THE SEPARATION OF THE RARE EARTHS BY PARTITION CHROMATOGRAPHY WITH REVERSED PHASES

PART I. BEHAVIOUR OF COLUMN MATERIAL

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The great similarities in the behaviour of the rare earth elements in aqueous solution have resulted in the separation of individual members being difficult to accomplish, and properties which can provide the basis of a method for the separation of the elements, usually differ so slightly through the series, that any fractionation process must be repeated many times to achieve isolation of a single lanthanide.

Thus early fractional crystallisation procedures proved long and tedious when valency differences could not be used[1], and it was only when the different distributions of the rare earths in solid cation-exchanger–aqueous complexing agent systems were exploited by chromatographic techniques, that practical separations were achieved[2]. Recently, however, it has been shown that certain liquid extractants can provide higher separation factors for the rare earths than have so far been obtained in cation-exchange systems[3], but again multiple equilibrations are required to isolate individual elements in the same valency state, and the difficulty of conveniently carrying out multiple small-scale liquid–liquid extractions has precluded their widespread application.

It would therefore appear that rare earth separations might be considerably simplified if liquid extractants could be incorporated into a scheme of chromatographic separation and thus combine the selectivity built into a suitable complexing agent with the technical advantages of chromatographic operation. The possibility of retaining a complexing agent on a solid supporting medium has already been considered[4–9], and columns of this type of material used for the separation of elements prior to analytical determination[10–13]. Clearly rare earth separations might be devised using this type of reversed phase partition technique, if a suitable complexing agent could be held sufficiently firmly on a solid support, and preliminary investigations indicated that the alkyl-phosphoric acid, di-(2-ethylhexyl) orthophosphoric acid (HDEHP), which has been shown to give the good average separation factor of 2.5 for adjacent rare earths[14], could be conveniently retained on a poly-(vinyl chloride/vinyl acetate) copolymer, (Corvic). Further, reaction between metal and ligand occurs rapidly, an essential requirement for elution peaks to be sharp. Reversed phase partition chromatography might also be expected to possess the advantages over conventional liquid–liquid extraction of reduced emulsification or physical entrainment of the extractant, reduced spill hazard, and more convenient operation in

restricted spaces (*e.g.* gloveboxes). In a short preliminary communication[15] the separation of all the rare earths by chromatographic elution from HDEHP–Corvic columns has been reported. In this paper some of the investigations carried out to assess the behaviour of the column material are described more fully.

EXPERIMENTAL

Column material

The poly-(vinyl chloride/vinyl acetate) copolymer, (Corvic, Imperial Chemical Industries Ltd.), used as solid support material was the commercially available product sieved to obtain particles of a suitable size (100–150 mesh).

HDEHP was obtained from two different commercial manufacturers and purified by a method based on that described elsewhere[16]. It was found that the distribution ratios for the extraction of a number of lanthanides from a perchloric acid phase into toluene solutions of the two different samples of HDEHP, after purification, matched within the limits of experimental error.

Column material was prepared by dissolving the requisite volume of HDEHP in a mixture of 3 ml of redistilled toluene and 5 ml of chloroform, and the resulting solution added to 10 g of the copolymer. Surplus organic solvent was evaporated off in a current of air and when constant weight had been achieved the powder containing the HDEHP stored for use. When required it was slurried with an aqueous phase and made up into a column in the usual way. Unless otherwise stated it will be assumed in this text that column material has been prepared by adding 2 ml of purified HDEHP to 10 g of the copolymer.

Radio tracers

Radio tracers were obtained by irradiating "Specpure" chemicals in a neutron flux of ~ 10^{12} n/cm^2/sec and after irradiation the γ-spectra and decay curves of these tracers examined for interfering radiations. Interference from impurities or daughter products was avoided by careful choice of irradiation and decay times, by the use of γ-spectrometry or by chemical separations. When chemical separation was necessary the required lanthanide was eluted from an HDEHP–Corvic column with perchloric acid at 60°.

Apparatus

All glassware was Pyrex. Chromatographic tubes used to contain the columns were 120 mm long × 5 mm diameter and were fitted with water jackets fed from a thermostat, so that the running temperature of the columns could be controlled. In all work reported in this paper, columns were maintained at 60° ± 0.5° since a series of preliminary experiments indicated that increasing the temperature increased the sharpness of the elution peaks. It was found that at 60° sharp elution peaks were obtained without bubble formation at the top of the column presenting any undue difficulty. Column effluents were passed through a drop counter to a fraction collector, and collected in volumes of 0.5 ml or less. The radioactivity of solutions was usually assayed by means of a 2 in. × 1$\frac{1}{2}$ in. NaI (Tl) well crystal, used with a simple scaler and timing set, but where γ-ray spectra were required a 3 in. × 3 in. NaI (Tl) crystal was used in conjunction with a 99 channel pulse analyser.

Capacity determinations

In order to obtain a value for the maximum quantity of element that could be extracted from aqueous solution by HDEHP–Corvic column material, 1.000 ± 0.003 g of polymer retaining the complexing agent was made up into a column and a standard solution of a lanthanide, "spiked" with radioactive tracer, was added as influent in very dilute perchloric acid. For different experiments both lanthanium and europium were used. When the activity of the effluent reached that of the influent, the column was washed with dilute perchloric acid until it was not possible to detect any further activity leaving the column, and the sorbed metal was eluted with 8 M perchloric acid. The effluent containing the metal that had been retained by the, column was then made up to a known volume and the metal concentration of this solution calculated after comparing the count of 2 ml with that of 2 ml of the original standard solution. In a series of experiments carried out with Corvic treated with toluene and chloroform but no HDEHP it was found that the amount of metal extracted was always less than 0.02 mg of lanthanide/g of column material.

Elutions

1.000 ± 0.003 g of HDEHP–Corvic column material was slurried with $N/500$ perchloric acid and made up to form a column 5 mm diameter × 10 cm long, thermostated to 60°. Lanthanide tracer was sorbed to form a thin band at the top of the column by adding a dilute solution of the metal in $N/500$ perchloric acid as influent, and the column was washed with $N/500$ perchloric acid. An elution curve was then obtained by eluting the lanthanide with the required aqueous phase, and monitoring the effluent for activity.

RESULTS AND DISCUSSION

It is essential that any column material that is to be used for chromatography may be prepared in reproducible form, and that its behaviour does not vary over the different time intervals that may elapse between preparation and use. Whilst liquid complexing agents are probably more readily purified than a solid material containing complexing groups chemically bound to the matrix, there might well be difficulty in obtaining reproducible behaviour from a column material prepared by sorbing the reagent onto a powdered solid. In order to assess the reliability of the method described in the experimental section for making up reproducible batches of column material, over 50 elutions of lanthanum from HDEHP–Corvic columns were carried out. The peak effluent volume for similar runs was found to vary by less than 3 % from the mean value, and to be independent, within the limits of experimental error, of the time that the column material had been allowed to stand between preparation and use (up to 11 days). Elution of europium from a sample of column material prepared 64 days before use was also carried out and the peak effluent volumes obtained were the same as obtained for freshly prepared material.

Capacity of column material

In order to assess the metal extraction capacity of HDEHP–Corvic mixtures, a series of batches of the column material were made up with different HDEHP loadings. HDEHP is known to be dimeric in benzene and naphthalene but monomeric in

ethylene glycol[16]. Assuming one exchangeable hydrogen ion for each acid dimer, the cation-exchange capacity of the column material, calculated from the added HDEHP is given in Table I, together with that found from metal adsorption measurements.

It can be seen in all cases that the added HDEHP appears to be available for complex formation with the rare earths and in fact more metal is extracted than would be expected on the assumption that 1 mole of M^{3+} combines with six formula weights

TABLE I

CAPACITY OF HDEHP–CORVIC MIXTURES OF DIFFERENT LOADINGS CALCULATED FROM AMOUNT OF HDEHP ADDED (A) AND METAL EXTRACTED AT SATURATION (B)

Mixture	Capacity of column material (m.quiv./g)		No. of determinations
	A	B	
1	0.070	0.090	5
2	0.099	0.150	4
3	0.135	0.223	7
4	0.194	0.276	5
5	0.247	0.322	16
6	0.298	0.408	4

(three dimer weights) of HDEHP. Investigations into the behaviour of HDEHP in liquid–liquid systems under metal rich conditions are severely limited by gel formation when the rare earth content of the organic phase is slightly in excess of the 1:6 metal–ligand ratio and therefore the reason for this behaviour is difficult to assess. No attempt has been made to calculate the degree of polymerisation of the HDEHP in the solid phase.

Flow rate

Reaction between HDEHP and the lanthanides is known to be rapid in liquid–liquid systems and if distribution of the elements also occurs quickly when the complexing agent is immobilised on a solid phase, efficient utilisation of the column will be favoured, resulting in sharp elution curves. The shape of the elution curves was found to improve as the running temperature of the column was increased, and 60° was eventually used as a convenient temperature at which good elutions could be achieved without any technical difficulty. Using the formula, number of theoretical plates $= 2 s (s - t)/d^2$, where $s =$ the volume of the eluate at peak maximum, $t =$ the interstitial column volume, and $d =$ half width of peak at 1/e of maximum solute concentration, the number of theoretical plates for different flow rates at 60° were calculated for the elution of lanthanides from HDEHP–Corvic columns. These results are recorded in Fig. 1. Completely constant flow rates were difficult to obtain due to the tendency of the columns to pack down slightly during flow of the liquid phase, and this gave rise to scatter of points, but it can be seen that at low flow rates the height of a theoretical plate is similar to that obtained when ion-exchangers are used for rare earth separations[17].

Elution of the elements

Distribution of a metal between an aqueous phase and a solid medium is usually most satisfactorily followed by batch extraction techniques and it has been found possible to investigate the behaviour of some complexes sorbed on solids by this method[8].
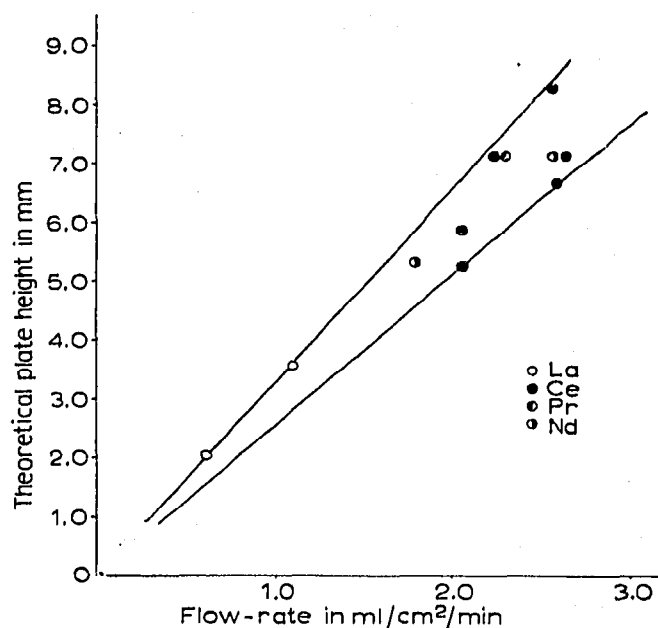

Fig. 1. Variation of plate height with flow rate.

However, after a number of preliminary extractions this technique was considered unsatisfactory for HDEHP–Corvic mixtures, since upon prolonged vigorous shaking, there was evidence that small quantities of HDEHP were washed off the more heavily loaded supports, consequently all distribution data were obtained from elution curves.

Equations have been derived for the chromatographic elution of elements from papers impregnated with ion-exchangers[18], and from phases consisting of complexing agents retained on columns[19] and paper strips[20]. In all cases the reaction between metal and column material is given by the equation:

$$M^{n+} + n \, HL_0 \rightleftharpoons ML_{n0} + n \, H^+$$
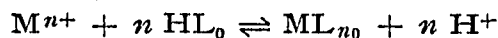
where the subscript o refers to species present in the solid phase. All these equations reduce to the form:

$$R_M = \log A_s/A_m + \log K^{11} + n \log [HL]_0 - n \log [H^+] \tag{1}$$

where the zone migration parameter $R_M = (1/R_F - 1)$ and A_s and A_m are the cross-sectional areas of the stationary and mobile phases respectively. Under conditions of constant ionic strength concentrations are often used in place of activities when the constant K^{11} then refers to a standard set of conditions.

Consequently it can be seen that if the column parameter A_s/A_m, the constant K^{11} and the HDEHP loading of the column do not vary there should be a linear

dependency of R_M upon the log of the hydrogen ion concentration of the aqueous elutrient, the slope being — n. Further, at constant acidity there should be an n'th power dependency of $(1/R_F — 1)$ upon $[HL]_0$, but in this case it is unlikely that concentrations may reasonably be used in place of activities. The value of n has been found to be 3 for the extraction of the lanthanides by HDEHP in liquid–liquid systems, and results obtained for the elution of europium from Corvic columns of different HDEHP loadings, which are presented on a plot of R_M *versus* log $[H^+]$ in Fig. 2, again indicate a value of 3 for n in all cases. Thus similar acid dependencies are obtained for column operation and for equilibrium liquid–liquid measurements and are independent of HDEHP loadings over the values investigated. Similar results have been reported using paper impregnated with HDEHP[20]. Whilst perchloric
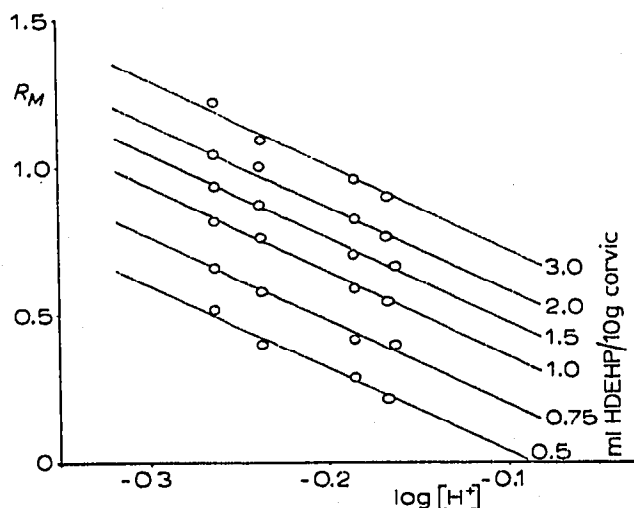

Fig. 2. Elution of europium by perchloric acid from Corvic columns retaining varying amounts of HDEHP.

acid only was used for these experiments and the ionic strength of the aqueous phase was not maintained constant, the differences that occurred were found not to affect the position of the peak maximum over quite large changes in perchlorate ion concentration. No attempt was made to relate R_M to $[HL]_0$ since the nature of the non-aqueous phase is not yet known, but from Fig. 2 it can be seen that an increase in column loading is accompanied by an increase in R_M.

CONCLUSIONS

Suitable columns for the chromatographic elution of the rare earths can be made up from HDEHP–Corvic mixtures. Batches can be prepared with reproducible elution behaviour, and the peak effluent volume of the eluted element does not appear to be dependent upon the time that is allowed to elapse between preparation and use of the column material over the periods investigated. The capacity of the columns used in these determinations is lower than that of a number of ion-exchangers but elution of the elements is by aqueous acid solutions and the height of an equivalent theoretical plate at low flow rates approaches that obtained in conventional ion-exchanger–complexing agent systems. However, the actual separation of individual

rare earths from each other will be dependent upon the good separation factors which are found when HDEHP is used for liquid extractions, prevailing when the HDEHP is sorbed on Corvic. Whilst the third power dependency of $(1/R_F - 1)$ on the hydrogen ion concentration of the eluting phase indicates close similarities in the performance of HDEHP in the liquid–liquid and liquid–solid systems, clearly for a more comprehensive comparison it is necessary to have data for the behaviour of all the rare earths in the two cases. This will be considered in the second paper in this series.

SUMMARY

The complexing agent di-(2-ethylhexyl) orthophosphoric acid, which is known to have a good average separation factor for adjacent rare earths, has been retained on a poly-(vinyl chloride/vinyl acetate) copolymer, and this mixture used as column material for chromatographic elution of the rare earths. This column material can be conveniently prepared with reproducible behaviour, sharp elution peaks being obtained at a running temperature of 60°, and a third power dependency of $(1/R_F - 1)$ upon the hydrogen ion concentration of the eluting phase is found at several different loadings of the polymer with complexing agents.

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