

REVERSED-PHASE PARTITION CHROMATOGRAPHY ON PAPER TREATED WITH DI-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID: A SYSTEMATIC STUDY OF 67 CATIONS IN HYDROCHLORIC ACID

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INTRODUCTION

After PEPPARD *et al.*¹ first showed, in 1957, that di-(2-ethylhexyl) orthophosphoric acid (HDEHP) was a very promising extractant for the fractionation of the trivalent lanthanides, a great deal of work was performed in many laboratories on the use of this compound in the separation of various cations.

The high degree of selectivity attainable with HDEHP when separating elements which show very similar chemical properties, made this compound a very effective tool for reversed-phase partition chromatography in the field of inorganic chemistry. Supports treated with a suitable organic solution of HDEHP have been used, in the form of a bed for column applications or in the form of a paper sheet for paper chromatography. It is not possible to list here all the examples given in the literature of the use of HDEHP-treated supports, since, due to their number, a special review would be required.

Many chemical elements have already been investigated in our laboratory as to their behaviour on reversed-phase chromatography with HDEHP-treated papers. With the purpose of completing a list of the behaviour of as many as 67 cations, our efforts were devoted to investigating the HDEHP-HCl system on paper.

This work, starting from our recent results, and extending further their development, is aimed at collecting all the experimental data obtained and correlating such data with some special aspects of liquid-liquid extraction phenomena.

EXPERIMENTAL

Reagents and equipment

The di-(2-ethylhexyl) orthophosphoric acid (HDEHP) was a Virginia-Carolina Chemical Co. (Richmond, U.S.A.) product supplied by Soc. Eigenmann and Veronelli (Milan). It was used as supplied, since no differences in experimental results were noticed² when HDEHP samples had been previously purified by a method derived from that described by STEWART AND CRANDALL³. All the reagents were analytical grade. A list of cations, not considered in our previous work, and the relative compounds used, is shown in Table I, together with the suppliers and final solutions obtained.

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TABLE I

SOLUTIONS USED TO APPLY THE CATIONS ON THE CHROMATOGRAMS

<i>Cation</i>	<i>Compound used</i>	<i>Final solvent</i>	<i>Final ion conc., equiv./l</i>	<i>Supplier</i>
Li ⁺	LiCl	H ₂ O	0.005	C. Erba
Na ⁺	NaCl	H ₂ O	0.005	C. Erba
K ⁺	KCl	H ₂ O	0.005	C. Erba
Rb ⁺	RbCl	H ₂ O	0.005	Fluka
Cs ⁺	CsCl	H ₂ O	0.005	B.D.H.
Y ³⁺	YCl ₃ · 6 H ₂ O	H ₂ O	0.08	Merck
Nd ³⁺	Nd ₂ O ₃	0.2 M HCl	0.075	B.D.H.
Tb ³⁺	Tb ₂ O ₃	0.1 M HCl	0.02	Fluka
Dy ³⁺	Dy ₂ O ₃	0.2 M HCl	0.002	Fluka
Ho ³⁺	Ho ₂ O ₃	0.1 M HCl	0.035	Fluka
Tm ³⁺	Tm ₂ O ₃	0.2 M HCl	0.02	Light
Lu ³⁺	Lu ₂ O ₃	0.1 M HCl	0.02	Light
UO ₂ ²⁺	UO ₂ (NO ₃) ₂ · 6 H ₂ O	5 M HCl	0.005	Merck
Ti ⁴⁺	TiCl ₄	0.1 M HCl	0.005	C. Erba
Hf ⁴⁺	metal	6 M HCl	0.02	Fluka
V ³⁺	V ₂ O ₃	conc. HCl	0.10	C. Erba
V ⁴⁺	VOSO ₄ · 5 H ₂ O	H ₂ O	0.10	Merck
Nb ⁵⁺	metal	conc. H ₂ SO ₄	0.10	B.D.H.
Cr ³⁺	CrCl ₃ · 6 H ₂ O	H ₂ O	0.10	C. Erba
Mo ⁶⁺	MoO ₃	0.1 M NaOH	0.10	C. Erba
W ⁶⁺	Na ₂ WO ₄ · 2 H ₂ O	H ₂ O	0.10	C. Erba
Mn ²⁺	MnCl ₂ · 4 H ₂ O	H ₂ O	0.005	C. Erba
Re ⁷⁺	metal	6 M HCl	0.01	B.D.H.
Ru ³⁺	RuCl ₃	1 M HCl	0.05	B.D.H.
Rh ³⁺	metal	conc. HCl	0.10	B.D.H.
Pd ²⁺	PdCl ₂	1 M HCl	0.05	C. Erba
Ir ⁴⁺	IrCl ₃	conc. HCl	0.10	C. Erba
Pt ⁴⁺	H ₂ PtCl ₆ · 6 H ₂ O	conc. HCl	0.005	C. Erba
Cu ²⁺	CuCl ₂ · 2 H ₂ O	H ₂ O	0.005	C. Erba
Ag ⁺	AgNO ₃	H ₂ O	0.10	C. Erba
Au ³⁺	HAuCl ₄ · 4 H ₂ O	0.1 M HCl	0.005	C. Erba
Zn ²⁺	ZnCl ₂	0.1 M HCl	0.005	C. Erba
Cd ²⁺	CdCl ₂ · 2.5 H ₂ O	H ₂ O	0.012	C. Erba
Hg ²⁺	HgCl ₂	H ₂ O	0.005	C. Erba
B ³⁺	Na ₂ B ₄ O ₇ · 10 H ₂ O	H ₂ O	0.10	C. Erba
Ge ⁴⁺	GeCl ₄	conc. HCl	0.10	B.D.H.
Sn ²⁺	SnCl ₂ · 2 H ₂ O	95 % ethanol	0.10	C. Erba
Pb ²⁺	Pb(NO ₃) ₂	0.1 M HCl	0.005	C. Erba
As ³⁺	As ₂ O ₃	conc. HCl	0.10	C. Erba
As ⁵⁺	As ₂ O ₅	conc. HCl	0.10	C. Erba
Sb ⁵⁺	Sb ₂ O ₅	conc. HCl	0.10	C. Erba
Bi ³⁺	Bi(NO ₃) ₃ · 5 H ₂ O	0.3 M HCl	0.10	C. Erba
Se ⁴⁺	H ₂ SeO ₃	H ₂ O	0.10	C. Erba
Te ⁴⁺	TeCl ₄	conc. HCl	0.10	B.D.H.

The chromatographic paper was Whatman No. 1 (CRL/1 type). It was treated with the appropriate cyclohexane solution of HDEHP, which had been previously equilibrated with hydrochloric acid by shaking 10 min with twice its volume of a 2.5 M HCl solution. The paper was immersed for about 30 sec in the equilibrated organic solution and then removed and allowed to drip. It was finally dried in a current of warm air.

The behaviour of the various cations on varying the HCl concentration in the eluent was mostly determined with paper treated with 0.100 *M* HDEHP.

In order to obtain experimental data on the role of HDEHP in the partition mechanism of the ions, simultaneous elutions⁴ were carried out on papers treated with cyclohexane solutions of HDEHP at different concentrations, *viz.* 0.100, 0.080, 0.060, 0.040, 0.025, 0.015 and 0.010 *M*; the HCl concentration in the eluent being chosen for each ion from the results obtained with 0.100 *M* HDEHP treated papers.

In the case of yttrium and uranium, an extensive investigation was carried out to determine the dependence of their R_F values on the hydrochloric acid concentration not only with paper treated with 0.100 *M* HDEHP, but also with paper treated with 0.075, 0.050, 0.025 and 0.010 *M* HDEHP, as has already been done for the alkaline earths⁴ and aluminium, gallium, indium, thallium and the transition metals of the iron group².

The equipment used has already been described in previous work⁵.

Chromatographic procedure

Spots with a volume of about 0.02 ml were applied on the paper, which corresponds approximately to 1×10^{-7} equivalents of the cation with a 0.005 *N* solution and to 2×10^{-6} equivalents with a 0.1 *N* solution. After development, the paper was dried in a current of warm air, and then sprayed with a solution suitable for the detection of the spots. The reagent solutions used for this purpose are listed in Table II.

TABLE II
SPRAY REAGENTS FOR DETECTION OF THE SPOTS

Compound	Reagent solution	Cations developed*
Dithizone	0.1 % soln. in chloroform	V ³⁺ ; V ⁴⁺ ; Nb ⁵⁺ ; Re ⁷⁺ ; Ru ³⁺ ; Rh ³⁺ ; Pd ²⁺ ; Ir ⁴⁺ ; Ag ⁺ ; Au ³⁺ ; Zn ²⁺ ; Cd ²⁺ ; Hg ²⁺ ; Ge ⁴⁺ ; Pb ²⁺ ; As ³⁺ ; As ⁵⁺ ; Sb ⁵⁺ ; Se ⁴⁺ ; Te ⁴⁺
Quercetin	0.1 % soln. in ethanol	Sc ³⁺ ; Ti ⁴⁺ ; Zr ⁴⁺ ; Hf ⁴⁺ ; Mn ²⁺ ; P ⁴⁺ ; Cu ²⁺ ; Sn ²⁺
8-Hydroxyquinoline	0.1 % soln. in 50 % ethanol	Y ³⁺ ; UO ₂ ²⁺ ; <i>rare earths</i>
Morin	0.1 % soln. in ethanol	Mo ⁶⁺ ; W ⁶⁺
Diphenylcarbazide	0.1 % soln. in ethanol	Cr ³⁺
Sodium alizarinsulphonate	0.1 % soln. in ethanol	B ³⁺
Ammonium sulphide	20 % soln. in water	Bi ³⁺

* Cations in italics can be detected only under U.V. light.

Except in the case of bismuth, which was sprayed with ammonium sulphide, the sprayed paper had to be exposed to ammonia fumes to make the spots visible.

Further details of the chromatographic technique are described in a previous paper⁶.

The elutions, all ascending, were made with hydrochloric acid (supplied by C. Erba, Milan) at different concentrations, ranging from $1 \cdot 10^{-4}$ to 10 *M*.

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

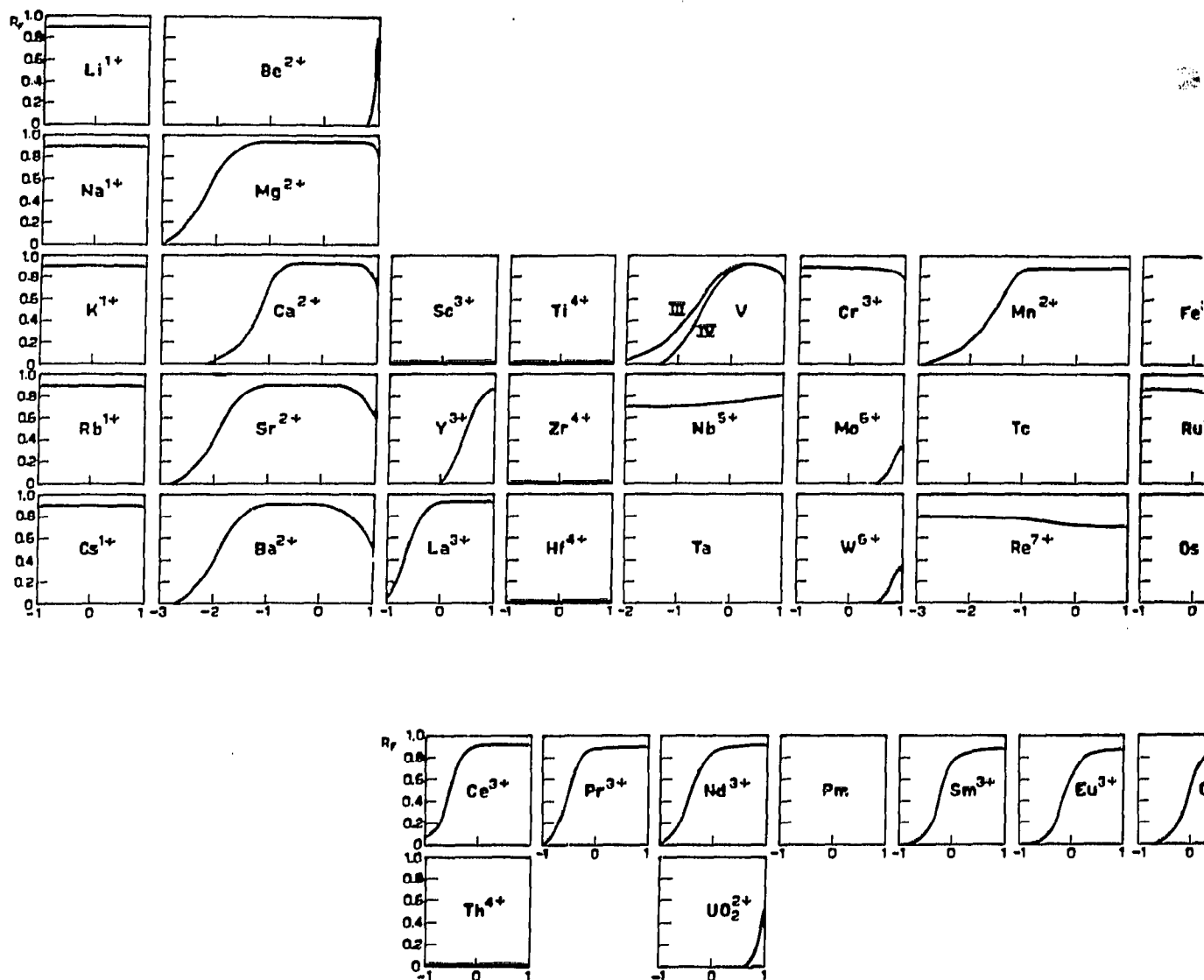


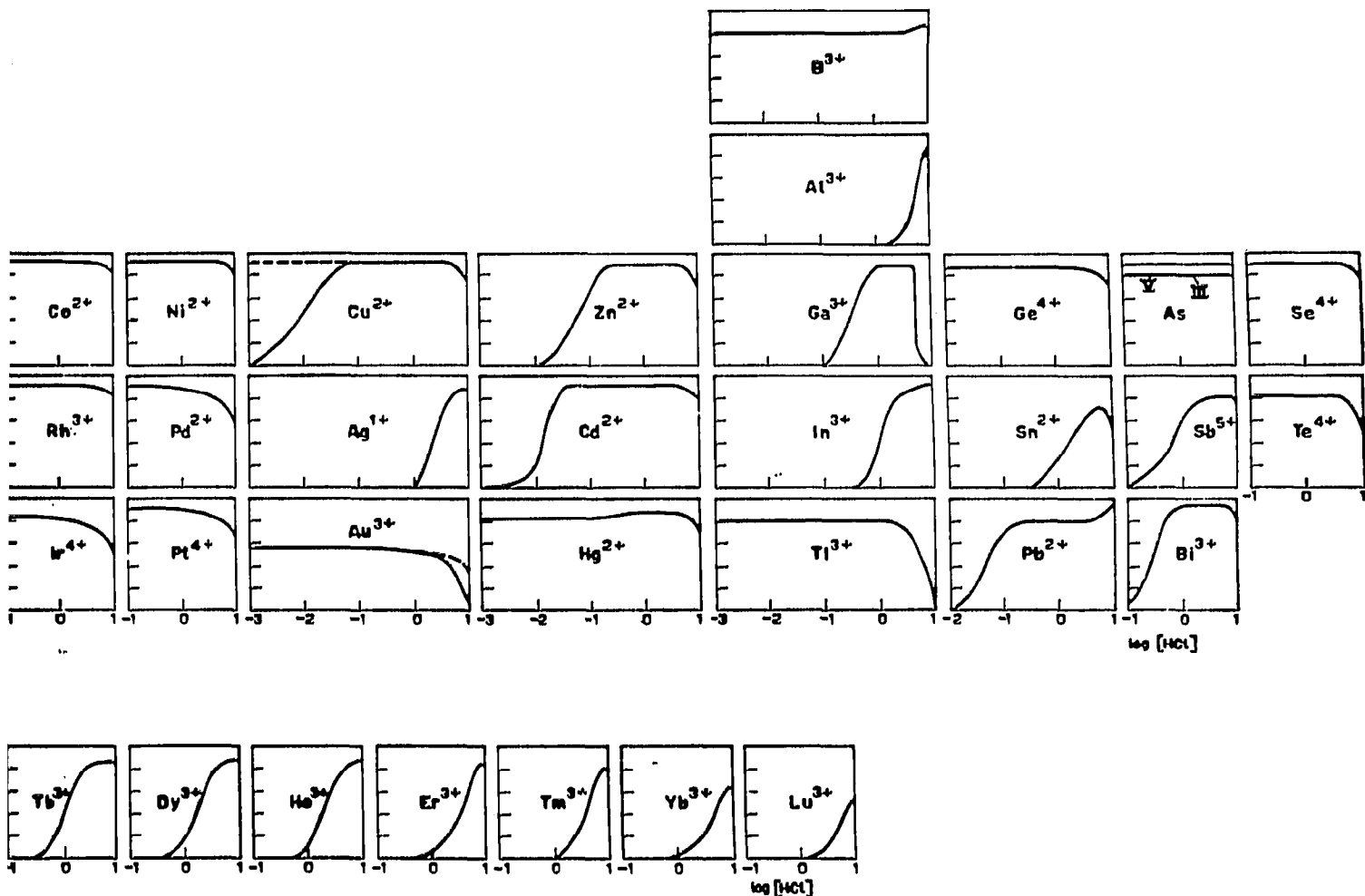
Fig. 1. Chromatography on paper treated with 0.1 *M* di-(2-ethylhexyl) orthophosphoric acid in cyclohexane; plot of the R_F values of the elements as a function of the logarithm of the molarity of the hydrochloric acid used as the eluent.

considered satisfactory, because of the shortness (about 9 cm) of the chromatograms. All the experiments were carried out at a room temperature of $23^\circ \pm 1^\circ$.

RESULTS

In Fig. 1, R_F values for all the cations studied both in the present and in previous work are plotted against the molarity of the HCl used as eluent, the papers being treated with an 0.100 *M* solution of HDEHP in cyclohexane. The cations are arranged according to their order in the Periodic Table.

Data on osmium are necessarily missing, since there were no methods of detection suitable for the low amounts of this cation which had to be used in order that the intrinsically low capacity of the treated paper was not overloaded. The other cations missing were those not available at the moment. Although the experiments



were carried out over a range of acidity from 10 M HCl to $1 \cdot 10^{-4} M$ for all cations, in drawing Fig. 1 the lower concentrations were often ignored, since the relative results showed no interesting features.

The general behaviour of the ions, as it appears in Fig. 1, compares well with the data in the literature on liquid-liquid extraction.

A good survey of the behaviour of elements in the liquid-liquid extraction with HDEHP from hydrochloric acid solutions was carried out by KIMURA⁷. By comparing our R_F results with the distribution coefficient values K reported in KIMURA's paper, a certain generalization can be made about the correspondence between these two variables. Roughly speaking, when in our experiments an element just leaves the start point, a value for K of about unity is found in KIMURA's table; and when an element reaches the front of the eluent, its extraction coefficient is of the order of $1 \cdot 10^{-3}$. It was found that the only disagreement between the two tables

occurs for mercury, which should, according to KIMURA's data, be partially retained on the paper, while in our experiments it always runs with the eluent.

Further comments on the results shown in Fig. 1 can be found in the discussions on the single groups of cations, reported below.

Fig. 2 reports the data obtained in the investigation of the behaviour of yttrium and uranium(VI) on papers treated with HDEHP at various concentrations in cyclohexane. As has been already mentioned, 0.100, 0.075, 0.050, 0.025 and 0.010 HDEHP molarities were studied.

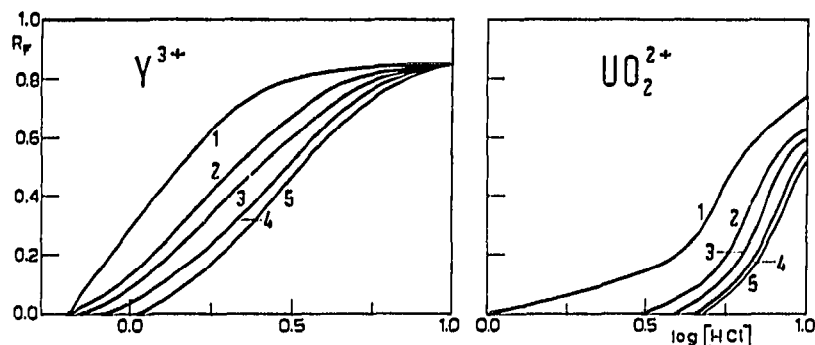


Fig. 2. R_F values for yttrium and uranium plotted vs. $\log M$ HCl. Paper treated with HDEHP solutions 0.010 M (curve 1), 0.025 M (curve 2), 0.050 M (curve 3), 0.075 M (curve 4), and 0.100 M (curve 5).

DISCUSSION

General

It is well-known that the behaviour of an ion in reversed-phase partition chromatography on supports impregnated with a given compound is closely related to its behaviour in liquid-liquid extraction by the same compound dissolved in a suitable solvent. The R_F values for a given ion on paper treated with a liquid extractant and eluted with a given aqueous solution are related to the extraction coefficients E_a° of the same ion in the analogous liquid-liquid system, through the well-known relationship:

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

where k is a constant depending on the chromatographic conditions.

As already pointed out⁴, the equilibrium accepted as representing the extraction mechanism of a cation with HDEHP may be written as:



The equilibrium constant K of this reaction, written in terms of activities, is:

$$K = \frac{\gamma_A [M(\text{DEHP})_b \cdot b \text{HDEHP} \cdot (c - b) (\text{HDEHP})_2] a_{\text{H}^+}^b}{\gamma_C [M^{b+}] [\text{MDEHP}]_{\text{eff}}^c} \quad (3)$$

where γ_A and γ_C are the activity coefficients of the adduct in the organic phase and of the metallic cation in the aqueous phase, respectively, and $[\text{HDEHP}]_{\text{eff}}$ is what

we called⁵ the effective HDEHP concentration and which is a measure of the activity of the HDEHP present on the paper sheet.

The extraction coefficient E_a^0 of the metallic ion is defined as:

$$E_a^0 = \frac{[M(\text{DEHP})_b \cdot b \text{ HDEHP} \cdot (c - b) (\text{HDEHP})_2]}{[M^{b+}]}$$

By substituting the left and right terms in this latter equation with their expressions obtainable from the eqns. (1) and (3) respectively, the following relationship is obtained:

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

where the term "const." in eqn. (4) = $\log K + \log k + \log (\gamma_C/\gamma_A)$; γ_C/γ_A being assumed to be practically constant in the ionic strength range pertaining to the experimental conditions considered for a given cation.

For a given element, plots of $\log (1/R_F - 1)$ against either $\log [\text{HDEHP}]_{\text{eff}}$ or $\log a_{\text{H}^+}$ can lead to the determination of the coefficients c and b of the eqn. (4) when either the HCl concentration in the eluent or the HDEHP concentration in the solution used to treat the paper are respectively kept constant. Thus, information on the extraction mechanism can be obtained.

Figs. 3 to 6 show such plots for the various cations considered in this work and whose R_F values in Fig. 1 increase as the HCl concentration is raised. The analogous plots for cations already considered in previous publications are omitted here, as they can be found in the respective papers^{2,4}. Data for rare earths are reported below.

The hydrogen ion activities in plots of Figs. 3 to 5 were calculated from the data reported by ROBINSON AND STOKES⁸. The effective HDEHP concentrations on the paper, used in Fig. 6, were calculated from the formula:

$$k [\text{HDEHP}]_{\text{eff}} = 0.14 + 1.5 [\text{HDEHP}]$$

mentioned in a previous paper⁵.

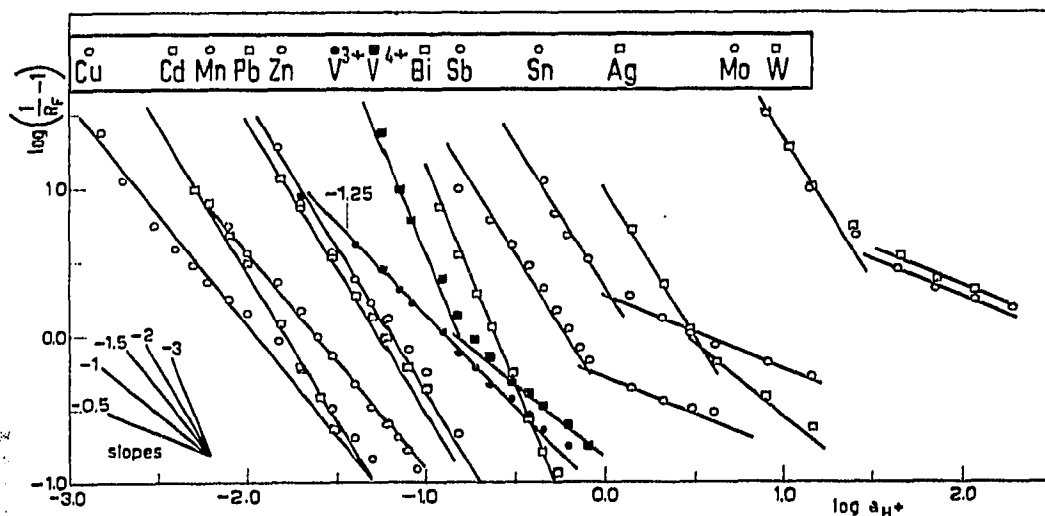


Fig. 3. Plots of $\log (1/R_F - 1)$ vs. $\log a_{\text{H}^+}$ for various cations. Paper treated with 0.100 M HDEHP.

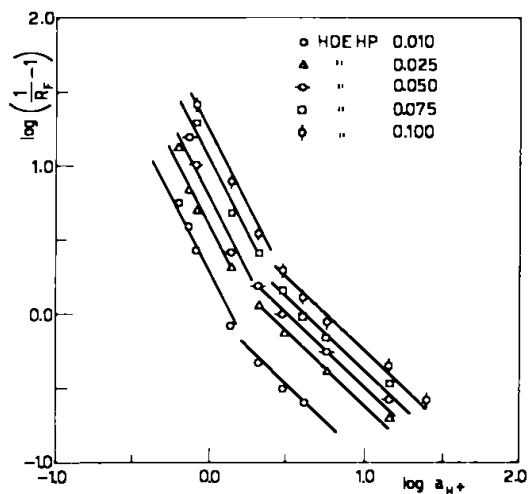


Fig. 4. Plots of $\log (1/R_F - 1)$ vs. $\log a_{H^+}$ for yttrium. Paper treated with HDEHP at various concentrations. Slopes -2 and -1 .

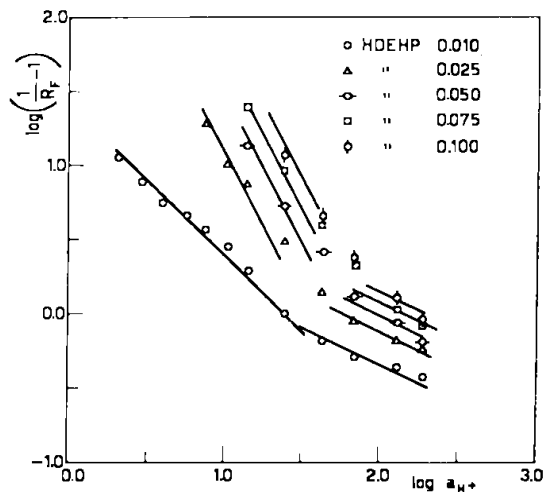


Fig. 5. Plots of $\log (1/R_F - 1)$ vs. $\log a_{H^+}$ for uranium. Paper treated with HDEHP at various concentrations. Slopes -2 , -1.5 , and -1 .

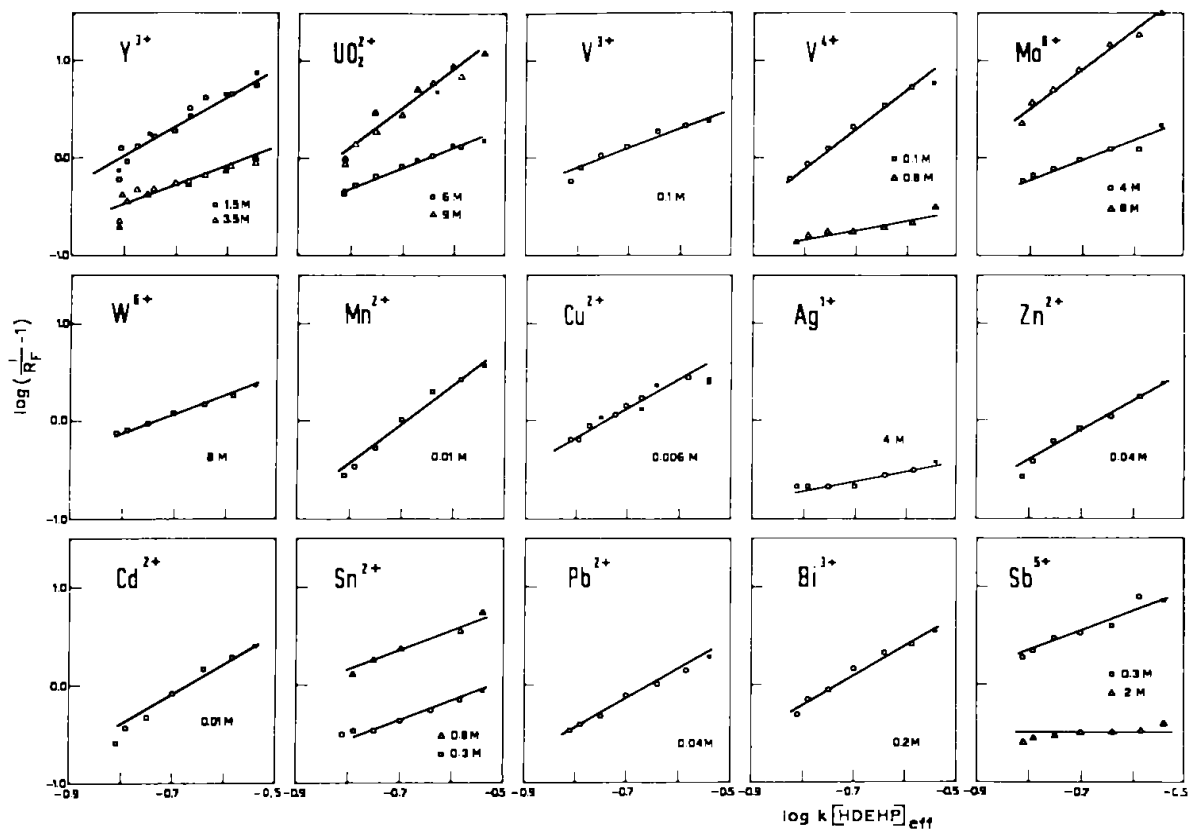


Fig. 6. Plots of $\log (1/R_F - 1)$ vs. $\log k[\text{HDEHP}]_{\text{eff}}$ for various cations. Different HCl concentrations, as quoted in the single plots. Open symbols refer to data obtained with simultaneous elutions with paper treated with HDEHP at different concentrations. Closed symbols refer to data obtained from Figs. 3 to 5. Slopes are found in Table III.

From the slopes of the curves in the Figs. 3-6 the values for the coefficients b and c of eqn. (4) were obtained. These are collected in Table III, together with the similar results obtained for the cations considered in previous publications. From a general standpoint, the results collected in Table III show that although a relationship such as that shown in eqn. (1) holds, the values for coefficient b for a given cation seldom agree with the charge of the cation itself.

The fact that the cations are likely to be partially complexed by the chloride ions present in the eluent solution has to be taken into account. A cation M^{b+} coordinating n Cl^- ions gives rise to a $MCl_n^{(b-n)+}$ complex which actually takes part in the exchange reaction. In this case, the mechanism of exchange may be represented

TABLE III

VALUES OF COEFFICIENTS b AND c OF EQUATION (4) FOR CATIONS ELUTED WITH HCl ON PAPER TREATED WITH 0.1 M HDEHP IN CYCLOHEXANE

Cation	Coefficient b		Coefficient c	
	Value	HCl molarity range	Value	HCl molarity
Mg ²⁺	1.5	0.001 -0.04	3.0	0.003
Ca ²⁺	1.5	0.008 -0.1	3.0	0.03
Sr ²⁺	2.0	0.002 -0.006	3.0	0.003
Ba ²⁺	1.5	0.006 -0.04	3.0	0.01
	2.0	0.002 -0.006	3.0	0.003
Y ³⁺	1.5	0.006 -0.04	3.0	0.01
	2.0	0.7 -2	3.0	1.5
UO ₂ ²⁺	1.0	2 -6	2.0	3.5
	2.0	5 -7	4.0	6.0
V ³⁺	1.0	7 -10	2.0	9.0
	1.25	0.01 -1	2.0	0.1
V ⁴⁺	3.0	0.05 -0.2	4.0	0.1
	1.0	0.2 -1	1.0	0.8
Mo ⁶⁺	2.0	4 -6	4.0	4.0
	0.5	6 -10	2.0	8.0
W ⁶⁺	2.0	4 -6	—	—
	0.5	6 -10	2.0	8.0
Mn ²⁺	1.5	0.004 -0.1	4.0	0.01
Fe ³⁺	2.0	2 -6	3.0	2.3
Co ²⁺	(1.5)	0.0001-0.03	—	—
Ni ²⁺	(1.5)	0.0001-0.03	—	—
Cu ²⁺	1.5	0.001 -0.05	3.0	0.006
Ag ⁺	2.0	1 -3	—	—
	1.0	3 -5	1.0	4.0
Zn ²⁺	2.0	0.01 -0.2	3.0	0.04
Cd ²⁺	2.0	0.004 -0.03	3.0	0.01
Al ³⁺	2.0	3.5 -5	3.0	4.0
	1.0	5 -10	3.0	6.0
Ga ³⁺	3.0	0.08 -0.2	3.0	0.08
	2.0	0.2 -1	3.0	4.0
In ³⁺	3.0	0.3 -1	3.0	0.5
	< 3.0	1 -3	< 3.0	—
Sn ²⁺	2.0	0.5 -1	2.0	0.8
	0.5	1 -5	2.0	3.0
Pb ²⁺	2.0	0.01 -0.1	3.0	0.04
Sb ⁵⁺	2.0	0.1 -1	2.0	0.3
	0.5	1 -3	0.0	2.0
Bi ³⁺	3.0	0.1 -0.7	3.0	0.2

by a reaction similar to reaction (2) in which the element M^{b+} and the coefficient b are substituted by $MCl_n^{(b-n)+}$ and by $(b - n)$, respectively. The slopes of the plots of $\log (1/R_F - 1)$ vs. $\log a_{H^+}$ will then give $(b - n)$ values. Furthermore, the combination of the two equilibria gives a value of b lying between the value of the charge of the cation and the same value minus n .

The same effect is obtained if partial hydrolysis of the cation occurs: the cationic species to be considered will then be $M(OH)_n^{(b-n)+}$, and reaction (2) will be modified in the same way as in the case of the $MCl_n^{(b-n)+}$ species.

In addition to the above, another reason for b coefficients differing from the stoichiometric values may be ascribed to a dehydration effect which takes place at high hydrochloric acid concentrations. This effect may be responsible for the decrease of the R_F values shown to different extent by almost all the elements. A general discussion on this effect which deserves further consideration will be given in a future paper⁹.

Except for Y(III) and UO_2 (II) and those cations already considered in previous papers on reversed-phase paper chromatography with HDEHP there are not many data on liquid-liquid extraction with HDEHP available in the literature for those cations listed in Table III, though, as already mentioned, a good survey on the behaviour of almost all cations was carried out by KIMURA⁷. However, if the general trend of the different cations, as shown in the previous section, agrees with KIMURA's results, the same cannot be said about the values of coefficients b and c in eqn. (4). The reason for this disagreement may be due to two important factors, which are now considered.

Firstly, in KIMURA's work the determination of the dependence of the extraction coefficients on the concentration of hydrochloric acid was carried out with a 50% HDEHP solution in toluene, this condition being appreciably different from ours. Secondly, consideration also has to be given to the fact that the reversed-phase chromatography gives R_F values differing from zero in a range of conditions in which liquid-liquid extraction gives extraction coefficients which are very low with respect to the ones usually considered: thus, the mechanism of extraction may be appreciably different in the two cases.

Both reasons reported above are quite obvious: nevertheless the discussion on the extraction of uranium(VI) with HDEHP from various acidic media, reported below in the paragraph dealing with uranium, may be a good illustration of them. A feature which further confirms this point is the fact that the disagreement is particularly found with ions which do not follow reaction (2), *i.e.* they are involved in the extraction mechanism as complexes with Cl^- or as partially hydrolyzed ions. It is obvious that ions which undergo these phenomena will behave in quite a different way at two different HCl concentrations.

Alkali and alkaline earth metals

Alkali metals run generally with the front of the eluent; when eluted with very dilute HCl, they show a slight retention by the paper (R_F values about 0.7), which probably has to be ascribed to a partition phenomenon in which little role is played by HDEHP.

A discussion on the behaviour of alkaline earths has been already reported in previous work⁴.

Scandium, yttrium and the lanthanides

Since scandium is strongly retained by HDEHP at any HCl concentrations, no results on the mechanism of its extraction can be derived from reversed-phase chromatographic data.

The behaviour of yttrium in liquid-liquid extraction systems involving HDEHP has been often reported in the literature^{1,10,11}, where the value 3 is given for both the coefficients b and c in eqn. (4). Its behaviour in reversed-phase chromatography is now discussed together with the behaviour of the rare earths.

Because of their importance in the nuclear field, the rare earths deserve a particular consideration. It has already been demonstrated also in this laboratory that reversed-phase chromatography on supports impregnated with HDEHP is a powerful means of separation of the rare earths. In this work, it is intended to complete the information about their behaviour on paper treated with HDEHP when eluted with HCl, and at the same time to rectify a mistake that unfortunately occurred during the compilation of a previous paper⁶.

Fig. 7 shows the behaviour of the rare earths in the form of R_F values plotted against the logarithm of the hydrochloric acid concentration of the eluent. It can be seen how their behaviour (as their atomic weight varies), is consistent with the one expected, and how yttrium falls between holmium and erbium following its usual peculiar behaviour towards rare earths.

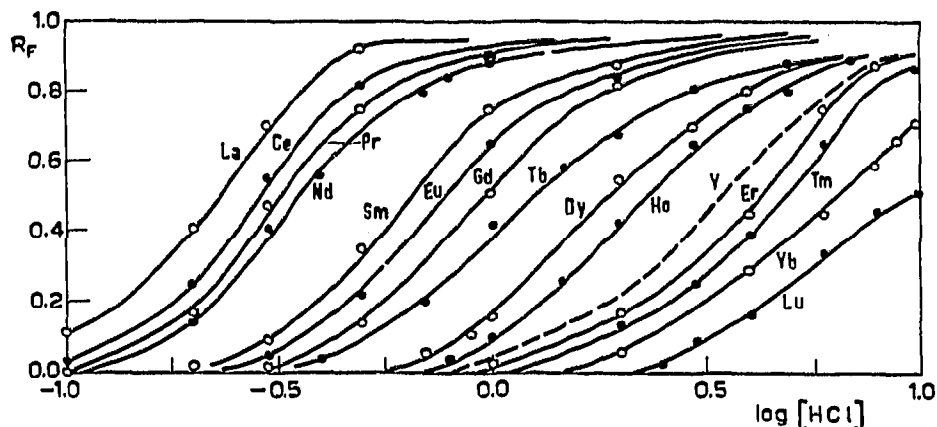


Fig. 7. R_F values for rare earths plotted *vs.* $\log M$ HCl. Paper treated with 0.100 M HDEHP. Yttrium behaviour is included.

In plotting these results, it was noticed that the curve referring to dysprosium, as reported in the previous publication⁶, was not consistent with the curves referring to the rare earths immediately before and after it. Reinvestigation permitted us to conclude that most probably in the earlier work yttrium instead of dysprosium was used.

Fig. 8 shows the plots of $\log (1/R_F - 1)$ against the atomic number Z of the rare earths. According to results in the literature^{1,6}, parallel straight lines are obtained showing that E_a° is a linear function of the atomic number. From the figure, the average separation factor between two adjacent rare earths is estimated as 1.9.

In order to check the mechanism responsible for their retention, $\log (1/R_F - 1)$ has been plotted against the logarithm of the hydrogen ion activity in the eluent,

and results are shown in Fig. 9. Fig. 10 shows some plots of $\log (1/R_F - 1)$ against the effective HDEHP concentration on paper; these are from R_F data obtained from simultaneous elution of elements on paper treated with HDEHP at different concentrations in cyclohexane. While all the rare earths are considered in Fig. 9, the plots in Fig. 10 refer only to Sm, Tb, Ho and Yb, the other rare earths behaving in a similar way.

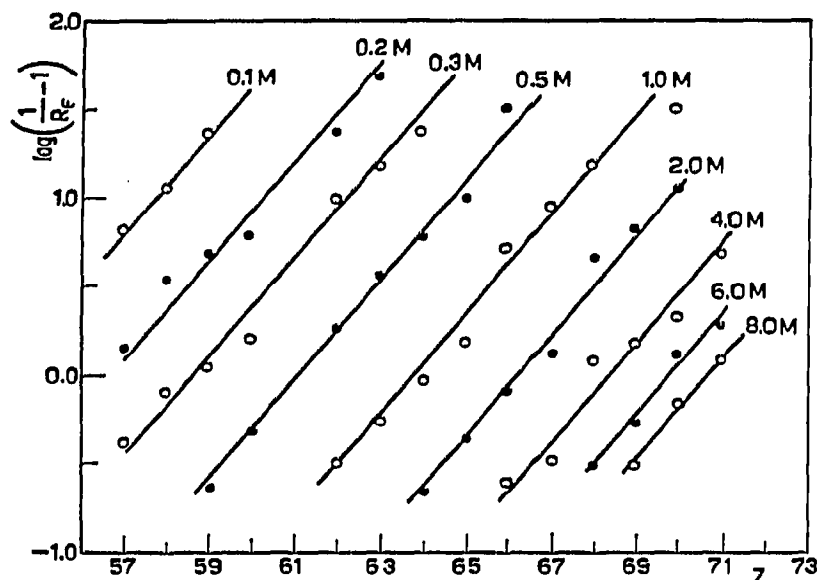


Fig. 8. Plots of $\log (1/R_F - 1)$ vs. atomic number Z for rare earths. Paper treated with 0.100 M HDEHP, elution with HCl at the indicated molarities. Average separation factor: $(1/R_F - 1)_{z+1} / (1/R_F - 1)_z = 1.9$.

The main feature arising from Fig. 9 is the fact that $\log (1/R_F - 1)$ against $\log a_{H^+}$ plots do not follow straight lines of slope -3 as would be expected from the ion exchange mechanism. They tend rather to follow curves which may be approximated to lines of slope -3 only in their upper part. In particular, it will be noticed that this disagreement with the usual ion exchange mechanism predictions is greater the greater the atomic number of the rare earths, that is the higher the hydrochloric acid concentration range involved.

Fig. 10 shows how the slopes of the curves obtained by plotting $\log (1/R_F - 1)$ against the logarithm of the effective HDEHP concentration on the paper vary when the eluent concentration is varied. As a general rule, the slope 3 (as expected from the ion exchange mechanism) is only obtained when the hydrogen ion activity of the eluent is kept within the range where the slope is -3 in Fig. 9. When the H^+ ion activity of the eluent is higher, slopes lower than 3 are obtained, reaching values as low as 1 or even less.

These results are in agreement with the results reported in the literature, although this may not become apparent at first sight since the extraction coefficients were usually plotted against the stoichiometric H^+ concentration in the aqueous layer and not against the H^+ activity which we have done, owing to the high HCl concentrations involved.

Liquid-liquid extraction of the rare earths by HDEHP from HCl, HNO_3 , H_2SO_4 and $HClO_4$ was first reported by PEPPARD *et al.*^{1,10}. Low acid concentrations

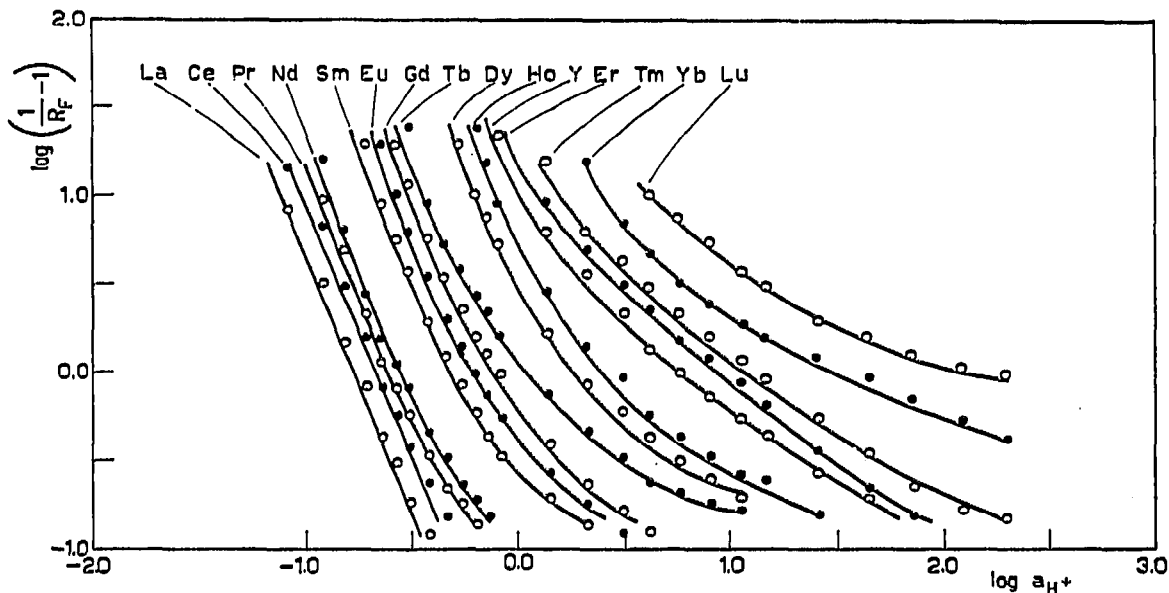


Fig. 9. Plots of $\log (1/R_F - 1)$ vs. $\log a_{H^+}$ for rare earths and yttrium. Paper treated with 0.100 M HDEHP. Slope of straight lines is -3 .

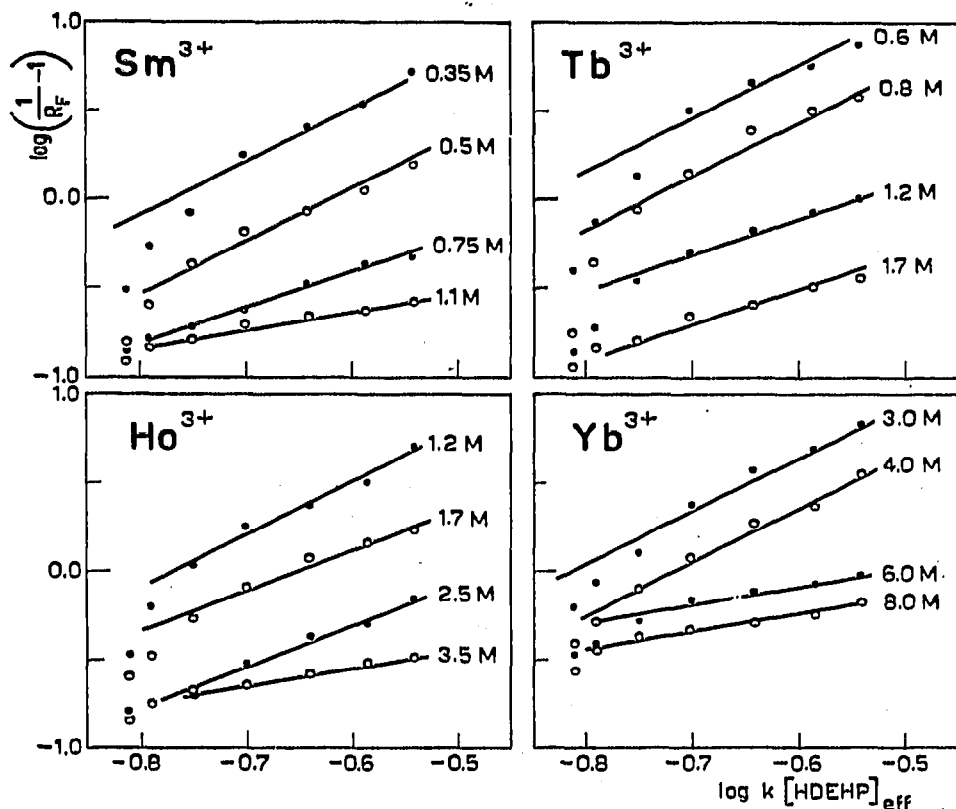


Fig. 10. Plots of $\log (1/R_F - 1)$ vs. $\log k[\text{HDEHP}]_{\text{eff}}$ for samarium, terbium, holmium, and yttrium at various HCl concentrations of the eluent. Data are obtained from simultaneous elutions with paper treated with HDEHP at different concentrations.

were used and the expected value of 3 for both coefficients b and c in eqn. (4) were found.

On the other hand, PIERCE AND PECK¹¹ and PIERCE, PECK AND HOBBS¹² report both liquid-liquid extraction and reversed-phase partition chromatography of rare earths on columns with impregnated inert supports and with HDEHP as the extractant; aqueous solutions were in HClO_4 or HCl , whose concentrations were rather high. The logarithm of the extraction coefficients in liquid-liquid extraction, and the logarithm of $(1/R_F - 1)$ in reversed-phase chromatography were plotted by these authors against the logarithm of the hydrogen ion concentration of the eluent, and straight lines were obtained. By substituting the H^+ activity for the H^+ concentration, curves similar to those in Fig. 9 can be obtained.

Results of reversed-phase chromatography on paper treated with di-*n*-butyl phosphate (a compound very similar to HDEHP), published by CVJETIČANIN¹³, after making the above mentioned substitution, also agree with our results. In this latter work, furthermore, the reported values of coefficients c for some rare earths eluted with 4 *M* HCl are lower than the values obtained for other rare earths eluted with the less concentrated 0.3 *M* HCl , the other experimental conditions being the same.

A value of 2.5 has been recently reported by CHENG *et al.*¹⁴ as the dependence of the elution volume on the H^+ activity in elutions of rare earths on HDEHP columns with HCl concentration in the eluent ranging from 0.2 to 0.3 *M*.

We feel that the disagreement between the values of b and c of eqn. (2) expected from the simple ion exchange mechanism, and the results presented here, can be explained by the dehydration effect already mentioned for the elements whose R_F decreases as the HCl concentration increases in the high concentration range. For a detailed discussion of this phenomenon we defer to future work⁹.

Thorium and uranium

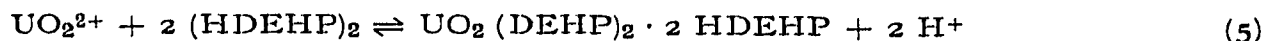
No comments can be made on the extraction mechanism of thorium(IV), since it is strongly retained by HDEHP at all the HCl concentrations.

As already mentioned, experiments carried out with uranium (VI) on paper treated with HDEHP solutions having concentrations varying from 0.100 to 0.010 *M* are shown in Fig. 2, and Fig. 5 shows the plots of $\log (1/R_F - 1)$ vs. $\log a_{\text{H}^+}$ from which the coefficient b in eqn. (4) may be obtained.

U(VI) behaves unusually when paper treated with 0.010 *M* HDEHP is used. This behaviour may be attributed to an insufficient loading of the paper when treated with such dilute HDEHP solutions. Insufficient loading is confirmed also when the results obtained for most cations are correlated with the HDEHP concentration on paper; in Fig. 6, for example, the values of $\log (1/R_F - 1)$ for very low HDEHP concentrations are lower than would be expected from the results at higher concentrations of the extractant.

The behaviour of U(VI) in liquid-liquid extraction with HDEHP has been frequently described in the literature: a brief survey of the reported data will confirm the importance of both the hydrochloric acid and the HDEHP concentration ranges in which experiments are carried out, and their effect on the mechanism of extraction for a given ion, thus confirming the reasons we stated above for the discrepancies between KIMURA's extraction data and our results.

Most of the work on the extraction of uranium(VI) by HDEHP has been done with dilute or moderately concentrated acid solutions (see for example the papers by BAES or PEPPARD, and their co-workers¹⁵⁻¹⁷): all the results obtained led to the conclusion that the reaction responsible for the extraction of the uranium was:



i.e. coefficients b and c in eqn. (4) are both equal to 2. Perchloric, sulphuric, nitric, and hydrochloric acids have been used, and the reaction just mentioned was true for all of them.

More recently, ASANO *et al.*¹⁸ have published some results obtained with the above mentioned acids used up to very high concentrations in the aqueous phase. It appeared that the reaction represented by eqn. (5) holds only if the H^+ activity is kept below the value 1; with higher H^+ activities, the behaviour of the distribution coefficients is highly dependent on the nature of the acid used: for HCl, in particular, a very much smaller slope than that of -2 , which holds at the lower concentrations, is obtained, having a value of about -0.1 . Similar abnormal behaviour with concentrated HNO_3 was also reported by GUREEV *et al.*¹⁹. Very recently, a paper by SATO²⁰ reported E_a° values for uranium(VI) extracted with HDEHP, at various low concentrations, from HCl solutions which ranged up to high concentrations. By plotting $\log E_a^\circ$ vs. $\log a_{\text{H}^+}$, straight lines can be obtained very similar to those shown in Fig. 5, having slopes -2 and -1 , the slope of -2 holding at the lower HCl concentration range for the highest HDEHP concentrations.

With respect to the influence of the HDEHP concentration on the extraction mechanism of U(VI), a recent paper by LASKORIN AND SMIRNOV²¹ deals with the liquid-liquid extraction of uranium(VI) from phosphoric acid solutions with HDEHP. In this work, the value 2 for the coefficient c is reported when the HDEHP concentration is about $0.1 M$, while a value of 4 for the same coefficient is reported with a more dilute (lower than $0.01 M$) HDEHP solution.

Titanium, zirconium and hafnium

R_F values equal to zero were found for these three ions for all HCl concentrations. No information on their extraction mechanism is therefore obtainable.

Vanadium and niobium

Values for coefficients b and c in the case of vanadium(IV) may be obtained from the papers of KIMURA⁷ ($b = 4$; $c = 1.5$), BLAKE *et al.*¹⁵ ($b = 4$; $c = 2$), and LASKORIN *et al.*²² ($b = 2$; $c = 2$). The values $b = 3$ and $c = 4$ were obtained from our data. The different experimental conditions are probably responsible for the discrepancies.

No literature data have been found for vanadium(III). Its behaviour in reversed-phase chromatography is very similar to that shown by vanadium(IV).

The slight retention of niobium(V) can probably be ascribed to the partition phenomena on paper already mentioned for alkali ions.

Chromium, molybdenum and tungsten

Chromium(III) runs with the front of the eluent; only at very high HCl con-

centrations does it show a slight retention due to the already mentioned dehydration phenomena.

It was not possible to find a detection reagent capable of revealing the spots of chromate at such low amounts as those dealt with. Therefore its behaviour was not recorded.

Molybdenum(VI) and tungsten(VI) behave similarly: only highly concentrated HCl solutions were capable of displacing them a little, in accordance with the results reported by LASKORIN and coworkers²³ for molybdenum, in liquid-liquid extraction systems. An attempt was made to obtain the values of the coefficients b and c in eqn. (4) from the R_F values, which never exceed 0.40. The results showed that the same mechanism is responsible for the extraction of both ions, but it is not, however, represented by reaction (2).

Manganese and rhenium

The values of 1.5 and 4 for coefficients b and c are found for manganese(II). Partial hydrolysis may be responsible for this behaviour.

Rhenium(VII) shows high R_F values. Its slight retention could be ascribed to the partition mechanism on paper mentioned for alkali ions.

Iron, cobalt and nickel

A discussion on the behaviour of the transition metals of the iron group has been already published². Worth mentioning here is a peculiarity of nickel and cobalt ions, which sometimes showed a double spot in the HCl concentration range from $1 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ M, when paper had been treated with 0.1 M HDEHP. One spot, as expected, ran with the front of the eluent, while the second, which appeared in some cases, had a lower R_F value, which decreased the lower the HCl concentration. This spot was only detected in some of the chromatograms out of a series of several similar ones simultaneously eluted under the same conditions. No explanation was found for this behaviour. When using paper treated with more dilute HDEHP solutions (from 0.075 M down), only the spot at the front of the eluent was detected.

A value of 1.5 for the coefficient b was obtained from the retained spots.

The behaviour of cobalt and nickel in liquid-liquid systems has been studied in a sulphate medium by MADIGAN²⁴, who reported the coefficient b to be lower than 2, in accordance with our results. Only nickel(II) has a value for coefficient b lower than 2 in KIMURA's data.

The strong dehydration effect on iron(III) is noticeable; another peculiarity of the iron(III) ion is the already reported² dependence of its R_F values on the elution time, due to the slow rate to equilibrium of the exchange reaction responsible for its retention.

Ruthenium, rhodium and palladium

Ruthenium(III), rhodium(III) and palladium(II) always run with the front of the eluent: they are partially retained in the high HCl concentration range because of dehydration effects.

Osmium, iridium and platinum

Osmium is not reported since no suitable developing reagent was found to detect it on the paper.

Iridium(IV) and platinum(IV) ions run with the front of the eluent, being somewhat retained in the high HCl concentration range because of the dehydration effect.

Copper, silver and gold

Copper(II) shows a second faint spot at the front of the eluent in the range of HCl concentrations in which it is normally retained by the stationary phase. This spot appears with paper treated not only with 0.1 M HDEHP, as for cobalt and nickel, but also with more dilute solutions. The presence of monovalent copper as an impurity may be an explanation of the spot at the front.

The value of coefficient b for copper is 1.5, in accordance with a value lower than 2 reported by MADIGAN²⁴ in the extraction of this ion with HDEHP from sulphate solutions. KIMURA's value is 2.

Silver(I) gave tailed spots when low R_F values were obtained. In this range of acidity a slope of -2 was obtained from the plot $\log (1/R_F - 1)$ vs. $\log a_{H^+}$ in Fig. 3. An explanation of both these facts may be incomplete dissolution of the silver salt at insufficiently high HCl concentrations.

Gold(III) has R_F values of around 0.6 in the whole HCl concentration range explored, up to about 3 M HCl. With HCl concentrations higher than 3 M, two spots, having different colours, are obtained, the former soon reaching a zero R_F value, the latter being less retained. The retention at low HCl concentrations may be ascribed to the partition phenomena already mentioned, for example, for alkali metals, while the doubling of the spots at the high HCl concentrations will be dealt with in another paper⁹, where the peculiar lowering of the R_F values for most elements, when very concentrated hydrochloric acid is used as the eluent, will be discussed.

Zinc, cadmium and mercury

Zinc(II) and cadmium(II) are the first ions considered in this discussion which have values for the coefficient b which are in agreement with a mechanism involving the eqn. (2). The same value of 2 is reported for coefficient b of both these ions by LEVIN AND SABOLOSKI²⁵, for extractions from H_2SO_4 solutions.

Mercury(II) runs with the front of the eluent for the whole HCl concentration range explored.

Boron, aluminium, gallium, indium and thallium

Boron(III) is not retained by HDEHP at any concentrations of HCl in the eluent.

The behaviour of aluminium(III), gallium(III), indium(III) and thallium(III) has already been discussed². It is worthwhile pointing out how gallium shows a greater lowering of R_F values, due to the dehydration effect, than all the other cations considered. The R_F value of thallium also considerably decreases in the high HCl concentration range. On the other hand, a partition phenomenon similar to that reported for alkali ions is thought to be responsible for the slight retention ($R_F \simeq 0.8$) shown by the latter ion in the whole HCl concentration range explored.

Although aluminium is reported¹⁶ to have a slow exchange reaction, no dependence of its R_F values on the elution time was noticed.

The peculiar behaviour of the above mentioned ions makes it possible to obtain many interesting separations of them; this has already been shown in a previous paper²⁶.

Germanium, tin and lead

Germanium(IV) was always found near the front of the eluent.

Tin(II) gave tailed spots in the whole range in which R_F values different from zero were obtained. Nevertheless both tin(II) and lead(II) show values for the coefficient b in eqn. (3) in accordance with the reaction (2).

Arsenic, antimony and bismuth

Both arsenic(III) and arsenic(V) ions run with the front of the eluent, arsenic(III) being slightly retained by a partition phenomenon in which little role is played by the extractant present on the paper.

The behaviour of antimony(V) does not follow reaction (2); furthermore, at the high HCl concentration values, coefficient c becomes zero, *i.e.* it is independent of the HDEHP concentration on the paper. A mechanism differing from ion exchange has to be postulated.

The value of the coefficient b for bismuth(III) is in accordance with the above mentioned reaction. In conclusion, the only ions which can be considered to exhibit such behaviour are zinc(II), cadmium(II), tin(II), lead(II), and bismuth(III), together with the already reported strontium(II) and barium(II).

Selenium and tellurium

Both selenium(IV) and tellurium(IV) run with the front of the eluent. They show, however, a different behaviour in the high HCl concentration range, when tellurium is retained more than selenium. Also a slight retention ($R_F \approx 0.8$) is shown by tellurium over the whole range considered, probably due to the partition effect already mentioned in the case of alkali metals.

CONCLUSIONS

The R_F data reported in Figs. 1, 2 and 7 are sufficient to suggest many interesting separations of ions by elution with hydrochloric acid of a suitable concentration on paper treated with HDEHP. Many examples of such separations have already been reported^{2, 4, 6, 26}.

The data are also useful to predict separations of mixtures of ions by eluting them on columns prepared with inert supports treated with HDEHP: the higher capacity of the columns allows the separation of relatively large amounts of substances.

Sometimes, however, especially when very concentrated eluting solutions are used, the results obtained with paper and with these columns do not coincide, since the supports used for the column do not always behave as really inert ones: columns of treated cellulose powder are naturally the ones whose behaviour is closest to that of the paper sheets.

The reversed-phase paper chromatographic technique may also give useful information which will help to elucidate both the mechanism of retention on paper or columns and the mechanism of extraction in the liquid-liquid systems.

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SUMMARY

The behaviour of 67 cations in reversed-phase partition chromatography on paper treated with di-(2-ethylhexyl) orthophosphoric acid was investigated. Hydrochloric acid was used as the eluent in a concentration range of 10 M to $1 \cdot 10^{-4}$ M. For 48 cations the quantity $(1/R_F - 1)$ was related to the hydrogen ions activity in the mobile phase and to the effective HDEHP concentration on the paper.

The chromatographic behaviour was correlated to that in analogous liquid-liquid extraction systems.

Particular attention was devoted to U(VI) and to the rare earths group of metals.

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