

REVERSED-PHASE CHROMATOGRAPHY OF ALKALINE EARTHS ON PAPER TREATED WITH DI-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID IN CHLORIDE MEDIUM

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INTRODUCTION

In a previous paper¹ the chromatographic behaviour of alkali metals and alkaline earths was investigated, using papers treated with organic solutions of di-(2-ethylhexyl) orthophosphoric acid (HDEHP), the eluent being acetic acid.

As in the case of the chromatographic separation of rare earths², similarity was found between results of liquid-liquid experiments reported in the literature and data obtained in chromatographic investigation.

In the present work the behaviour of alkaline earths in reversed-phase paper chromatography has been further investigated, using hydrochloric acid solutions as the eluents. The R_F values of calcium, strontium, barium, magnesium and beryllium were determined as functions of the HDEHP concentration and of the molarity of the hydrochloric acid used as eluent.

EXPERIMENTAL

Reagents, equipment and treatment of paper

The reagents and equipment used in this work have already been described¹.

Chromatographic paper was treated with cyclohexane solutions of HDEHP previously equilibrated with 2.5 *M* HCl solutions according to the usual procedure². Paper sheets were carefully washed with a 1 *M* HCl solution and rinsed with distilled water before treatment with HDEHP.

Chromatographic procedure

Application of spots, chromatographic procedure and development of spots were generally the same as described previously¹. For the detection of Ba²⁺ spots, however, tetrahydroxyquinone³ was preferred to sodium alizarinsulphonate. The spots became immediately visible on spraying a 0.1 % solution in ethanol of this reagent on paper previously exposed to ammonia vapours.

The main work was performed with five different concentrations of HDEHP in cyclohexane, namely 0.010, 0.025, 0.050, 0.075 and 0.100 *M*; experiments were also performed with intermediate concentrations.

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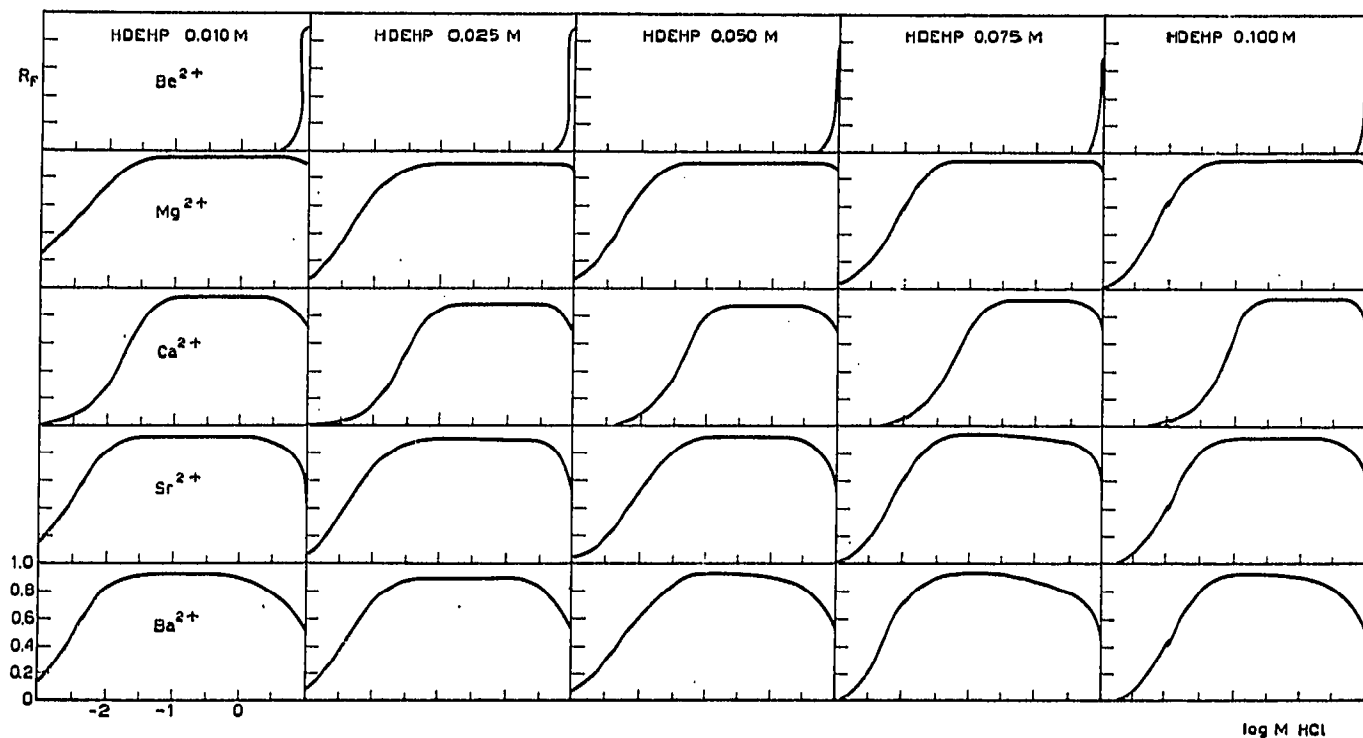


Fig. 1. R_F values of alkaline earth ions plotted *vs.* $\log M \text{ HCl}$. Paper treated with HDEHP.

Each result was checked at least once under the same conditions, except for a few cases in which the relative position of results at various concentrations left no doubt as to their reliability. Reproducibility of the R_F values within $\pm 3\%$ was considered satisfactory, because of the shortness of the chromatograms and of the difficulty often encountered in obtaining an exact view of the real shape of the eluted and developed spots.

RESULTS AND DISCUSSION

Typical experimental R_F values for alkaline earth ions are collected in Table I as functions of the molarity of the hydrochloric acid used as eluent for papers treated with 0.010 M, 0.025 M, 0.050 M, 0.075 M and 0.100 M solutions of HDEHP in cyclohexane.

In Fig. 1, the results are plotted against the log of the hydrochloric acid concentration. Although experiments were carried out in a range of acidity from 1 M to $1 \cdot 10^{-4}$ M HCl, concentrations lower than $1 \cdot 10^{-3}$ M were omitted in plotting Fig. 1 since the results were of little interest.

The results collected in Fig. 1 agree qualitatively with those reported by PEPPARD *et al.* for the liquid-liquid extraction of calcium, strontium and barium⁴.

The decrease in R_F values at very high hydrochloric acid concentrations, particularly noticeable in the case of strontium and barium, was also verified when acetic acid was used as eluent; this problem was also discussed in the previous paper¹.

By applying the equation

$$\log E_a^0 = \log \left(\frac{1}{R_F} - 1 \right) + k \quad (1)$$

TABLE I

R_F VALUES FOR ALKALINE EARTH IONS AS FUNCTIONS OF THE MOLARITY OF THE HCl ELUENT.
PAPER TREATED WITH HDEHP.

Operating temperature $23^\circ \pm 1^\circ$

| HDEHP molarity | Cations | R_F | | | | | | | | | |
|-------------------|------------------|--------------|------|------|------|------|------|------|-------|-------|--------|
| | | HCl molarity | | | | | | | | | |
| | | 10 | 7 | 2.5 | 1 | 0.1 | 0.04 | 0.01 | 0.004 | 0.001 | 0.0002 |
| 0.010 | Be ²⁺ | 0.85 | 0.28 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Mg ²⁺ | 0.87 | 0.85 | 0.94 | 0.94 | 0.92 | 0.92 | 0.73 | 0.49 | 0.20 | 0.20 |
| | Ca ²⁺ | 0.79 | 0.81 | 0.89 | 0.95 | 0.93 | 0.80 | 0.25 | 0.10 | 0.03 | 0.00 |
| | Sr ²⁺ | 0.53 | 0.78 | 0.85 | 0.90 | 0.89 | 0.92 | 0.80 | 0.48 | 0.12 | 0.10 |
| | Ba ²⁺ | 0.56 | 0.67 | 0.81 | 0.90 | 0.89 | 0.87 | 0.80 | 0.45 | 0.12 | 0.10 |
| 0.025 | Be ²⁺ | 0.84 | — | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Mg ²⁺ | 0.88 | 0.90 | 0.93 | 0.89 | 0.85 | 0.88 | 0.71 | 0.60 | 0.16 | 0.10 |
| | Ca ²⁺ | 0.75 | 0.90 | 0.91 | 0.84 | 0.59 | 0.35 | 0.13 | 0.06 | 0.00 | 0.00 |
| | Sr ²⁺ | 0.59 | 0.87 | 0.93 | 0.88 | 0.83 | 0.84 | 0.69 | 0.58 | 0.15 | 0.10 |
| | Ba ²⁺ | 0.54 | 0.83 | 0.92 | 0.88 | 0.84 | 0.84 | 0.69 | 0.62 | 0.19 | 0.10 |
| 0.050 | Be ²⁺ | 0.71 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Mg ²⁺ | 0.88 | 0.88 | 0.93 | 0.93 | 0.91 | 0.89 | 0.82 | 0.66 | 0.31 | 0.00 |
| | Ca ²⁺ | 0.71 | 0.85 | 0.87 | 0.88 | 0.80 | 0.54 | 0.19 | 0.06 | 0.00 | 0.00 |
| | Sr ²⁺ | 0.49 | 0.82 | 0.91 | 0.90 | 0.92 | 0.86 | 0.70 | 0.50 | 0.24 | 0.07 |
| | Ba ²⁺ | 0.50 | 0.75 | 0.90 | 0.90 | 0.95 | 0.86 | 0.69 | 0.58 | 0.33 | 0.06 |
| 0.075 | Be ²⁺ | 0.70 | 0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Mg ²⁺ | 0.95 | 0.95 | 0.92 | 0.92 | 0.91 | 0.91 | 0.75 | 0.27 | 0.13 | 0.04 |
| | Ca ²⁺ | 0.85 | 0.92 | 0.92 | 0.92 | 0.71 | 0.32 | 0.08 | 0.00 | 0.00 | 0.00 |
| | Sr ²⁺ | 0.59 | 0.80 | 0.87 | 0.90 | 0.95 | 0.93 | 0.78 | 0.24 | 0.06 | 0.00 |
| | Ba ²⁺ | 0.55 | 0.67 | 0.81 | 0.84 | 0.92 | 0.91 | 0.78 | 0.30 | 0.10 | 0.00 |
| 0.100 | Be ²⁺ | 0.78 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Mg ²⁺ | 0.88 | 0.92 | 0.93 | 0.93 | 0.96 | 0.93 | 0.83 | 0.65 | 0.32 | 0.02 |
| | Ca ²⁺ | 0.69 | 0.89 | 0.93 | 0.93 | 0.67 | 0.35 | 0.16 | 0.04 | 0.02 | 0.00 |
| | Sr ²⁺ | 0.57 | 0.77 | 0.88 | 0.95 | 0.95 | — | 0.77 | 0.44 | 0.17 | 0.01 |
| | Ba ²⁺ | 0.59 | 0.67 | 0.84 | 0.90 | 0.95 | — | 0.77 | 0.43 | 0.17 | 0.01 |

where E_a° is the extraction coefficient of a given element in the liquid-liquid system, and k is a constant that depends on the experimental conditions, the chromatographic R_F value can be used to elucidate some aspects of the extraction mechanism².

The equilibrium generally accepted as representing the extraction mechanism of metallic cations by dialkyl esters of orthophosphoric acid, may be written as



where M^{b+} is the cation having the valency b , and HY is the extractant molecule disregarding its degree of polymerization.

PEPPARD *et al.*^{5,6} have proved HDEHP to be dimeric in solvents such as cyclohexane, which is used in this work. Thus eqn. (2) may be written as



where the extracted species has been indicated without giving any information as to how the extractant is bound to the metallic atom. According to PEPPARD *et al.*⁷ single ionization of the dimer $(\text{HDEHP})_2$ occurs, followed by chelation with the metal. More recently McDOWELL AND COLEMAN⁸ have suggested double ionization of the dimer together with coordination of the other molecules of the acid, in the monomeric form, around the metal, to satisfy the metal coordination number. As in the case of the acetate system¹, the latter hypothesis has been adopted here.

From eqns. (1) and (3) the following relationship can be written

$$\log \left(\frac{1}{R_F} - 1 \right) = c \log [\text{HDEHP}]_{\text{eff}} - b \log [\text{H}^+] + K \quad (4)$$

where $[\text{HDEHP}]_{\text{eff}}$ is the effective HDEHP concentration on paper and K is a term containing the logarithm of the equilibrium constant of reaction (3).

In the case of liquid-liquid systems the analogous equation, $\log E_a^\circ = c \log [(\text{HDEHP})_2] - b \log [\text{H}^+] + \text{constant}$, was shown to hold in the case of the HDEHP extraction of lanthanides (III) and actinides (III) as summarized by PEPPARD AND MASON⁹. The expected value 3 for b , and the same value for c was found in that case. The same results were obtained in the paper chromatography of rare earth elements provided that the HDEHP concentration was expressed as the effective concentration, $[\text{HDEHP}]_{\text{eff}}$, of the extractant in the stationary phase and not as the nominal concentration of the solution used to treat the paper^{1,2}.

Liquid-liquid extraction of alkaline earth ions with HDEHP solutions^{4,8} from inorganic acid solutions gave the expected value of 2 for b and the value of c was 3.

To investigate the analogous chromatographic behaviour, in Figs. 2, 3, 4 and 5 the plots have been reported of $\log (1/R_F - 1)$ vs. $\log [\text{H}^+]$ for Ca^{2+} , Mg^{2+} , Sr^{2+} and Ba^{2+} respectively. Beryllium was not included because, as shown in Fig. 1, it is firmly held by the stationary phase throughout a wide range of HCl and HDEHP concentrations. Hydrogen ion concentration, in the range considered, may be assumed to be equal to the hydrochloric acid concentration. In these figures straight lines with different slopes were drawn and the experimental results compared to them. It can be noted for later discussion that very few of these lines have the expected slope of -2 .

On the other hand in the plot shown in Fig. 6 of $\log (1/R_F - 1)$ against the

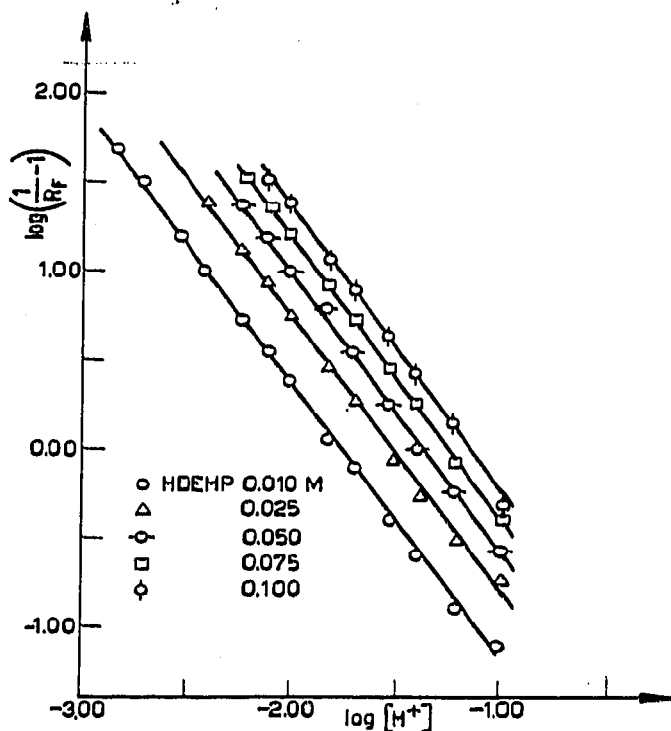


Fig. 2. Plot of $\log (1/R_F - 1)$ vs. $\log [H^+]$ for calcium. Paper treated with HDEHP at various concentrations. Slope = -1.5.

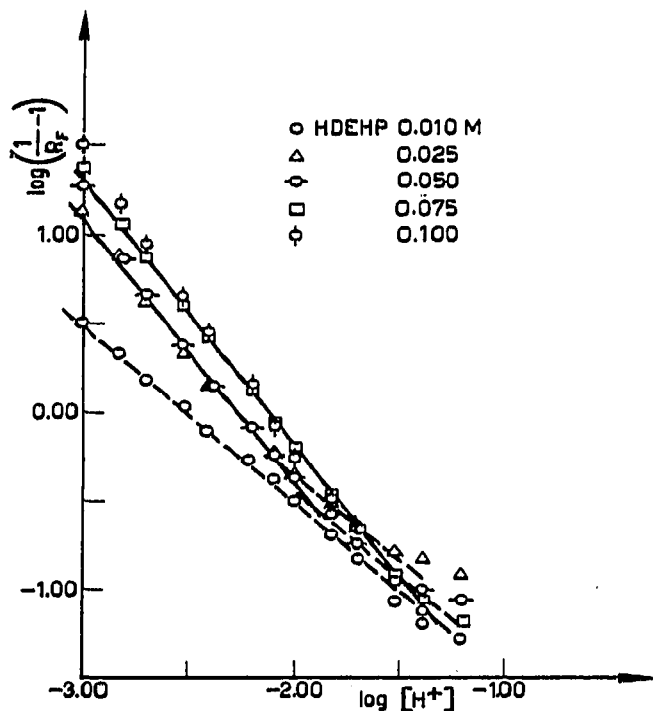


Fig. 3. Plot of $\log (1/R_F - 1)$ vs. $\log [H^+]$ for magnesium. Paper treated with HDEHP at various concentrations. Slopes = -1.5 (solid lines); -1.0 (dashed lines).

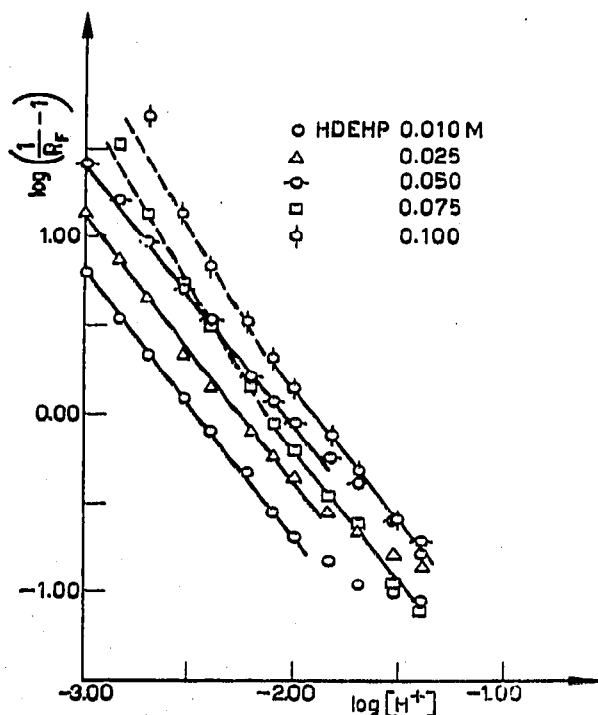


Fig. 4. Plot of $\log (1/R_F - 1)$ vs. $\log [H^+]$ for strontium. Paper treated with HDEHP at various concentrations. Slopes = -1.5 (solid lines); -2.0 (dashed lines).

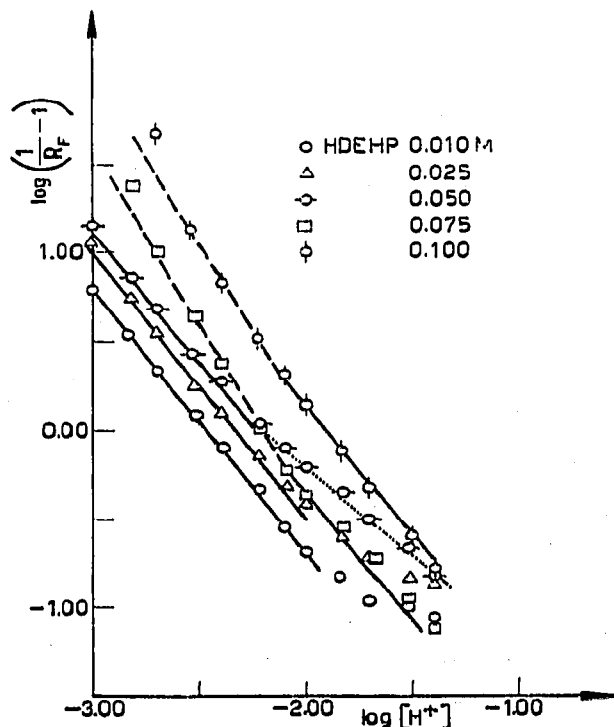


Fig. 5. Plot of $\log (1/R_F - 1)$ vs. $\log [H^+]$ for barium. Paper treated with HDEHP at various concentrations. Slopes = -1.5 (solid lines); -2.0 (dashed lines); -1.0 (dotted line).

logarithm of the effective HDEHP concentration on paper, straight lines having the expected slope of + 3 can be drawn. The effective HDEHP concentration was evaluated following the procedure reported in the previous paper¹. The two curves refer to Ca^{2+} and Sr^{2+} ; Ba^{2+} and Mg^{2+} , when eluted with HCl under the same conditions as Sr^{2+} , give analogous curves which lie very close to that of strontium. In order to have more information on this behaviour, simultaneous elutions were carried out with

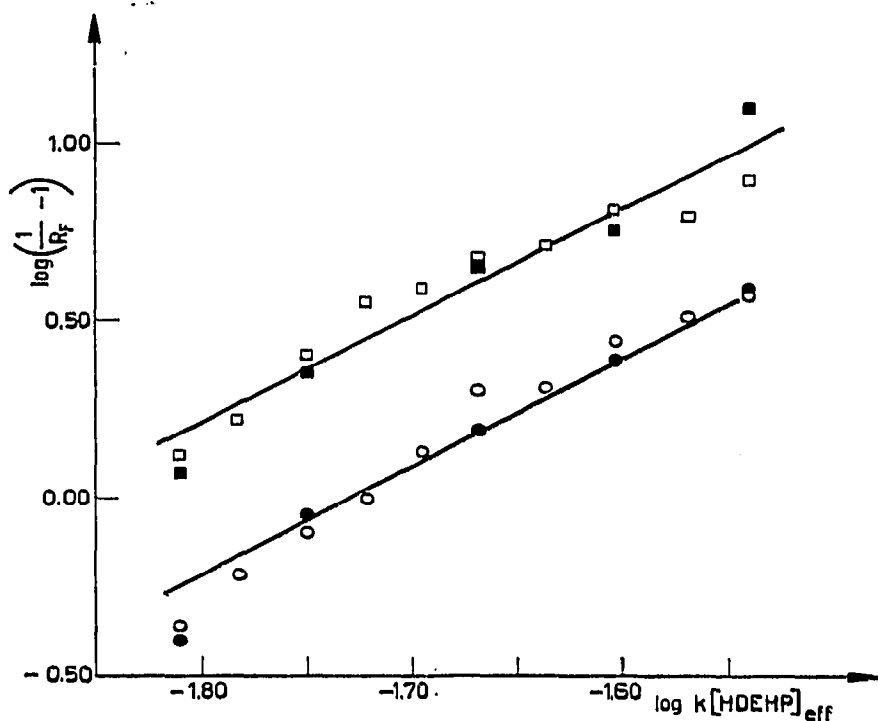


Fig. 6. Plot of $\log(1/R_F - 1)$ vs. $\log k [\text{HDEHP}]_{\text{eff}}$ for calcium eluted with $0.03 M$ HCl (circles), and strontium eluted with $0.003 M$ HCl (squares). Data from Table II (open symbols) and data from plots in Figs. 2 and 4 (closed symbols).

paper treated with HDEHP solutions at ten different concentrations. Whatman CRL/1 paper strips were used, cut from complete sheets each treated with a different HDEHP concentration. The results are collected in Table II. From this table, data referring to calcium and strontium are shown in Fig. 6 as open symbols. The closed symbols refer to data derived from plots given in Figs. 2 and 4.

From the results of Figs. 2 to 6 it appears that although a relationship such as that shown in equation (4) holds, the values obtained for b are often lower than the stoichiometric value 2 characteristic of the ion involved and confirmed in the liquid-liquid experiments referred to above.

The strontium and barium lines showed the expected -2 slope, giving a value of 2 for b , only when paper treated with 0.075 and $0.100 M$ HDEHP was used and eluted with HCl at a concentration less than $0.01 M$.

In some cases a value of b smaller than the cation valency was also reported in the literature for liquid-liquid extraction with HDEHP. PEPPARD *et al.*¹⁰ have shown that in the extraction of thorium(IV) by HDEHP in toluene from aqueous nitrate, perchlorate and chloride solutions, an inverse third (instead of fourth) power dependence of E_a° on H^+ concentration occurs when the acidity is high. This dependence

TABLE II

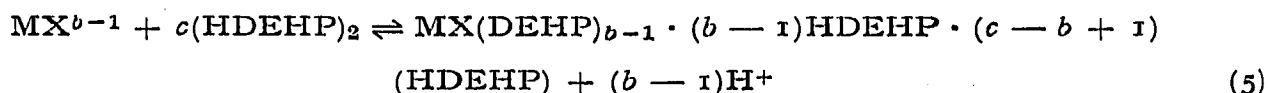
R_F VALUES FOR ALKALINE EARTH IONS ELUTED WITH HCl, AS FUNCTIONS OF HDEHP CONCENTRATION OF THE SOLUTION USED TO TREAT THE PAPER.

Operating temperature $23^\circ \pm 1^\circ$

| HCl molarity | Cations | R_F | | | | | | | | | |
|-----------------|------------------|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | HDEHP molarity | | | | | | | | | |
| | | 0.010 | 0.017 | 0.025 | 0.033 | 0.041 | 0.050 | 0.061 | 0.075 | 0.087 | 0.100 |
| 0.03 | Ca ²⁺ | 0.67 | 0.60 | 0.53 | 0.48 | 0.40 | 0.31 | 0.31 | 0.25 | 0.22 | 0.20 |
| 0.01 | Mg ²⁺ | 0.81 | 0.83 | — | 0.71 | 0.68 | — | 0.62 | 0.65 | 0.66 | — |
| | Ca ²⁺ | 0.28 | — | — | 0.11 | 0.09 | 0.08 | 0.04 | — | 0.02 | — |
| | Sr ²⁺ | 0.77 | 0.77 | 0.71 | 0.70 | 0.74 | 0.66 | 0.59 | 0.59 | 0.56 | 0.47 |
| | Ba ²⁺ | 0.79 | 0.75 | 0.70 | 0.68 | 0.71 | 0.65 | 0.66 | 0.62 | 0.65 | 0.62 |
| 0.003 | Mg ²⁺ | 0.51 | 0.46 | 0.34 | 0.29 | 0.26 | 0.25 | 0.19 | 0.21 | 0.20 | 0.15 |
| | Sr ²⁺ | 0.42 | 0.36 | 0.28 | 0.21 | 0.20 | 0.17 | 0.15 | 0.13 | 0.14 | 0.11 |
| | Ba ²⁺ | 0.46 | 0.41 | 0.30 | 0.30 | 0.22 | 0.25 | 0.18 | 0.21 | 0.21 | 0.14 |

extends to the low acidity with nitrate systems. Such results were explained by postulating that thorium is extracted as both metallic cation Th⁴⁺ and ThX³⁺ complex with the acid anion X⁻. This hypothesis was experimentally confirmed by means of infrared absorption measurements, which revealed the presence of NO₃⁻ in the extracted species for thorium, cerium, hafnium, and zirconium¹¹. Further examples are given for neptunium extracted as Np(NO₃)³⁺ in the HDEHP (toluene) *versus* perchlorate + nitrate system⁹ and for beryllium with HDEHP (toluene) in nitrate, sulphate and chloride systems^{12,13}. In this case, plots of log E_a° vs. log[H⁺] show E_a° values at high acid concentration greater than expected from the -2 slope that is obtained with more dilute solutions.

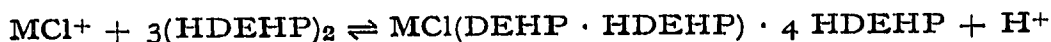
Though only the behaviour reported for beryllium concerns a chloride system in the field of alkaline earths, and thus directly refers to the present investigation, the great number of examples reported already suggest that in this case also, as in that of an acetate system, the formation of a compound where the cation is surrounded by both the inorganic anion and HDEHP is responsible for the slopes found in Figs. 2 to 5. It therefore follows that, together with the equilibrium represented by equation (2), the following equilibrium should also hold



The combination of the two equilibria gives a value of b in eqn. (4) lying between 2 and 1, as actually results from this investigation.

As reported above, the value 3 of the coefficient c was expected on the basis of liquid-liquid extraction data. There is, however, a tendency to a minor slope at high HDEHP concentration. At very high HDEHP concentrations a second-power dependence was found to exist between E_a° and the extractant concentration for alkaline earths^{14,15} in chloride systems.

In conclusion, from eqns. (3) and (5) the equilibria can be written as:



These equations would explain the mechanism of the retention of alkaline earth ions on paper treated with HDEHP and eluted with hydrochloric acid. High concentrations of acid, as well as low amounts of HDEHP on paper, seem to favour the second equilibrium. Moreover, the value 3 of the $(HDEHP)_2$ coefficient is affected at a high extractant concentration. Probably at still higher concentrations, a value between 3 and 2 should be postulated (and hence some different kind of equilibrium) to justify the experimental results.

Application to chromatographic separations

From the results described above, it appears that many interesting chromatographic separations are feasible.

Various chromatograms were obtained by the ascending technique on 3×40 cm strips cut from Whatman No. 1 paper sheets perpendicularly to the machine direction. The paper was treated with HDEHP in the same way as the CRL/r sheets used in the basic work. Conditions were chosen on the basis of the curves reported in Fig. 1. The chromatographic behaviour of elements included in the present experiments other than alkaline earths was known from work carried out in our laboratory, part of which has been published elsewhere².

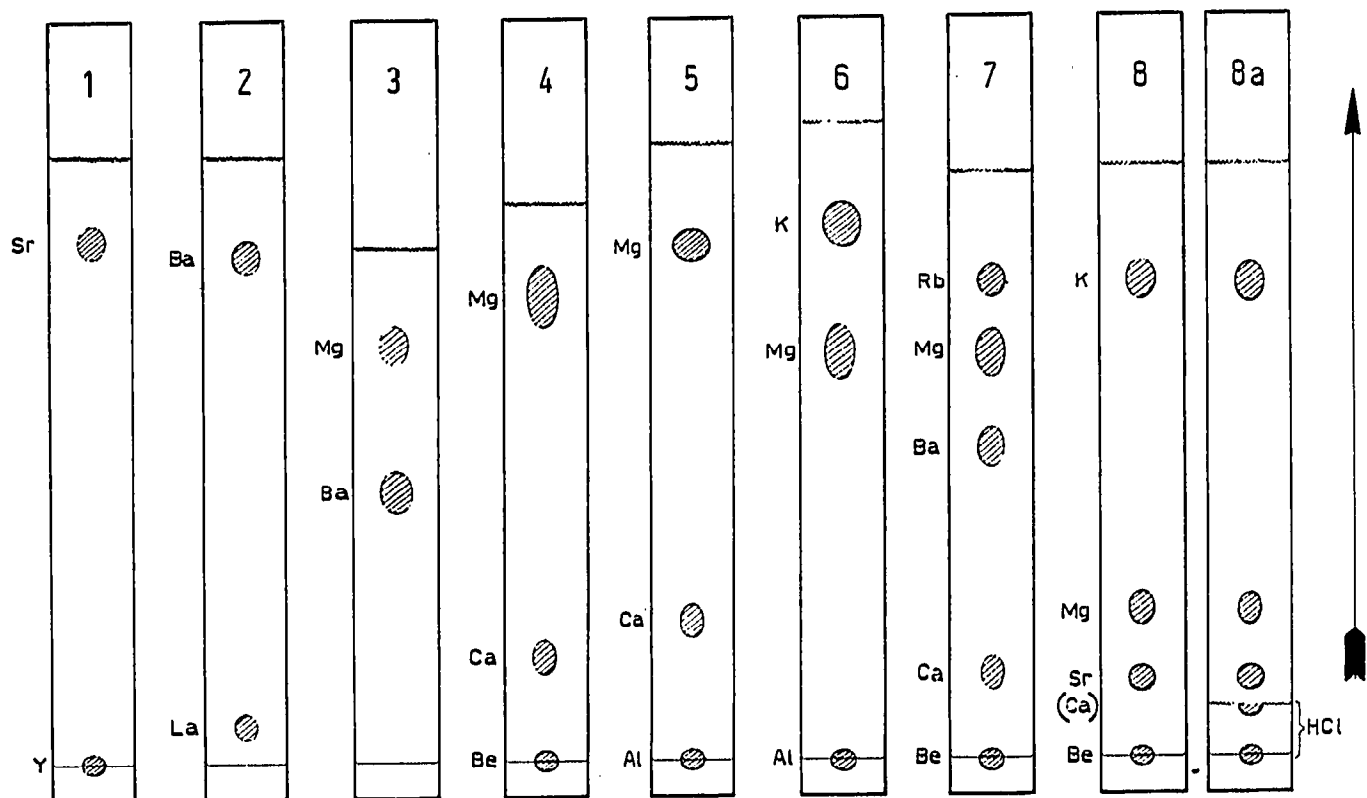


Fig. 7. Diagrams of the separations quoted in Table III.

TABLE III
 ASCENDING CHROMATOGRAMS OBTAINED WITH 3 X 40 CM PAPER STRIPS TREATED WITH HDEHP
 Operating temperature $23^{\circ} \pm 1^{\circ}$

| No. | Separations | Run (cm) | HDEHP (M) | Eluent | R_F |
|-----|----------------|-------------|--------------|-----------------------------------------|--------------------------------------------------------|
| 1 | Y-Sr | 34.5 | 0.100 | 0.10M HCl | Y = 0.00; Sr = 0.85 |
| 2 | La-Ba | 34.5 | 0.100 | 0.10M HCl | La = 0.06; Ba = 0.83 |
| 3 | Ba-Mg | 29.2 | 0.075 | 9M HCl | Ba = 0.52; Mg = 0.80 |
| 4 | Be-Ca-Mg | 31.8 | 0.100 | 0.05M HCl | Be = 0.00; Ca = 0.18; Mg = 0.82 |
| 5 | Al-Ca-Mg | 35.0 | 0.100 | 0.05M HCl | Al = 0.00; Ca = 0.22; Mg = 0.83 |
| 6 | Al-Mg-K | 36.3 | 0.100 | 0.01M HCl | Al = 0.00; Mg = 0.63; K = 0.83 |
| 7 | Be-Ca-Ba-Mg-Rb | 33.2 | 0.010 | 3.2M CH ₃ COOH | Be = 0.00; Ca = 0.14; Ba = 0.53; Mg = 0.69; Rb = 0.82 |
| 8 | Be(Ca)-Sr-Mg-K | 33.7 | 0.100 | 2.5M CH ₃ COOH | Be(Ca) = 0.00; Sr = 0.13; Mg = 0.25; K = 0.80 |
| 8a | Be-Ca-Sr-Mg-K | 33.7 | 0.100 | 2.5M CH ₃ COOH 0.25M HCl* | Be = 0.00; Ca = (0.08); Sr = 0.13; Mg = 0.25; K = 0.80 |

* Elution 8a is the same as elution 8 in which an additional HCl elution for a distance of 2.7 cm has been performed to resolve the Be-Ca pair.

Table III collects data of some of the separations obtained, and their diagram is shown in Fig. 7.

In order to compare the acetate system¹ with the chloride system two separations with acetic acid as eluent were also included. They show how the HDEHP-acetic acid system offers even more possibilities of separation than the HDEHP-hydrochloric acid system.

Since the separation obtained by a single elution with acetic acid on paper treated with 0.010 *M* HDEHP (No. 8 in Fig. 7) has the disadvantage of the small retention capacity of paper, the chromatogram was repeated with 0.100 *M* HDEHP treated paper. A double elution was performed first with more concentrated acetic acid, and then, to resolve the pair Ca²⁺-Ba²⁺, with hydrochloric acid.

In conclusion, in spite of a somewhat greater versatility of the HDEHP-acetate system with respect to the separation of alkaline earths, the chloride systems are of certain interest, since in most cases a chloride solution of the elements is available.

SUMMARY

Reversed-phase chromatography of alkaline earth metals on paper treated with di-(2-ethylhexyl) orthophosphoric acid (HDEHP) has been investigated, using hydrochloric acid as eluent in a range of concentrations from 10 *M* to $1 \cdot 10^{-4}$ *M*.

The quantity $(1/R_F - 1)$ has been related to the hydrogen ion concentration in the mobile phase, and to the effective HDEHP concentration on the paper.

The chromatographic behaviour has been correlated with that of liquid-liquid extraction systems.

Chromatographic separations of alkaline earths from each other, and from other cations, were performed. Two of them were obtained with acetic acid elutions.

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