

# REVERSED-PHASE CHROMATOGRAPHY OF ALKALI METALS AND ALKALINE EARTHS ON PAPER TREATED WITH DI-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID IN ACETATE MEDIUM

E. CERRAI AND G. GHERSINI

*Laboratori C.I.S.E., Segrate, Milan (Italy)\**

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## INTRODUCTION

Reversed-phase chromatography with paper supporting di-(2-ethylhexyl) orthophosphoric acid (HDEHP) was found useful for the separation of rare earths<sup>1</sup>.

The investigation has now been extended to the separation of alkali and alkaline earth metals. Paper treated with organic solutions of HDEHP was used and  $R_F$  values were determined as functions of the HDEHP concentration and of the acidity of the eluent. Aqueous solutions of acetic acid at different molarities were used as the eluents.

## EXPERIMENTAL

### *Reagents and equipment*

Di-(2-ethylhexyl) orthophosphoric acid (HDEHP) was a Virginia-Carolina Chemical Co. (Richmond, U.S.A.) product supplied by Soc. Eigenmann and Veronelli (Milan), and was used in cyclohexane solution.

The alkali and alkaline earth metals were used as RP grade chlorides, supplied by Carlo Erba (Milan). Stock 0.1 *M* solutions of pure chlorides, titrated with  $\text{AgNO}_3$ , were diluted to obtain 0.005*N* solutions. Since the drops applied to the paper were no more than 0.2 ml each, up to  $1 \cdot 10^{-7}$  equivalent of each element was spotted.

Chromatographic paper Whatman No. 1, CRL/1 type, was used for multiple experiments, whilst ordinary  $3 \times 40$  cm Whatman No. 1 paper strips were used for normal ascending and descending chromatograms.

For multiple experiments with CRL/1 type sheets, the chromatographic assembly shown in Fig. 1 was used. It consists of a Witt apparatus, in which a pyrex crystallizer is placed. A glass device on the crystallizer supports the sheet of paper. A long-stemmed separating funnel is fitted in the cover, and a stopcock is used to prevent increase of pressure in the apparatus when the eluting solution is transferred from the funnel to the crystallizer. A battery of five of these assemblies enabled us to perform up to fifteen different multiple developments a day. Ascending and descending chromatograms with single paper strips were carried out with ordinary glass ground-cover columns.

\* Address: C.I.S.E., Casella Postale 3986, Milano, Italia.

*Treatment of paper and chromatographic procedure*

Treatment of chromatographic paper with HDEHP has been already described<sup>1</sup>. In normal experiments, HDEHP solutions in cyclohexane were equilibrated for 20 min with a 2.5M solution of acetic acid. Since the experiments being performed

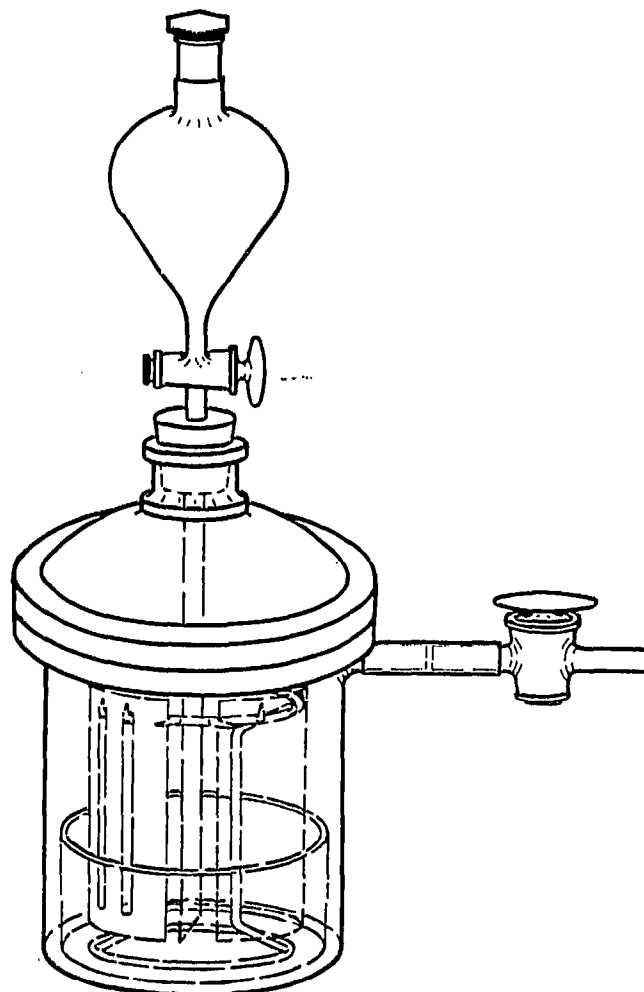


Fig. 1. Experimental apparatus for multiple development.

dealt with alkali and alkaline earth metals, paper sheets were carefully washed before HDEHP treatment with a 1 M solution of acetic acid, following the procedure described elsewhere in which 0.1M HCl was used<sup>2</sup>. After drying, the paper was immersed in the equilibrated HDEHP solution for 30 sec, then allowed to drip and dried in a current of warm air.

Spots were applied using 0.01 to 0.02 ml of solution (*i.e.* 0.5 —  $1.0 \cdot 10^{-7}$  equiv.). Each sheet of the CRL/1 type paper was hung on the glass device and placed for ascending elution inside the assembly shown in Fig. 1. At first, a small amount of the acid was allowed to enter the apparatus to saturate the atmosphere; after 15 min its level was raised to touch the paper, and development began.

When the front had moved about 9 cm, the paper was quickly removed from the apparatus and, after the front had been marked, was dried first with warm air and then in an oven at 40 to 50° for several hours.

Much trouble was encountered in revealing the spots, because of the very small amount of ions used, together with a slight acidity retained by the paper even after prolonged drying. To detect  $\text{Li}^+$  spots, an alcoholic solution of 0.1 g/100 ml of 1-amino-5-hydroxyanthraquinone was sprayed on the paper<sup>3</sup>. The spots became visible on exposing the strips to ammonia vapours. Better results were sometimes obtained by dipping the strips in a 0.1 *N* NaOH solution.  $\text{Na}^+$  spots were detected as sodium zinc uranyl acetate, visible in U.V. light. Strips were dipped into the developing solution prepared according to BARBER AND KOLTHOFF<sup>4</sup>. Checks were also performed using <sup>22</sup>Na tracer.  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  spots were made visible as alkali lead cobaltinitrites; the paper was sprayed with the solution recommended by MILLER AND MAGEE<sup>5</sup>.  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  spots were clearly visible in U.V. light after spraying the strips with 0.1% 8-hydroxyquinoline solution in 50% alcohol, and exposing them to ammonia vapours<sup>6</sup>. To detect  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , the strips were treated with a 0.5% sodium alizarinsulphonate solution in water<sup>7</sup>. The spots became visible a few minutes after spraying and exposing the strips to ammonia vapours.

Most of the work was performed with two different concentrations of HDEHP in cyclohexane solutions, namely 0.100 and 0.010 *M*; experiments were also performed with 0.075, 0.050 and 0.025 *M* HDEHP, with particular attention to 0.050 *M*.

Elutions were made using different concentrations of acetic acid. When the concentration of the acid used was low, de-aerated water was used to prevent any effect of dissolved  $\text{CO}_2$  on the pH determination. Each point was checked at least once under the same conditions, except in 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. Where bigger discrepancies appeared, as in the case of very high acetic acid concentrations, several chromatograms were run and the average result was taken.

## RESULTS AND DISCUSSION

### General

Experimental  $R_F$  values for alkali and alkaline-earth ions are shown in Table I as functions of the molarity of the acid eluent for paper treated with 0.010 and 0.100 *M* HDEHP. In Fig. 2 results are plotted against the log of acetic acid concentration.

As already pointed out<sup>1</sup>, the relationship between the extraction coefficient  $E_a^0$  for a given element in a liquid-liquid extraction and the  $R_F$  value in a chromatographic system in which the same extractant is used as the stationary phase and the same inorganic solution is used as the eluent, can be written as:

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

where  $k$  is a constant that depends on the experimental conditions. Information can therefore be obtained on the extraction mechanism, responsible for the retention by the stationary phase of the cations involved, by studying the behaviour of the quantity  $(1/R_F - 1)$  as a function both of the concentration of hydrogen ion in the aqueous phase (since HDEHP acts as a cationic exchanger) and of the concentration

TABLE I

 $R_F$  VALUES FOR ALKALI AND ALKALINE EARTH IONS AS FUNCTIONS OF THE MOLARITY OF THE  $\text{CH}_3\text{COOH}$  ELUENTPaper treated with 0.010 and 0.100M HDEHP. Operating temperature  $23^\circ \pm 1^\circ$ 

HDEHP molarity	Cations	$R_F$									
		$\text{CH}_3\text{COOH}$ molarity									
		0.01	0.03	0.05	0.1	0.2	0.3	0.5	1	2.5	3
0.010	Li <sup>+</sup>	0.64	0.72	—	0.86	0.91	0.87	0.93	0.90	0.88	0.90
	Na <sup>+</sup>	0.91	0.90	—	0.95	0.94	0.92	0.95	0.95	—	0.95
	K <sup>+</sup>	0.66	0.71	0.75	0.82	0.85	0.85	0.95	0.90	—	0.92
	Rb <sup>+</sup>	0.56	0.67	0.70	0.80	0.87	0.86	0.84	0.87	—	0.89
	Cs <sup>+</sup>	0.56	0.68	0.72	0.82	0.87	0.85	0.85	0.88	—	0.87
	Be <sup>2+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mg <sup>2+</sup>	0.08	0.23	0.17	0.31	0.38	0.46	0.51	0.54	0.77	0.75
	Ca <sup>2+</sup>	0.03	0.04	0.02	0.05	0.05	0.08	0.07	0.08	0.14	0.20
	Sr <sup>2+</sup>	0.12	0.14	0.20	0.25	0.33	0.39	0.40	0.45	0.59	0.63
	Ba <sup>2+</sup>	0.08	0.13	0.20	0.24	0.35	0.37	0.40	0.52	0.54	0.60
0.100	Li <sup>+</sup>	0.30	0.47	0.61	0.65	0.73	0.75	0.70	0.80	0.81	0.83
	Na <sup>+</sup>	0.95	—	0.95	—	0.95	0.95	—	0.93	0.92	0.92
	K <sup>+</sup>	0.48	0.62	0.67	0.75	0.80	0.79	0.78	0.74	0.77	0.82
	Rb <sup>+</sup>	0.46	0.62	0.65	0.73	0.76	0.78	0.78	0.74	0.77	0.82
	Cs <sup>+</sup>	0.43	0.57	0.65	0.70	0.75	0.78	0.76	0.74	0.77	0.82
	Be <sup>2+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mg <sup>2+</sup>	0.02	0.02	0.02	0.02	0.06	0.14	0.14	0.21	0.26	0.28
	Ca <sup>2+</sup>	—	—	—	0.00	0.00	0.00	0.00	0.00	0.02	0.02
	Sr <sup>2+</sup>	—	—	—	0.02	0.05	0.09	0.14	0.14	0.14	0.12
	Ba <sup>2+</sup>	—	—	—	0.02	0.06	0.08	0.08	0.11	0.14	0.10

of the stationary phase on the chromatographic support. Thus the  $\log (1/R_F - 1)$  values were evaluated and plotted against the logarithm of the  $\text{H}^+$  concentration. Owing to the dissociation equilibrium of  $\text{CH}_3\text{COOH}$ , the second-power of the  $\text{H}^+$  concentration is proportional to the acetic acid concentration in the whole range of acetic acid solutions used as eluents.

After the first series of results with 0.010 and 0.100M HDEHP treated papers, additional experiments became necessary with paper treated with intermediate concentrations of HDEHP in cyclohexane between 0.100 and 0.010M. Such chromatograms were made with paper treated with 0.075, 0.050 and 0.025M HDEHP.

In correlating the quantity  $\log (1/R_F - 1)$  with  $\log [\text{HDEHP}]$  it was decided to use for the concentration of the stationary phase its actual concentration on the paper and not the concentration of the extractant when in the organic solution during the paper treatment. This latter method had been used in correlating data for Dy, Gd and Sm in previous work<sup>1</sup>, and though the expected linearity of  $\log (1/R_F - 1)$  vs.  $\log M$  HDEHP was found, the slope was much less than the expected value of + 3. It was qualitatively explained on the basis of a difference between the behaviour of HDEHP when in the organic solution and when fixed on the cellulose. Further attention has now been given to this.

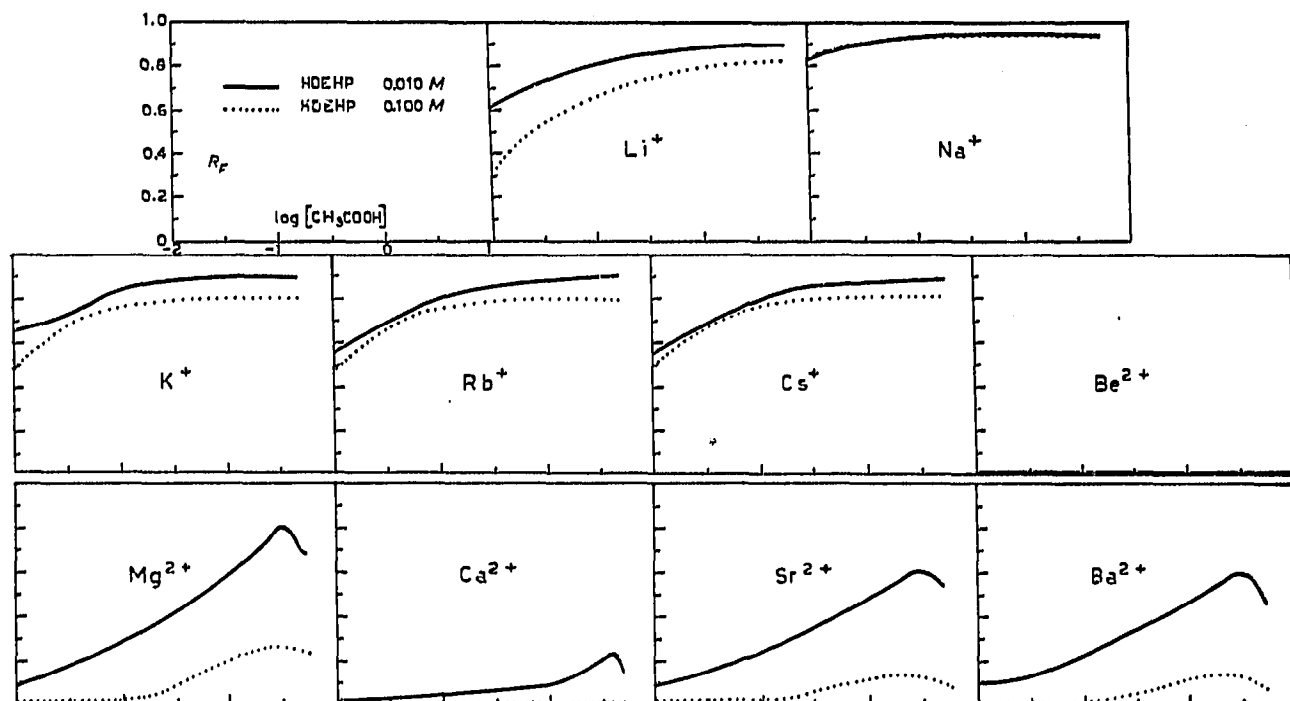


Fig. 2.  $R_F$  values of alkali and alkaline earth ions plotted vs.  $\log M$   $\text{CH}_3\text{COOH}$ . Paper treated with HDEHP.

Provided that the HDEHP concentration in the treatment solution is directly proportional to the "effective" concentration on the paper, the slope of  $\log (1/R_F - 1) = f(\log [\text{HDEHP}])$  does not change when the concentration in the organic solution is used for that on the paper. But if such a direct proportionality does not hold, the slope mentioned above can be affected to some extent. Experiments are therefore being performed in our laboratory to determine the "effective" concentration of extractant on the paper,  $[\text{HDEHP}]_{\text{eff}}$ , as a function of the concentration of the extractant in the cyclohexane solution,  $[\text{HDEHP}]$ . At present, preliminary experiments with beryllium ion, which is strongly retained by HDEHP on paper, have shown that a linear relationship exists between the two quantities. Paper strips ( $2.5 \times 5$  cm) treated with cyclohexane solutions having different concentrations of HDEHP were completely immersed in 20 ml of acidic solutions containing a few  $\mu\text{g}$  per ml of beryllium. The amount of beryllium retained per surface area unit was determined by measuring the ion loss in the respective solutions. Beryllium was determined by colorimetry. By assuming that the amount of  $\text{Be}^{2+}$  retained per  $\text{cm}^2$  of paper is directly proportional to the "effective" HDEHP concentration, the following experimental relationship was found:

$$C_{\text{Be}} = k[\text{HDEHP}]_{\text{eff}} = 0.14 + 1.5[\text{HDEHP}] \quad (2)$$

in which  $C_{\text{Be}}$  is the concentration of  $\text{Be}^{2+}$  on the paper ( $\mu\text{g}/\text{cm}^2$ ) and  $k$  is the proportionality constant between beryllium concentration and  $[\text{HDEHP}]_{\text{eff}}$ . Such an equation holds for  $[\text{HDEHP}]$  from 0.010 to 0.100M in cyclohexane.

From the results reported above it appears that when  $\log [\text{HDEHP}]_{\text{eff}}$  is needed for correlating data with  $\log (1/R_F - 1)$ , the quantity  $\log C_{\text{Be}}$  can be used, since  $\log k$

is an additional term which does not affect the slope obtained. On the other hand, where  $\log [\text{HDEHP}]$  is used for  $\log [\text{HDEHP}]_{\text{eff}}$  the slope is actually affected. Thus, by correcting the results of the rare earth experiments referred to above, using this equation, the expected slope  $+3$  can be found. In the present work this correction has been applied when the quantity  $k [\text{HDEHP}]_{\text{eff}}$  is indicated.

#### Alkaline earth ions

Plots reported in Fig. 2 show that all the alkaline earth ions,  $\text{Be}^{2+}$  excluded, present a maximum  $R_F$  at a given molarity of the acetic acid eluent.

Figs. 3 and 4 show  $\log (1/R_F - 1)$  values plotted against  $\log [\text{H}^+]$  up to  $2M$  acetic acid (see below), for  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  respectively, at the five HDEHP concentrations considered. In Fig. 3 the behaviour of  $\text{Ca}^{2+}$  is also shown at the lowest HDEHP concentration, which is the only case in which this element presents  $R_F$  values higher than zero.

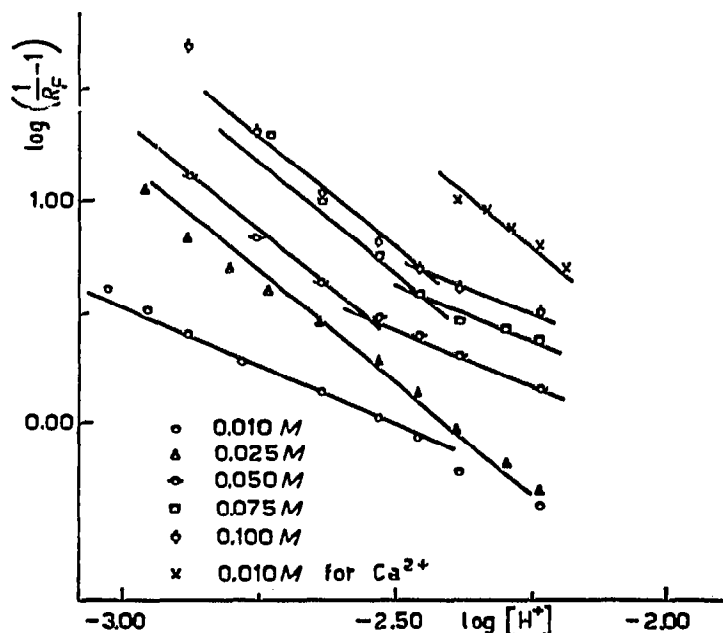


Fig. 3. Plot of  $\log (1/R_F - 1)$  vs.  $\log [\text{H}^+]$  for magnesium. Paper treated with HDEHP at various concentrations. Calcium is also shown at  $0.010 M$  HDEHP.

Straight lines are indicated in the two plots having slopes  $-2.0$  and  $-1.0$ ; such lines fit the experimental points with a sufficient agreement, and it appears that the quantity  $(1/R_F - 1)$  (*i.e.*  $E_a^0$ ) is inversely proportional to the square of the  $\text{H}^+$  concentration, if the concentration of HDEHP in cyclohexane is more than  $0.025M$  and provided that the acetic acid concentration is kept low. In fact, when the acetic acid concentration is raised, the quantity  $(1/R_F - 1)$  tends to become inversely proportional to the  $\text{H}^+$  concentration.

At low HDEHP concentrations ( $0.010$  and  $0.025 M$ )  $\text{Sr}^{2+}$  presents an inverse first-power dependency and  $\text{Mg}^{2+}$  shows a slope of  $-1$  at  $0.010M$  and  $-2$  at  $0.025 M$ , which is quite unexpected. Experimental results for  $\text{Ba}^{2+}$  are similar to those of  $\text{Sr}^{2+}$ , whilst  $\text{Be}^{2+}$  never moves from the starting point.

In Fig. 5 the  $\log (1/R_F - 1)$  values for  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  are plotted as functions of the logarithm of the effective concentration of HDEHP on paper,  $[\text{HDEHP}]_{\text{eff}}$ . This

concentration is expressed as  $\mu\text{g Be}^{2+}/\text{cm}^2$  (see above). Acetic acid of strengths 1.8M and 0.2M were chosen as the eluents, as these were considered representative of concentrated and dilute acid behaviour respectively. In both cases the slope + 3.0 shows that a third-power dependency holds between  $(1/R_F - 1)$  and  $[\text{HDEHP}]_{\text{eff}}$ .

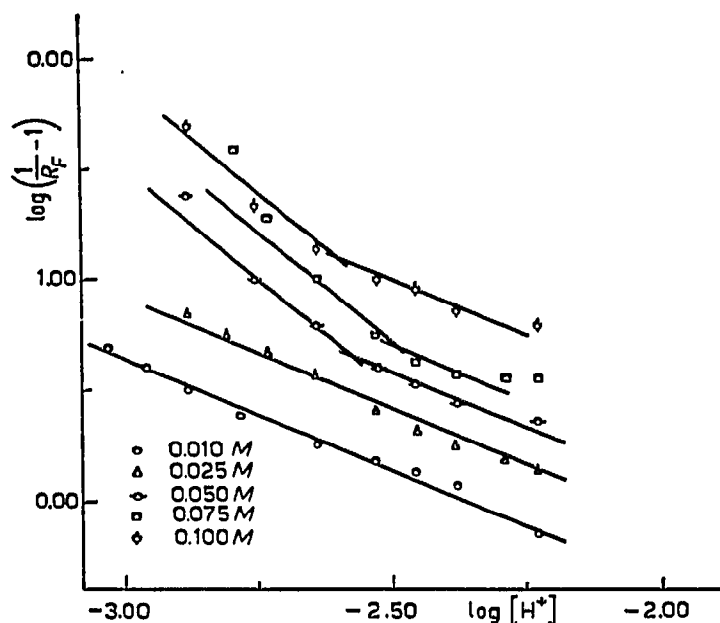


Fig. 4. Plot of  $\log(1/R_F - 1)$  vs.  $\log[\text{H}^+]$  for strontium. Paper treated with HDEHP at various concentrations.

Both the slope  $-2.0$  of Figs. 3 and 4 and the slope  $+3$  of Fig. 5 can be explained in terms of the analogy between the liquid-liquid and the chromatographic systems. According to PEPPARD *et al.*<sup>8</sup> the extraction of calcium ion from an aqueous solution

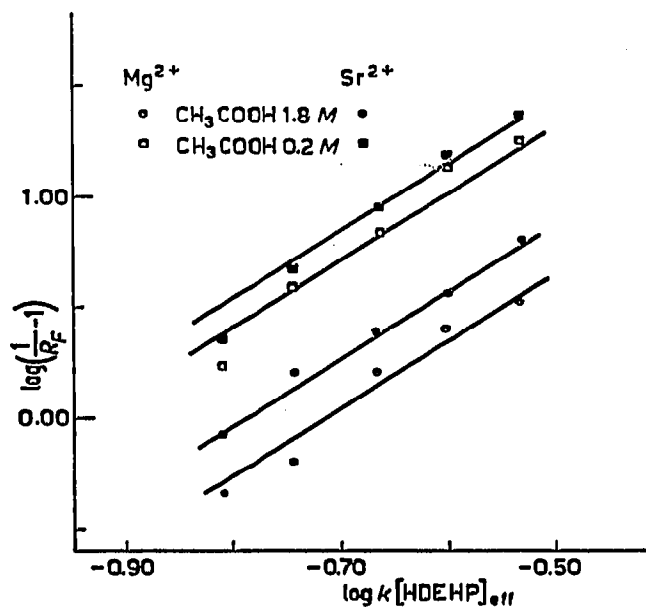
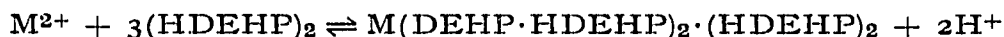
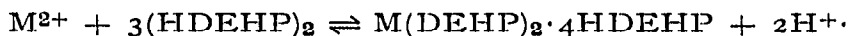


Fig. 5. Plot of  $\log(1/R_F - 1)$  vs.  $\log k_1[\text{HDEHP}]_{\text{eff}}$  for magnesium and strontium at two  $\text{CH}_3\text{COOH}$  concentrations.

by acid esters of phosphorous oxyacids in an organic phase follows the equation:



where  $M^{2+}$  is the calcium ion. In a more recent study on the extraction of strontium from acidic aqueous solutions with HDEHP, McDOWELL AND COLEMAN<sup>9</sup> suggest a reaction scheme which also leads to the same reaction coefficients without giving any special significance to hydrogen bonding between ligands within the complex. Such a scheme may be represented by the equation:



In both cases the extraction coefficient is inversely proportional to the square of the hydrogen ion concentration in the equilibrated aqueous phase and proportional to the cube of the HDEHP concentration in the organic phase.

The slope  $-1.0$  found in Figs. 3 and 4 where acetic acid is more concentrated may be explained by the formation of a different compound in the organic phase. The formation of a compound where the cation is surrounded both by  $CH_3COO^-$  and by HDEHP, may be the reason for this different behaviour toward hydrogen ions, while still maintaining the same dependency on HDEHP concentration. Following the scheme by McDOWELL AND COLEMAN cited above, the cation may form ionic bonds with both  $CH_3COO^-$  and  $(DEHP \cdot HDEHP)^-$  whilst four HDEHP molecules are coordinated. Consequently the following reaction is suggested as a possible mechanism:



from which the dependency on the hydrogen ion concentration becomes first power.

PEPPARD *et al.*<sup>10</sup> in the case of Th-nitrate systems had also considered a partial combination of the cation with the aqueous phase acid and the extraction of a combined ion of this kind by the organic extractant. The peculiar effect of acetic acid on the extraction of  $Sr^{2+}$  with HDEHP was also pointed out by MCHENRY AND POSEY<sup>11</sup> who showed that the distribution coefficients were affected not only by the  $H^+$  concentration but by the acetic acid concentration as well. On the other hand, SCHULZ *et al.*<sup>12</sup> studying the extraction of  $Sr^{2+}$  with HDEHP from a  $0.5N$   $CH_3COONa$  solution acidified with  $HNO_3$ , report a plot of  $\log E_a^\circ$  vs. pH which has a slope of  $+1.0$ , that is,  $E_a^\circ$  is inversely first power dependent on the  $H^+$  concentration. In the same work, the log of the distribution coefficients of  $Sr^{2+}$  and  $Ca^{2+}$  from a  $1M$  citric acid solution show almost a  $+1$  slope vs. pH. A slope smaller than 2 was also found by WISHOW AND HORNER<sup>13</sup> for the first portion of the plot of  $\log E_a^\circ$  of  $Sr^{2+}$  vs. pH of an aqueous phase containing tartaric acid.

Furthermore, results reported by HARDY *et al.*<sup>14</sup> on the extraction of  $Be^{2+}$  with HDEHP from aqueous solutions containing  $HCl$ ,  $H_2SO_4$  and  $HNO_3$  show that  $E_a^\circ$  values at high acid concentrations are greater than expected from the inverse second power dependency on the acid concentration shown with more dilute solutions. They suggest that at high aqueous acid concentrations complexes containing the anion of the aqueous acid are probably also extracted.



*Alkali ions*

The results obtained with alkali ions are quite different from the results with alkaline-earth ions. Since the extraction coefficients are very low, the  $R_F$  values of alkali ions tend to unity. In fact  $\text{Na}^+$  consistently runs with the front of the eluent, except at the lowest acetic acid concentrations;  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Li}^+$  show a retention somewhat higher than  $\text{Na}^+$ , which increases slightly from  $\text{K}^+$  to  $\text{Li}^+$ .

An attempt was made to obtain some information about their behaviour, by calculating the  $(1/R_F - 1)$  function along the ascending portion of the alkali ion curves of Fig. 2. Thus in Fig. 6  $\log (1/R_F - 1)$  is plotted against  $\log [\text{H}^+]$  for  $\text{K}^+$  at the five HDEHP concentrations studied;  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{Li}^+$  behave similarly.

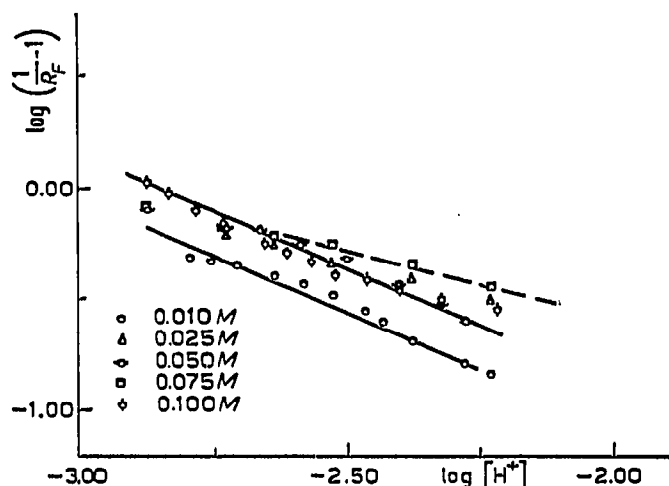


Fig. 6. Plot of  $\log (1/R_F - 1)$  vs.  $\log [\text{H}^+]$  for potassium. Paper treated with HDEHP at various concentrations.

It is evident that the dependence of  $(1/R_F - 1)$  or  $E_a^\circ$  upon the hydrogen ion concentration is less than that shown by alkaline earths. In Fig. 6 two lines (solid) of slope  $-1.0$  are drawn, by analogy with the results obtained by MCDOWELL AND COLEMAN<sup>9</sup> for the extraction of  $\text{Na}^+$  with HDEHP in benzene. Whilst points obtained with  $0.010M$  HDEHP follow this slope quite closely the same cannot be said for the other HDEHP concentrations, where lower negative slopes fit better (broken line in Fig. 6).

SCHULZ *et al.*<sup>12</sup> report a plot of the extraction coefficient for  $\text{Na}^+$  with HDEHP from an aqueous phase containing  $\text{CH}_3\text{COONa}$ , against the acidity of the aqueous solution, which shows an inverse square root dependency upon the hydrogen ion concentration, that is a  $+0.5$  slope in the  $\log E_a^\circ$  vs. pH plot.

Nothing can be said about the dependency of  $(1/R_F - 1)$  on the HDEHP concentration. It is interesting, however, that in Fig. 6 only points at  $0.010M$  HDEHP are separated from the others, and this shows that the extraction coefficient is practically independent of the HDEHP concentration in the portion of the curve considered. The absence of relation between  $R_F$  and the HDEHP concentration, may be explained by recalling results reported by BLAKE *et al.*<sup>15</sup> on the effective solubility in water of sodium salts of HDEHP. Thus  $R_F$  values would depend solely upon the solubility of the organic salts in the acid solution.

### Systems containing concentrated acetic acid

Particular attention was given to what happens when elutions are performed with very concentrated acetic acid. It was found that  $R_F$  values for alkaline earth ions present a maximum at acetic acid concentrations near  $3M$  (see Fig. 2), while reproducibility of results was good enough up to  $4M$  acetic acid. For higher concentrations it was not possible to obtain reliable results. Development of paper strips with 8-oxyquinoline and sodium alizarinsulphonate showed strange spots all over the paper which had been in contact with the acid. It was therefore decided to investigate the behaviour of the HDEHP treated papers with concentrated acetic acid. Since from various experimental results it looked as if HDEHP had lost its retention capacity after an elution with concentrated acid, three possibilities were taken into account, (i) the HDEHP somehow reacting with the acetic acid (ii) the paper being damaged and (iii) the HDEHP being eluted away from the paper.

HDEHP ( $0.100M$ ) equilibrated with  $10M$   $CH_3COOH$  was prepared and paper sheets were washed with acid of the same concentration. A series of elutions with  $Mg^{2+}$  spots was made, with  $1M$  and  $10M$   $CH_3COOH$ , and results showed that while every development made with  $10M$  acetic acid gave unsatisfactory results, experiments carried out using HDEHP and/or paper which had been previously in contact with  $10M$  acetic acid, gave  $R_F$  values in agreement with results obtained under normal conditions.

These results pointed to the HDEHP being eluted away from the paper by the concentrated acetic acid as the most probable possibility. Drops of  $0.1M$  HDEHP on paper strips were eluted with acetic acid at various high concentrations and the spots were detected as phosphomolybdate complexes<sup>2</sup>. Although the HDEHP spot was found at the starting point, a faint blue spot immediately behind the front of the solvent appeared at acid concentrations higher than  $3M$ , this spot increasing in dimension and intensity as the acid concentration was raised. When the latter exceeded  $7M$ , the original HDEHP spot disappeared. Fig. 7 shows elutions with  $6M$ ,  $7M$  and  $8M$  acetic acid.

The partial elution of HDEHP by concentrated acetic acid was considered re-

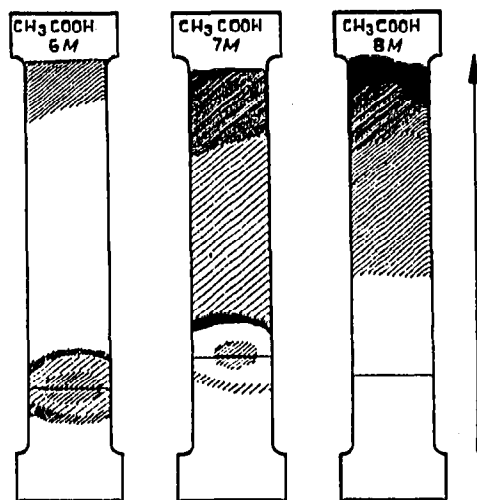


Fig. 7. Spots of HDEHP  $0.1M$  (in cyclohexane, eluted with  $CH_3COOH$  at various concentrations. The shading is proportional to the intensity of the blue colour shown after development as phosphomolybdate complex.

sponsible for the bad results obtained when dealing with acid concentrations higher than 2M. It should be noted that the decrease of  $R_F$  values for alkaline earths after their maximum cannot be put down to a phenomenon of this kind, since such a hypothesis would lead to an increase rather than a decrease of  $R_F$  values. In addition, an increase of  $E_a^\circ$  values with the acid concentration in extraction experiments with HDEHP was also found by HARDY *et al.*<sup>14</sup> for  $\text{Be}^{2+}$  and  $\text{HNO}_3$ . MCHENRY AND POSEY<sup>11</sup> found this also in their extraction of  $\text{Sr}^{2+}$  from acetic acid solutions.

#### Application to chromatographic separations

From the experimental results described above it appears that some separations are possible of alkali and alkaline earth ions. Some ascending and descending chromatograms were carried out with paper strips ( $3 \times 40$  cm) cut from Whatman No. 1 paper sheets. The strips were treated with 0.050M and 0.100M HDEHP in cyclohexane. Elutions with 3M and 0.2M acetic acid were performed.

TABLE II

$R_F$  VALUES OBTAINED IN ASCENDING AND DESCENDING CHROMATOGRAPHY ON PAPER TREATED WITH HDEHP

Paper strips  $3 \times 40$  cm. Each column refers to an individual chromatogram. Operating temperature  $23^\circ \pm 1^\circ$

HDEHP 0.050 M	$\text{CH}_3\text{COOH } 2M$						$\text{CH}_3\text{COOH } 0.1M$			
	$R_F$ from Fig. 2		$R_F$				$R_F$ from Fig. 2		$R_F$	
Li <sup>+</sup>	0.90	n.d.	n.d.	0.89	n.d.	n.d.	n.d.	0.76	n.d.	n.d.
Na <sup>+</sup>	0.94	n.d.	0.98	n.d.	0.94	0.94	n.d.	0.94	0.92	n.d.
K <sup>+</sup>	0.90	0.82	n.d.	n.d.	n.d.	n.s.	0.88	0.82	0.81	n.d.
Rb <sup>+</sup>	0.90	0.82	n.d.	n.d.	n.d.	n.s.	0.88	0.82	0.81	n.d.
Cs <sup>+</sup>	0.90	0.82	n.d.	n.d.	n.d.	0.88	n.s.	0.82	0.81	n.d.
Be <sup>2+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg <sup>2+</sup>	0.46	0.34	0.32	0.41	0.44	0.46	0.46	0.14	0.14	0.14
Ca <sup>2+</sup>	0.00	0.00	0.02	0.03	0.04	0.03	0.03	0.00	0.01	0.00
Sr <sup>2+</sup>	0.30	0.17	0.18	0.23	0.27	0.29	n.s.	0.10	0.11	0.12
Ba <sup>2+</sup>	0.30	0.17	0.18	0.23	0.27	n.s.	0.23	0.10	0.11	0.12
Run (cm) ascend, descend.	33.1		34.0	29.4	25.8	31.0	26.1	32.1		32.6
HDEHP 0.100 M										
Li <sup>+</sup>	0.81	n.d.	0.82	n.d.	n.d.	0.84		0.70	n.d.	
Na <sup>+</sup>	0.94	n.d.	0.95	0.93	0.93	0.92		0.94	n.d.	
K <sup>+</sup>	0.80	0.78	n.d.	n.s.	n.s.	0.85		0.78	0.73	
Rb <sup>+</sup>	0.80	0.78	n.d.	0.81	n.s.	n.s.		0.78	0.73	
Cs <sup>+</sup>	0.80	0.78	n.d.	n.s.	0.80	n.s.		0.78	0.73	
Be <sup>2+</sup>	0.00	0.00	0.00	0.00	0.00	n.s.		0.00	0.00	
Mg <sup>2+</sup>	0.26	0.27	0.22	0.24	0.28	0.34		0.05	0.07	
Ca <sup>2+</sup>	0.00	0.01	0.00	0.02	0.01	0.02		0.00	0.00	
Sr <sup>2+</sup>	0.14	0.12	0.09	0.14	0.14	0.18		0.04	0.07	
Ba <sup>2+</sup>	0.14	0.12	0.09	0.14	0.14	n.s.		0.04	0.07	
Run (cm) ascend, descend.	32.0		35.0	29.6	29.2	26.6		32.2		

n.d. = element not developed, n.s. = element not spotted.

The results are reported in Table II. It was not possible to detect  $\text{Li}^+$  and  $\text{K}^+$  ( $\text{Rb}^+$ ,  $\text{Cs}^+$ ) together on the same chromatogram, because of the closeness of the spots and the incompatibility of the developing reagents. Amongst the many types of separations which can be carried out under the conditions reported in Table II, can be cited Ca-Sr, Mg-Ba-Ca, Mg-Ca, Na-Ca-Sr, Cs-Sr, Cs-Ca-Sr.

From the curves in Fig. 2 it is also possible to choose better conditions under which to perform these and other separations. Most alkali and alkaline earth ions can be separated from each other by means of relatively short elutions with appropriate HDEHP and  $\text{CH}_3\text{COOH}$  concentrations.

#### CONCLUSIONS

The experimental results reported in this paper show the great similarity between the extraction properties of HDEHP in liquid-liquid systems and the chromatographic behaviour of paper treated with HDEHP which holds also in systems involving alkali and alkaline earth ions.

As in the case of paper chromatography or column separation of rare earths with cellulose<sup>1,16,17</sup> or Kel-F powder<sup>18</sup> treated with HDEHP, the influence of the  $\text{H}^+$  concentration in the aqueous phase and of the effective concentration of HDEHP on the support can be related to hypotheses derived from liquid-liquid extraction investigations.

The use of more concentrated acetic acid gives rise to peculiarities in the chromatographic behaviour, which are here discussed. The behaviour of paper treated with HDEHP towards very concentrated acetic acid solutions limits the concentration of the eluent which can be used.

Within a considerable range of acidities, from an upper limit ( $3M$   $\text{CH}_3\text{COOH}$ ) to reasonable dilutions ( $0.1M$   $\text{CH}_3\text{COOH}$ ), many interesting separations of alkali and alkaline earth metals can be carried out.

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#### SUMMARY

The chromatographic behaviour of alkali and alkaline earth metals on paper treated with di(2-ethylhexyl) phosphoric acid (HDEHP) has been investigated, using acetic acid as the eluent in the range of concentrations from  $2M$  to  $0.01M$ .

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

A behaviour similar to that shown in liquid-liquid extraction with HDEHP solutions was found, provided that the acetic acid concentration was kept low. The peculiar behaviour shown with concentrated acetic acid has been discussed.

No direct proportionality has been obtained between the HDEHP molarity in the solution used to treat the paper and the effective concentration of HDEHP on the paper which acts during elution.

The instability of HDEHP on paper with very concentrated acetic acid has been also investigated.

Some chromatographic separations of alkali and alkaline earth metals have been carried out, and others have been suggested.

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