reagents and procedure

The MHDPO, $(C_6H_{13})_2P(O)-CH_2-P(O)(C_6H_{13})_2$, used was synthesized following the procedure by RICHARD *et al.*⁶. This compound was previously referred to as HDPM and the present abbreviation was adopted in order to prevent confusion with acidic compounds such as di-2-ethylhexyl orthophosphoric acid (HDEHP). The rare earth oxides used to prepare 0.1 *M* nitric and hydrochloric acid solutions of the rare earths were Ames Laboratory oxides (Ames, Iowa).

Schleicher and Schuell chromatographic paper (No. 589-C, Blue Ribbon, sheets or disks) was used. It was impregnated with the MHDPO by soaking the paper in a 0.1 or 0.2 *M* carbon tetrachloride solution (except for solvation number studies) and then allowing the papers to air dry. The papers were spotted, developed and the spots detected as previously described⁵. Arsenazo (0.1 % solution) was used

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 1787.

almost exclusively, however, to locate the rare earth spots after development. The sheets were developed for 18 to 20 h using the ascending technique.

RESULTS AND DISCUSSION

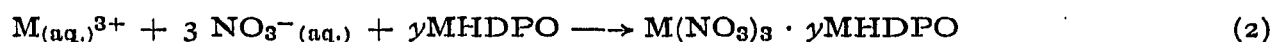
Nitric acid media

The R_F values for the rare earth nitrates, uranyl nitrate and thorium nitrate on papers treated with 0.1 and 0.2 *M* MHDPO are given in Table I. The R_F values given are all averages of at least two separate runs. The values usually agreed within $\pm 0.02 R_F$ units. The anomalous values for cerium are attributed to the oxidation of cerium(III) to cerium(IV) on the paper⁵.

The function $(1/R_F - 1)$ has been related to the partition coefficient, K_D , through the eqn. (1)⁷ where $v_{org.}$ and $v_{aq.}$ are the volumes of the organic and aqueous phases, respectively.

$$K_D = \frac{v_{org.}}{v_{aq.}} (1/R_F - 1) \quad (1)$$

If the overall reaction for the partition of the rare earth nitrates is given by eqn. (2),



the partition coefficient can then be expressed in terms of the equilibrium constant, K_e , for the above reaction by eqn. (3),

$$K_D = \frac{K_e(NO_3^-)^3 (MHDPO)^\gamma \gamma_{\pm}^4 \cdot \gamma_e^\gamma}{\gamma_c} \quad (3)$$

where γ_{\pm} is the mean ionic activity coefficient for the metal salt, and γ_e and γ_c are the activity coefficients for the extractant and for the complex, respectively. Based on the assumption that, at a given nitric acid concentration, the function $1/R_F - 1$ is linearly related to K_D , it follows that log-log plots of $1/R_F - 1$ versus the concentration of MHDPO should give the solvation number γ . Actually, the equilibrium concentration of free MHDPO should be used, but the initial concentration may be used if the fraction not complexed by nitric acid remains constant. For any given acid concentration this should be the case, and the use of the initial MHDPO concentration should not affect the slope. Log-log plots of $1/R_F - 1$ and the MHDPO concentration on the paper at various acid concentrations are shown in Fig. 1. The concentration of MHDPO (initial concentration) was determined spectrophotometrically⁸.

The data plotted in Fig. 1 give a family of straight lines with a slope of nearly one. The data for dysprosium were almost identical to those for gadolinium and were not plotted for the sake of greater clarity.

Although data on the extent of association of aqueous nitric acid and activity coefficient data in this media are available⁹, the lack of data on the mean ionic activity coefficients of the rare earth nitrates in concentrated nitric acid, and the lack of any

TABLE I
R_F VALUES FOR RARE EARTH, URANYL AND THORIUM NITRATES

Element	Nitric acid concentration													
	1.0 M	3.0 M	5.0 M	6.0 M	9.0 M	12.0 M	16.0 M	0.1	0.2	0.1	0.2	0.1	0.2	
MHDPO concentration														
Y	0.06	0.03	0.09	0.04	0.13	0.06	0.16	0.09	0.26	0.15	0.40	0.27	0.64	0.48
La	0.04	0.02	0.14	0.08	0.42	0.24	0.60	0.35	0.93	0.75	1.00	0.95	1.00	1.00
Ce	0.03	0.02	0.07	0.05	—	—	0.30	0.18	0.30	0.19	0.30	0.20	0.36	0.23
Pr	0.03	0.02	0.08	0.05	—	—	0.38	0.20	0.76	0.54	0.95	0.86	1.00	0.98
Nd	0.03	0.02	0.09	0.04	0.21	0.09	0.31	0.14	0.68	0.46	0.91	0.79	1.00	0.95
Sm	0.05	0.01	0.10	0.03	—	—	0.25	0.10	0.48	0.30	0.74	0.61	0.93	0.90
Eu	0.05	0.02	0.11	0.04	—	—	0.22	0.10	0.41	0.25	0.64	0.48	0.87	0.80
Gd	0.07	0.02	0.11	0.04	0.17	0.08	0.21	0.11	0.37	0.24	0.56	0.46	0.78	0.75
Tb	0.07	0.03	0.07	0.05	0.11	0.06	0.14	0.09	0.28	0.18	0.50	0.31	0.74	0.55
Dy	0.06	0.03	0.06	0.05	—	—	0.12	0.08	0.25	0.16	0.42	0.27	0.69	0.50
Ho	0.06	0.03	0.05	0.04	—	—	0.10	0.07	0.20	0.13	0.37	0.22	0.63	0.40
Er	0.07	0.03	0.04	0.03	—	—	0.09	0.06	0.18	0.11	0.32	0.19	0.53	0.34
Tm	0.08	0.03	0.04	0.03	—	—	0.08	0.05	0.15	0.08	0.26	0.15	0.44	0.26
Yb	0.09	0.04	0.04	0.02	—	—	0.07	0.04	0.12	0.07	0.21	0.12	0.36	0.23
Lu	0.09	0.04	0.05	0.02	0.04	0.03	0.05	0.04	0.10	0.06	0.18	0.11	0.33	0.19
U(VI)	0.00	0.00	0.00	0.00	—	—	0.01	0.00	0.01	0.00	0.01	0.01	0.04	0.03
Th(IV)	0.00	0.00	0.00	0.00	—	—	0.01	0.00	0.01	0.00	0.01	0.01	0.02	0.01

assurance that the ratio $v_{\text{org.}}/v_{\text{aq.}}$ in eqn. (1) remains constant at various acid concentrations makes any useful theoretical relationship between $1/R_F - 1$ and the nitrate ion or nitric acid concentration rather unlikely. Empirically, it was found that plots of $1/R_F - 1$ versus the nitric acid concentration were nearly linear at low acid concentrations with somewhat greater (negative) slopes for the lighter rare earths, as shown in Fig. 2 for several selected rare earths. The data for those rare earths not shown gave similarly shaped plots which fell between those shown. These plots were omitted for the sake of greater clarity.

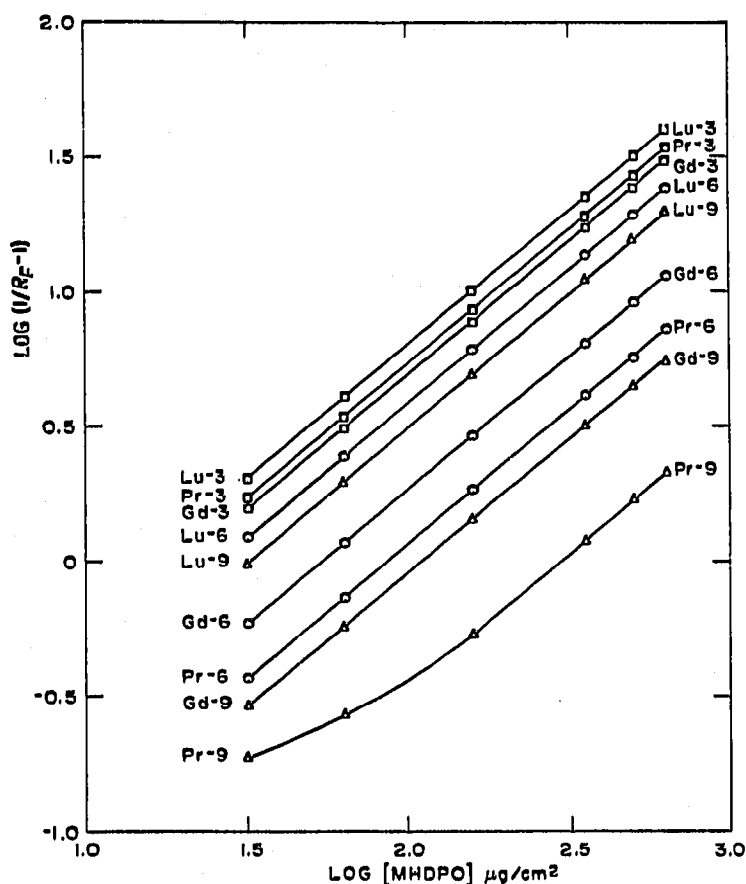


Fig. 1. Solvation number study for rare earth-MHDPO adducts in nitric acid. (\square — \square) 3 M HNO_3 ; (\circ — \circ) 6 M HNO_3 ; (\triangle — \triangle) 9 M HNO_3 .

The separation factor, β , (defined as the ratio of $1/R_F - 1$ values) for any two rare earths increased with acid concentration. This is more evident in Fig. 3 where the separation factors between the various rare earths and gadolinium are plotted against the acid concentration. The largest $1/R_F - 1$ value was always used in numerator and the negative β values refer to rare earths which are more tightly retained than gadolinium. The data plotted in Figs. 2 and 3 were obtained on the paper treated with 0.2 M MHDPO. Similar plots were obtained on the paper treated with 0.1 M MHDPO.

The increase in the separation factors with acid concentration is similar to what is observed in the case of TBP but, unlike TBP, the partition coefficient decreases with increasing acid concentration. Some caution should be used in comparing

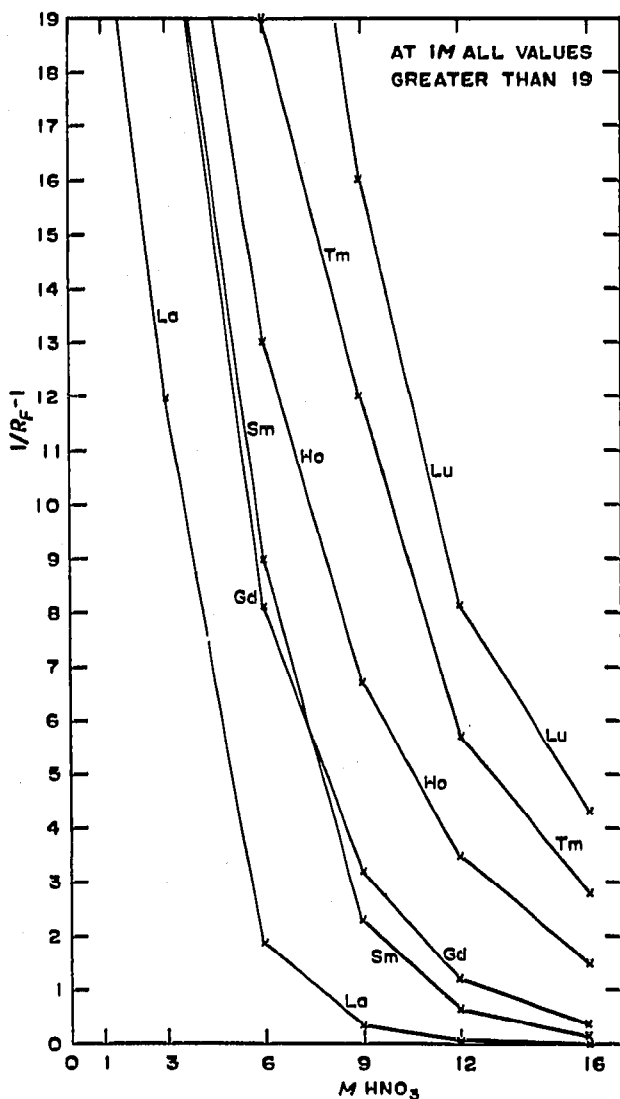


Fig. 2. Effect of nitric acid concentration on $1/R_F - 1$ for various rare earths.

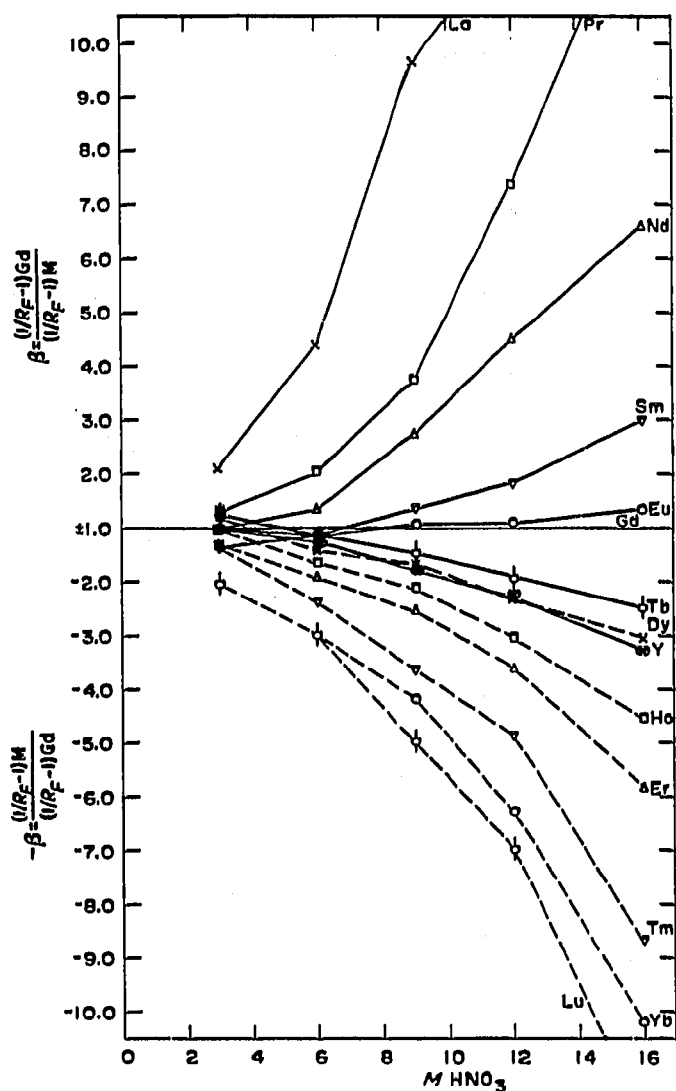


Fig. 3. Effect of nitric acid concentration on separation factors between the rare earths and gadolinium.

separation factors obtained in the above manner with those obtained by liquid-liquid extraction methods or by column chromatography. Although the trends are usually the same, the absolute value of the separation factors can certainly vary. Some separation factors for the rare earths reported in the literature with di-2-(ethylhexyl)-orthophosphoric acid (HDEHP) obtained using paper⁷ and column chromatography¹⁰ are shown in Table II and illustrate this point. No doubt the differences in the supporting phase (paper and kieselguhr) could account for the differences. CERRAI *et al.*¹¹ obtained almost identical separation factors on columns packed with cellulose powder as they did on paper.

It seems probable, however, that separation factors calculated from the ratio of $1/R_F - 1$ values are more subject to error than those obtained by careful column studies. The ratio $v_{\text{ORG}}/v_{\text{AQ}}$ undoubtedly varies from the start to the solvent front on

TABLE II

COMPARISON OF SEPARATION FACTORS FOR RARE EARTHS BY PAPER AND COLUMN CHROMATOGRAPHY USING HDEHP AS A STATIONARY PHASE*

Rare earth couple	Cervai and Testa ^{7**}	Sochacka and Siekierski ¹⁰
La-Ce	2.46	2.8
Ce-Pr	1.38	1.5
Pr-Nd	1.59	1.3
Nd-Sm	2.11	5.9 ^{***}
Sm-Eu	2.03	2.2
Eu-Gd	1.65	1.7
Gd-Tb	3.85	5.5
Tm-Yb	3.33	3.1

* Mobile phase was hydrochloric acid and the maximum separation factors obtained are reported regardless of acid concentration.

** Separation factors calculated from R_F data by present authors.

*** Nd-Sm factor in this case is the sum of Nd-Pm and Pm-Sm.

paper, thus K_D is not strictly linear with $1/R_F - 1$ (eqn. 2). This would decrease the separation factor of two rare earths having high and low R_F values, respectively, if $v_{org.}/v_{aq.}$ increased with distance from the start line as seems likely for ascending chromatography. The average velocity of the mobile phase also varies with time of development (it was observed to decrease fairly rapidly). Thus, although paper chromatography can be used for a rapid evaluation of the trends in the separation factors of different elements, the absolute magnitude of separation factors found for column separations may be considerably different, particularly where the R_F values are rather far apart.

The effect of the rate of development on the $1/R_F - 1$ values for three rare earths is illustrated in Fig. 4. The rate was varied by notching the paper (hence re-

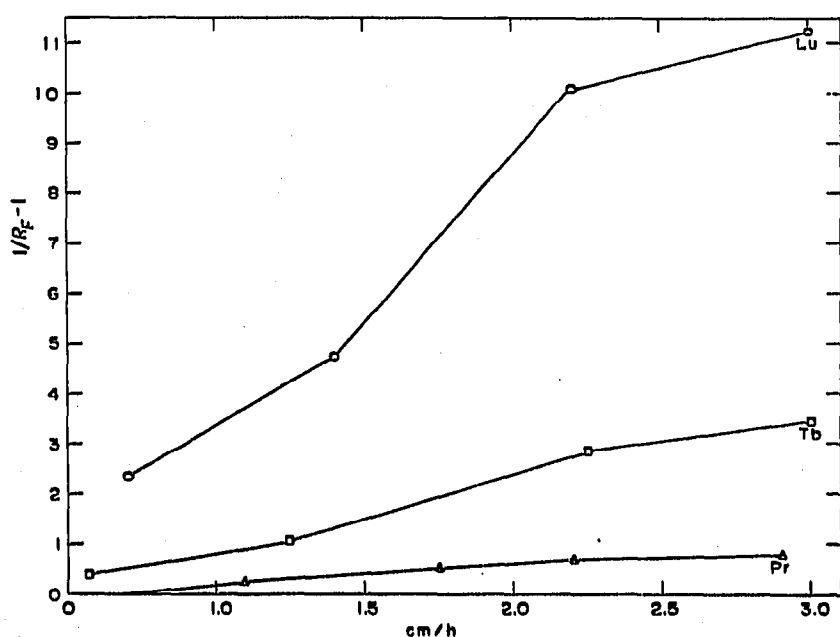


Fig. 4. Effect of rate of development on $1/R_F - 1$ values.

stricting the flow of the mobile phase) between the bottom and the point at which the spot was applied. The rate given is the average rate from start to finish.

Although not immediately apparent from Fig. 4, the separation factor of terbium and lutetium actually decreases with increasing rate while the opposite is true for the terbium-praeseodymium couple.

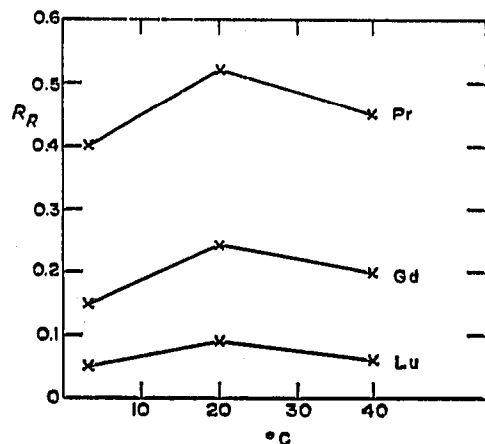


Fig. 5. Effect of temperature on R_R values for three rare earths.

The effect of temperature on the R_F values of the same three rare earths was studied using radial chromatography. The results obtained are shown in Fig. 5. The rate of development increased with temperature which would partially account for the decrease in R_R from 20 to 40°. The initial increase in R_R is in the opposite direc-

TABLE III

R_F VALUES FOR RARE EARTH, URANYL AND THORIUM CHLORIDES

Element	Hydrochloric acid concentration									
	1.0 M		3.0 M		6.0 M		9.0 M		12.0 M	
	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2
Y	0.82	0.63	0.78	0.70	0.75	0.54	0.42	0.34	0.50	0.34
La	0.76	0.63	0.68	0.57	0.80	0.62	0.51	0.46	0.64	0.60
Ce	0.70	0.46	0.65	0.54	0.73	0.52	0.46	0.39	0.52	0.44
Pr	0.68	0.52	0.64	0.55	0.73	0.51	0.43	0.39	0.53	0.42
Nd	0.75	0.62	0.70	0.56	0.70	0.51	0.40	0.36	0.49	0.36
Sm	0.68	0.52	0.61	0.45	0.62	0.43	0.34	0.29	0.44	0.30
Eu	0.68	0.54	0.68	0.56	0.63	0.43	0.35	0.29	0.44	0.28
Gd	0.71	0.58	0.76	0.65	0.69	0.51	0.42	0.36	0.48	0.31
Tb	0.72	0.62	0.76	0.65	0.66	0.47	0.38	0.32	0.44	0.27
Dy	0.75	0.63	0.80	0.70	0.66	0.50	0.37	0.29	0.43	0.26
Ho	0.78	0.69	0.84	0.77	0.70	0.52	0.37	0.32	0.44	0.28
Er	0.80	0.67	0.86	0.76	0.70	0.54	0.38	0.31	0.42	0.27
Tm	0.79	0.60	0.85	0.79	0.67	0.52	0.33	0.26	0.43	0.21
Yb	0.79	0.70	0.85	0.72	0.62	0.48	0.30	0.23	0.38	0.18
Lu	0.81	0.69	0.85	0.71	0.63	0.48	0.28	0.27	0.37	0.14
U(VI)	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.00
Th(IV)	0.02	0.00	0.02	0.00	0.02	0.00	0.02	0.00	0.03	0.00

tion, however, and suggests the metal adducts with the extractant are more stable at lower temperatures.

Hydrochloric acid system

R_F data on papers treated with 0.1 and 0.2 M MHDPO for the rare earth, uranyl and thorium chlorides are shown in Table III. The acid concentration of the mobile phase was varied from 1 to 12 M . Plots of $1/R_F - 1$ as a function of the acid concentration for several selected rare earths are shown in Fig. 6. The $1/R_F - 1$

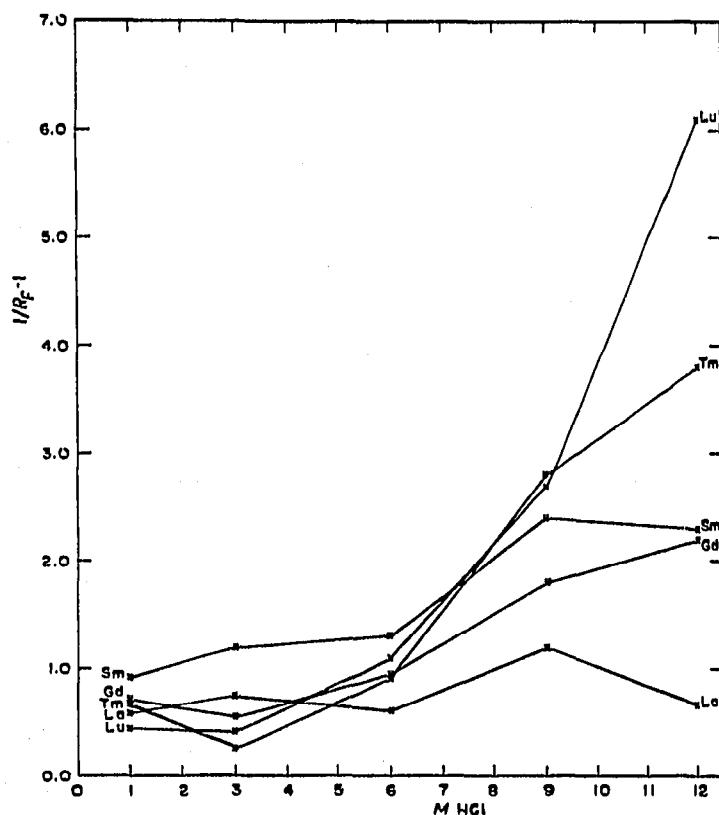


Fig. 6. Effect of hydrochloric acid concentration on $1/R_F - 1$ values for various rare earths.

values for all the rare earths fell between those for lanthanum and lutetium at high acid concentrations and between those of samarium and thulium at 3 M hydrochloric acid. Generally, the order of increasing retention with increasing atomic number was observed at high acid concentrations similar to the order in the nitric system. The order is not strictly followed, even at 12 M acid, as is evident from the R_F data in Table III. At lower acid concentrations, the order is quite complex with the order of the extreme light and heavy members inverted. The maximum for samarium and minimum for thulium at 3 M hydrochloric are extreme values for the rare earth chlorides at this acid concentration. The same behavior occurred on the papers treated with 0.1 M MHDPO up to 9 M acid, but in this case the $1/R_F - 1$ values decreased from 9 M to 12 M acid.

An attempt to determine the solvation number in the chloride system by plotting $\log(1/R_F - 1)$ as a function of $\log(\text{MHDPO})$ resulted in the plots shown in Fig. 7. The data for dysprosium were almost identical to those for gadolinium and

were not plotted for the sake of greater clarity. The MHDPO concentration was again determined spectrophotometrically⁸. The observed slopes are approximately one in 6 and 9 *M* acid at higher MHDPO concentrations. In 1 *M* acid the slope does not increase at higher MHDPO concentrations but rather decreases. It is almost zero for lutetium and drops noticeably for gadolinium. The observed slopes are considerably less than one at all acid concentrations at lower MHDPO concentrations.

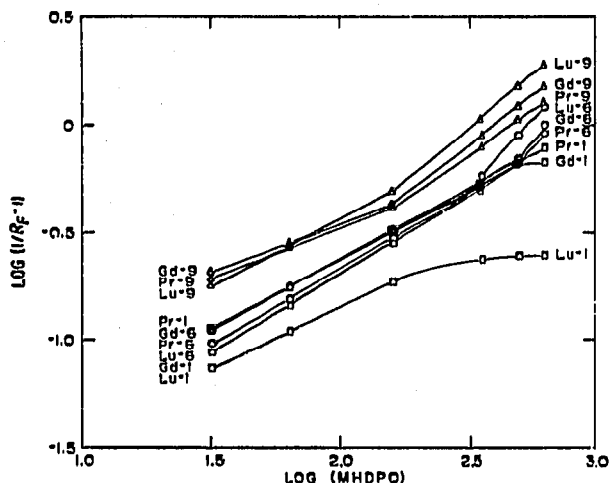


Fig. 7. Solvation number study for rare earth-MHDPO adducts in hydrochloric acid. (\square — \square) 1 *M* HCl; (\circ — \circ) 6 *M* HCl; (\triangle — \triangle) 9 *M* HCl.

The reasons for these rather anomalous results are not known but may be partially caused by a kinetically slow step in the partition of the chlorides into the MHDPO phase.

Interpretation of data

The $1/R_F - 1$ values for the rare earths in hydrochloric and nitric acid differ considerably and even show opposite trends with increasing acid concentration. Furthermore, the retention order is inverted at low acid concentrations from that observed in more concentrated acids. This is most apparent in the chloride system (and appears to be more complex than a simple inversion) but is also evident at 1 *M* nitric as can be seen by inspection of Table I.

SIKIERSKI¹² has pointed out that two factors are of most importance in the partition of inorganic salts into neutral organic solvents. These are:

1. The difference in solvation free energies in water and the organic solvent for both cation and anion.
2. The complex forming tendency of the anion.

It would appear that these factors also offer at least a qualitative explanation for the differences in the chromatographic behavior of the rare earth nitrates and chlorides.

The solvation free energies for the perchlorate, nitrate and chloride anions should increase in the order given. The complex-forming tendency should increase in the same order with the tendency of the nitrate and chloride anions to form complexes with the rare earth cations being about equal^{13,14}.

The first term should become increasingly less important as the acid concen-

tration increases and the nature of the "aqueous" phase changes from essentially a dilute water solution of the acid to the concentrated acid. In the latter case the rare earth cations should be essentially unhydrated and the differences in the "solvation" energies of the cations or the nitrate and chloride anions in concentrated nitric or hydrochloric acid should be small. The partition coefficients based on $1/R_F$ data are, actually, roughly the same, and the same retention order is also observed in both concentrated nitric and hydrochloric acids (decreasing from lutetium to lanthanum).

The rare earth nitrates are well extracted from dilute acid, but the chlorides are very poorly extracted. This could easily result from the differences in the free energies of solvation of the chloride and nitrate anions. It is important to note, as pointed out by SIEKIERSKI¹⁵, that "the difference in the free energy of hydration of two cations, equal to 5.5 kcal, is equivalent to the ratio of partition coefficients equal to 10^4 ." In view of the fact that three anions are extracted with each rare earth cation, it seems quite apparent that even relatively small differences in the solvation energies could account for the observed differences in the partition coefficients. The rare earth perchlorates have been reported to be much better extracted than the nitrates⁵ which is consistent with the above view.

The decrease in the partition coefficients for the rare earth nitrates with increasing nitric acid concentration is not only opposite to what is expected on the basis of the solvation energy factor but also to what might be expected on the basis of the mass action law (eqn. 2). Apparently the competitive extraction of nitric acid takes precedence over both these factors. Nitric acid has been shown to be well extracted by MHDPO even from dilute solutions⁴. Hydrochloric acid, however, is not well extracted from dilute solutions and never as well extracted as nitric acid⁴. Apparently the competitive extraction of hydrochloric acid is of lesser importance than the solvation and mass action effects.

Although the thermodynamic stabilities of the nitrate and chloride complexes with the rare earth cations may be about the same, true equilibrium may not be attained during the chromatographic process and there is no reason that the rates of formation or dissociation of the complexes should be the same. SIEKIERSKI AND SOCHACKA¹⁴ used this reasoning to explain the greater plate height observed when hydrochloric, rather than nitric, acid was used as the mobile phase for the separation of the rare earths on columns packed with HDEHP. The anomalous results obtained in the solvation number studies in hydrochloric acid, Fig. 7, may also be due, at least partially, to kinetic factors, as already suggested.

SIEKIERSKI AND SOCHACKA¹⁴ conjectured that the nitrate and chloride complexes, although of approximately the same thermodynamic stability, differed structurally. They postulated that the nitrate ions were coordinated to the hydrated rare earth cations in the second coordination sphere, possibly via hydrogen bonding to water molecules in the first coordination sphere. The partition kinetics for the two complexes might then be quite different. On the basis of their results, SIEKIERSKI AND SOCHACKA¹⁴ concluded equilibrium with the extractant was established rapidly provided the inner coordination sphere contained only water molecules, but slowly if the inner coordination sphere contained chloride ions.

If there were a slow absorption step, the rare earths in the mobile phase would have larger R_F values than they would if true equilibrium were attained during the chromatographic process. This effect would be relatively more important for higher

concentrations of extractant on the paper. It should also be most evident at low acid concentrations and for the heavy rare earths¹⁴. The results on the solvation number studies, Fig. 7, are at least consistent with this reasoning.

SUMMARY

Reversed-phase partition chromatography was used to separate the rare earths, thorium and uranium on papers treated with methylenebis(di-*n*-hexylphosphine oxide), MHDPO. The separation factors between adjacent rare earths were found to increase with the acid concentration in both nitric and hydrochloric media with the larger separation factors in nitric acid. Opposite trends were observed in hydrochloric and nitric acid. In the former case the partition coefficient increased with acid concentration, but in the latter case it decreased. This was explained on the basis of the solvation energies of the cations and anions, the mass action effect and the competitive extraction of nitric and hydrochloric acid. Solvation number studies indicated a 1:1 adduct between MHDPO and the rare earth nitrates. Corresponding studies on the rare earth chlorides gave anomalous results. It was postulated this was caused by non-equilibrium conditions.

REFERENCES

- 1 T. H. SIDDALL, III, *J. Inorg. Nucl. Chem.*, 26 (1964) 1991.
- 2 T. H. SIDDALL, III, *J. Inorg. Nucl. Chem.*, 25 (1963) 883.
- 3 H. SAISHO, *Bull. Chem. Soc. Japan*, 34 (1961) 859.
- 4 J. E. MROCHEK AND C. V. BANKS, *J. Inorg. Nucl. Chem.*, 27 (1965) 589.
- 5 J. W. O'LAUGHLIN AND C. V. BANKS, *Anal. Chem.*, 36 (1964) 1222.
- 6 J. J. RICHARD, K. E. BURKE, J. W. O'LAUGHLIN AND C. V. BANKS, *J. Am. Chem. Soc.*, 83 (1961) 1722.
- 7 E. CERRAI AND C. TESTA, *J. Chromatog.*, 8 (1962) 232.
- 8 J. W. O'LAUGHLIN, F. W. SEALOCK AND C. V. BANKS, *Anal. Chem.*, 36 (1964) 224.
- 9 W. DAVIS, JR. AND H. J. DE BRUIN, *J. Inorg. Nucl. Chem.*, 26 (1964) 1069.
- 10 R. J. SOCHACKA AND S. SIEKIERSKI, *J. Chromatog.*, 16 (1964) 376.
- 11 C. CERRAI, C. TESTA AND C. TRIULZI, *Energia Nucl. (Milan)*, 9 (1962) 377.
- 12 S. SIEKIERSKI, *J. Inorg. Nucl. Chem.*, 12 (1959) 129.
- 13 D. F. PEPPARD, G. W. MASON AND I. HUCHER, *J. Inorg. Nucl. Chem.*, 24 (1962) 881.
- 14 S. SIEKIERSKI AND R. J. SOCHACKA, *J. Chromatog.*, 16 (1964) 385.
- 15 S. SIEKIERSKI, *Nukleonika*, 9 (1964) 601.

J. Chromatog., 21 (1966) 460-470