# REVERSED-PHASE EXTRACTION CHROMATOGRAPHY USING Br⁻-CONTAINING ELUANTS

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## SUMMARY

Forty-three ions have been chromatographed on thin layers of silica gel impregnated with Alamine 336, Amberlite LA-1, Primene JM-T, Alamine oxide (AlamO), tri-$n$-octylphosphine oxide (TOPO) or tri-$n$-octylarsine oxide (TOAsO), and on non-impregnated silica gel using aqueous HBr and acidified LiBr solutions as eluants. The $R_F$ spectra and a number of separations are reported. Percentage extraction *versus* $M$ Br⁻ data and preliminary results of spectroscopic measurements for the system: extractant–Co(II)–Br⁻ are also recorded.

The behaviour of each of the six extractant–Br⁻ systems investigated resembles that of the corresponding chloride system. The sorption strength increases in the order: Primene < Amberlite ≤ AlamO ≤ Alamine. The strength of TOPO is comparable to that of Alamine for a large majority of the ions studied; the remaining ions are strongly sorbed on TOPO-impregnated silica gel, whereas sorption is weak in the case of Alamine. The behaviour of TOAsO distinctly deviates from that of all other extractants; the preferential uptake of a second molecule of HBr plays a decisive role here.

Sorption proceeds through anion-exchange with the amines and, probably, also with AlamO. With TOPO, both solvation and anion-exchange appear to play a role.

## INTRODUCTION

In a recent paper[1], the extraction properties of AlamO and TOAsO are described and compared with those of amines and TOPO. Using reversed-phase chromatography, it is demonstrated that (a) the behaviour of the amine oxide and a moderately sorbing amine in HCl systems is almost identical and (b) the three oxides show distinct differences among themselves. As a continuation of this work, the present paper reports on chromatography in bromide systems. Some data on liquid–liquid extraction have been included.

## MATERIALS AND METHODS

### Materials

Alamine 336-S (General Mills, Kankakee, Ill., U.S.A.) is a special quality (99–100%) mixture of tertiary amines having alkyl groups which consist of $C_8$-$C_{10}$ straight

chains; its mean mol.wt. is 392. Amberlite LA-1 is a mixture of dodecenyltrialkyl-methylamines with a mean mol.wt. of 372. Primene JM-T consists of a relatively large number of trialkylmethylamines (18–24 carbon atoms); the fractions having a mean mol.wt. of about 300 are isolated by repeated vacuum distillation. Primene and Amberlite LA-1 are supplied by Rohm and Haas (Philadelphia, Pa., U.S.A.).

AlamO is synthesised[1,2] by oxidation of Alamine 336-S with 30% $H_2O_2$ in absolute ethanol. After keeping the mixture at 45° for 3 days, the clear solution is poured into distilled water. AlamO, which separates as an oily upper layer, is diluted with toluene and repeatedly washed with aq. NaOH and distilled water. Solutions of AlamO in chloroform are prepared after evaporation of the toluene at a temperature below 50°. Standardisation is done by equilibration with an equal volume of about 2 N $HClO_4$, and subsequent determination of the amount of acid taken up by the organic phase (cf. the method given below). TOPO (K and K, Plainview, N.Y., U.S.A.) is a white crystalline product with a mol.wt. of 387 and a melting point of 51–52°.

TOAsO is synthesised[1,3] by the oxidation of tri-n-octylarsine with 30% $H_2O_2$. The impure oxide is crystallised from n-hexane and treated with absolute ethanol. After rigorous drying, the product has a melting point of 68–69°.

*Extraction of HBr*

The extractant (15 ml of a 0.1 M solution) in chloroform or toluene is shaken for 20 min with an equal volume of an aqueous HBr (with or without added LiBr) solution of the desired normality. After separation of the phases, an aliquot portion of the organic phase is diluted with 70 ml of ethanol and titrated with aqueous 0.1 N NaOH. The end-point is determined potentiometrically.

*Extraction of Co(II)*

An aqueous 0.04 M $CoBr_2$ solution (15 ml) is shaken for 20 min with an equal volume of a 0.1 M solution of the described extractant in toluene. After separation of the phases, an aliquot portion of the organic phase is stripped with 0.1 N $HNO_3$. The aqueous extract is evaporated to dryness and Co(II) is determined titrimetrically with EDTA, using murexide as an indicator.

Absorption spectra are recorded on a Zeiss PMQ II or a Perkin-Elmer 402 spectrometer.

*Chromatography*

A freshly prepared solution of the extractant in chloroform — either equilibrated with an aqueous 2 N HBr solution or used without prior equilibration (cf. next section) — is thoroughly mixed with Type DO silica gel (Fluka, Buchs, S.G., Switzerland) such that the silica gel–chloroform ratio is 1:6 (w/v) and chromato-plates are prepared by dipping microscope slides in the resulting suspension. After evaporation of the chloroform, the back of the slides is wiped clean and a series of scores is made in the thin layers. Spots are applied using a paper wick impregnated with the sample solution, which contains 1–10 mg of ion per ml.

Ascending chromatography is carried out for a 3-cm run in perspex or in Hellendahl staining jars, using solutions of 0.2–9 N HBr, and 2–10 M LiBr acidified with 0.5 N HBr as eluants. Note that HBr solutions occasionally turn brown-red on

standing. These are discarded, since their use as eluants leads to distinctly altered $R_F$ spectra.

Detection is done using visualisation procedures already described[4,5]. Details concerning the experimental technique have been reported[6].

RESULTS AND DISCUSSION

*Extraction of HBr*

Data on the extraction of HBr by 0.1 $M$ solutions of the various extractants in chloroform (chromatography) and toluene (extraction) are presented in Fig. 1.
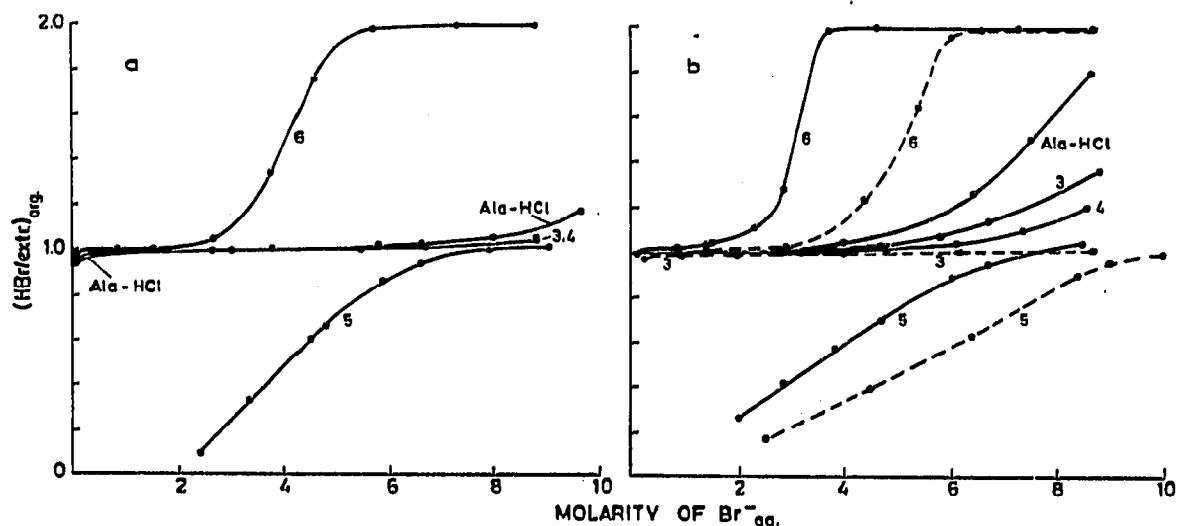


Fig. 1. Extraction of HBr by 0.10 $M$ solutions of various extractants in (a) chloroform and (b) toluene. Aqueous phase: ————, HBr; – – – –, LiBr acidified with 0.4 $N$ HBr. Extractants: Alamine (3); AlamO (4); TOPO (5); TOAsO (6). As a means of comparison, some results on the extraction of HCl by Alamine (————, Ala–HCl) are included.

*Equilibration*

Equilibration of liquid anion-exchangers with an aqueous acid solution prior to their use as stationary phases has been common practice since CERRAI AND TESTA[7] stated that conversion of amines into the appropriate salt form makes the elution more regular and the solvent front well defined. As is well known, the formation of amine salts of mineral acids is easily accomplished by shaking the amine with a dilute aqueous acid solution (Fig. 1; ref. 8). The data in Fig. 1 indicate that the conversion of TOAsO and AlamO into their respective 1:1 bromide salts is also virtually complete at low aqueous HBr concentrations; therefore, equilibration with a dilute hydrobromic acid solution is a suitable technique here too[9]. Complications due to the rapid uptake of a second molecule of hydrobromic acid by TOAsO will be discussed in the following sections.

Neutral organophosphorus compounds such as TOPO, extract the halogen acids, HCl and HBr, rather poorly (Fig. 1; *cf.* ref. 10), an (HX–TOPO)$_{org.}$ = 1:1 ratio being reached at relatively high acid normalities only. In view of this distinctly different situation, it was thought interesting to compare the behaviour of non-equilibrated TOPO as a stationary phase with TOPO equilibrated with approx. 6 $N$ HBr, *i.e.* an acid solution of sufficiently high normality to reach this 1:1 ratio.
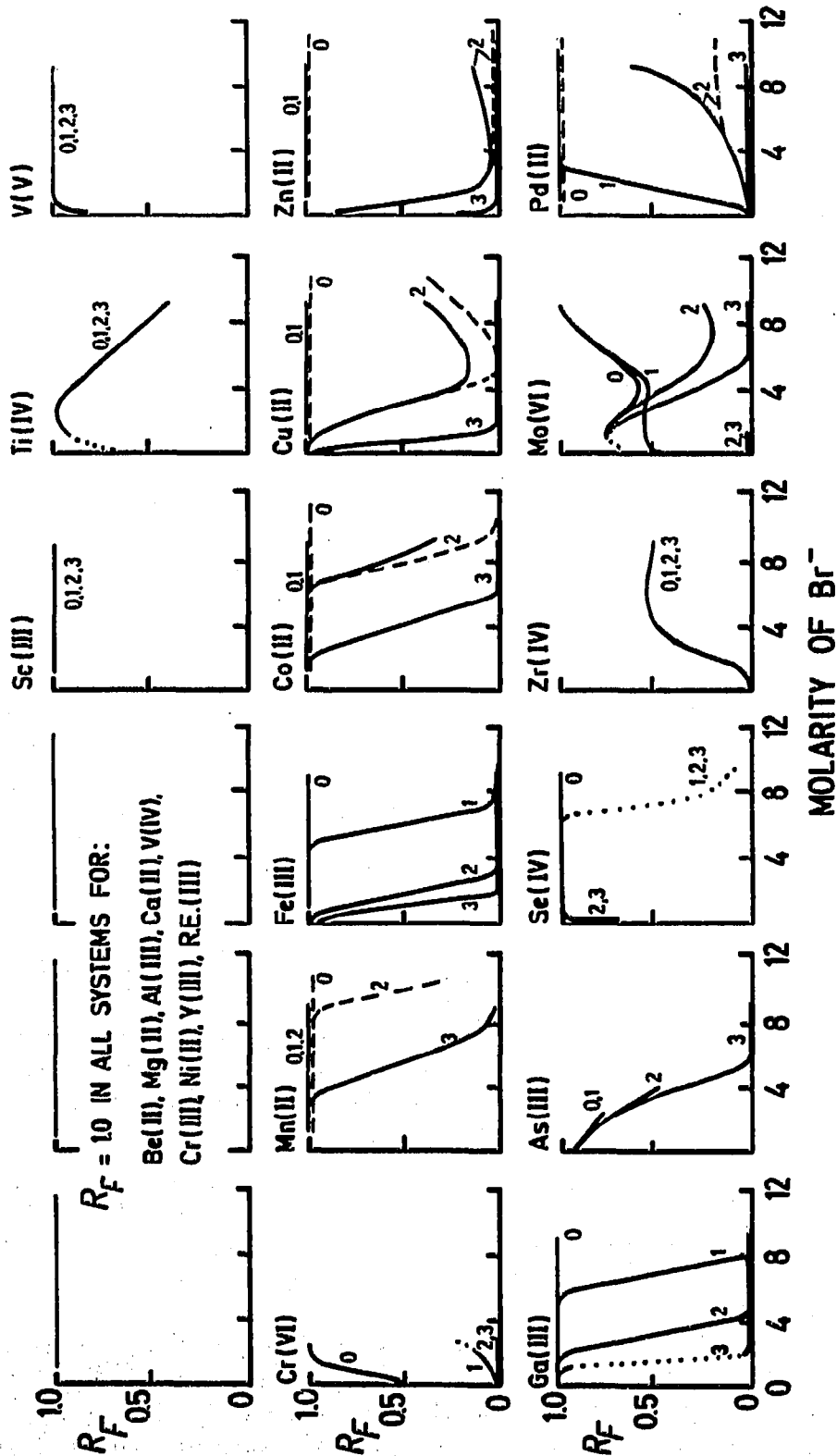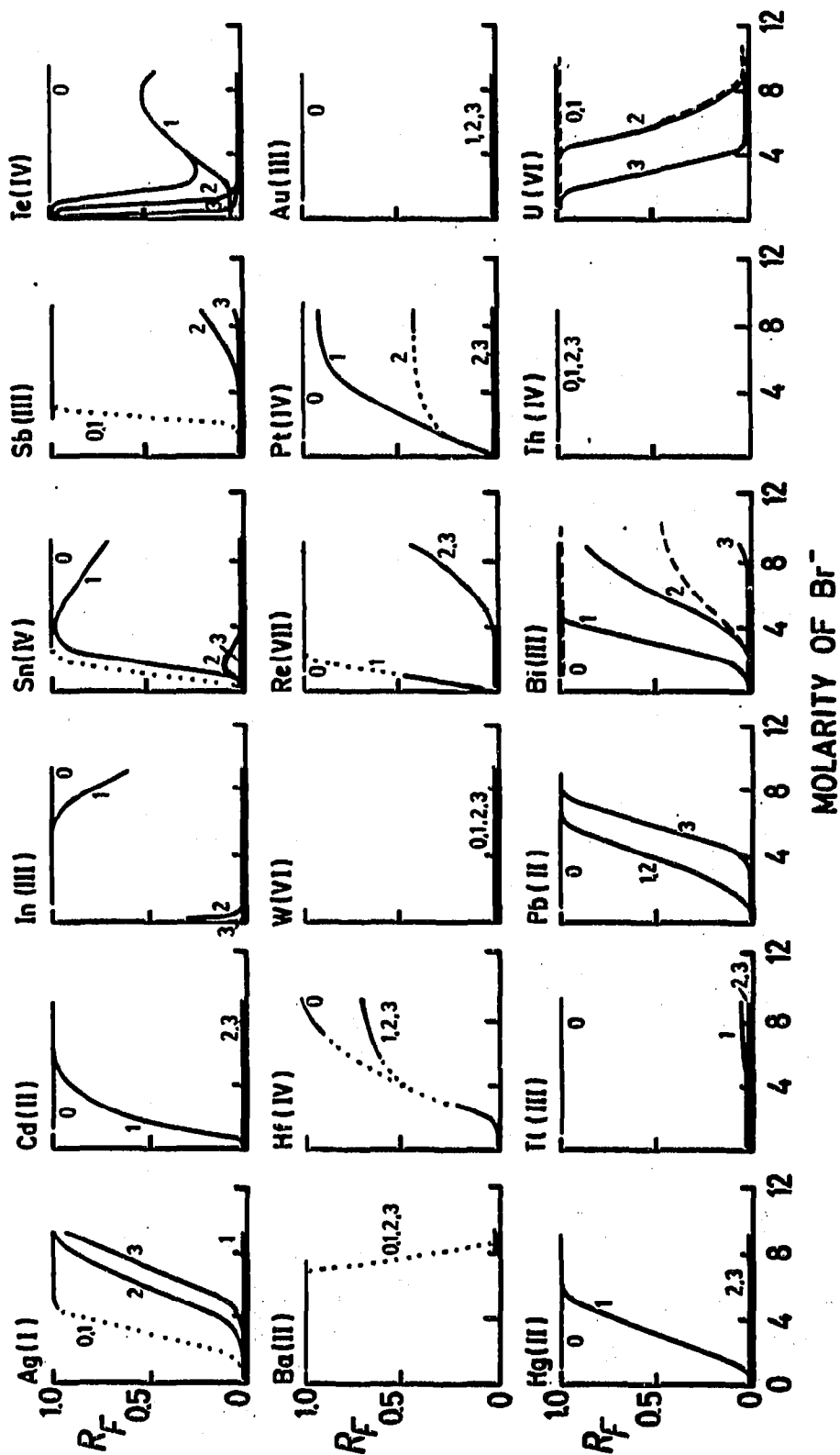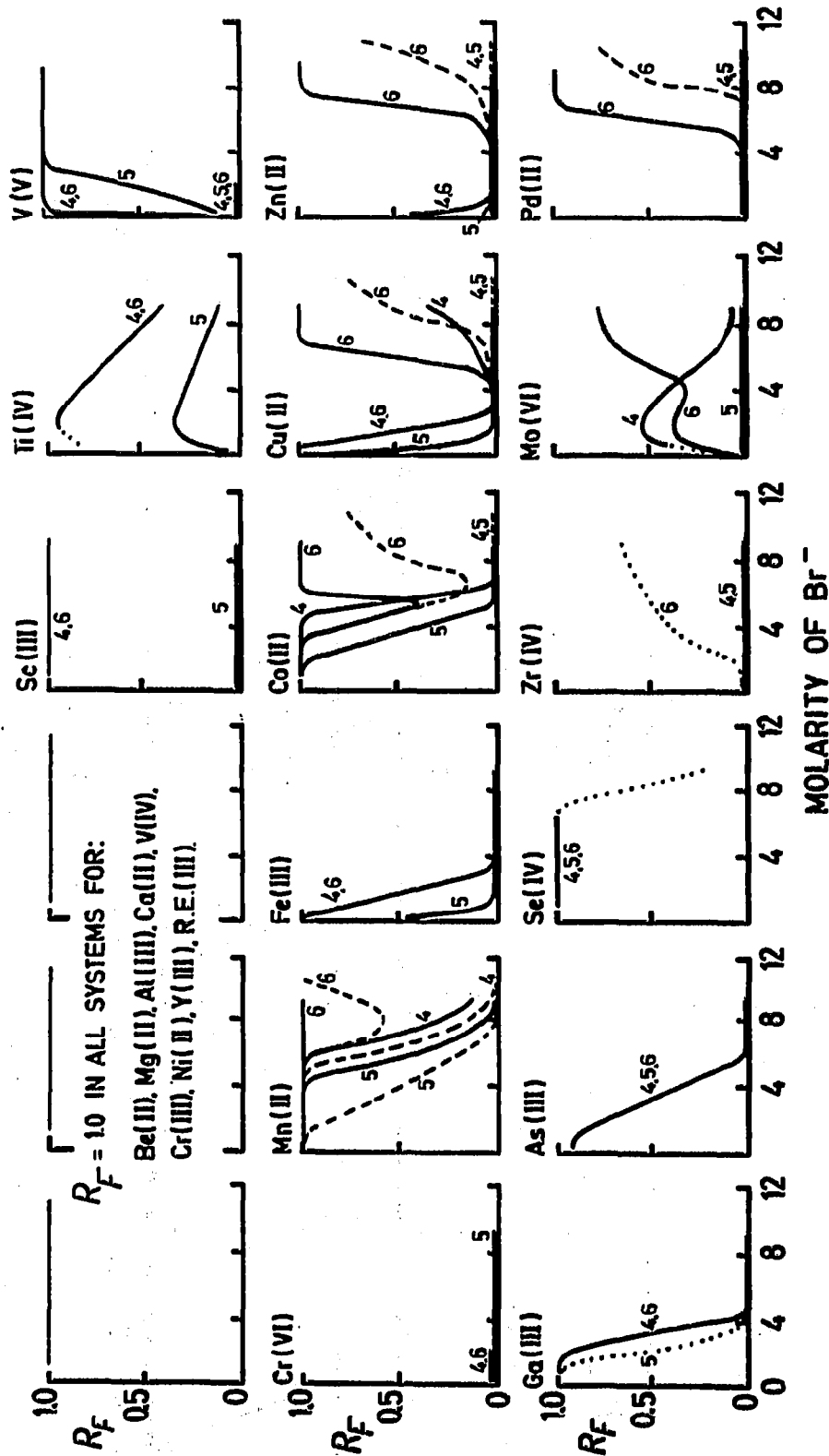
Fig. 2. $R_F$ versus $M$ Br⁻ spectra in thin-layer chromatography, using silica gel impregnated with Primene (1), Amberlite LA-1 (2) or Alamine (3), and non-impregnated silica gel (0). Eluants: ————, HBr; – – – –, acidified LiBr. Diffuse spots are indicated by dots.

$R_F = 1.0$ IN ALL SYSTEMS FOR:

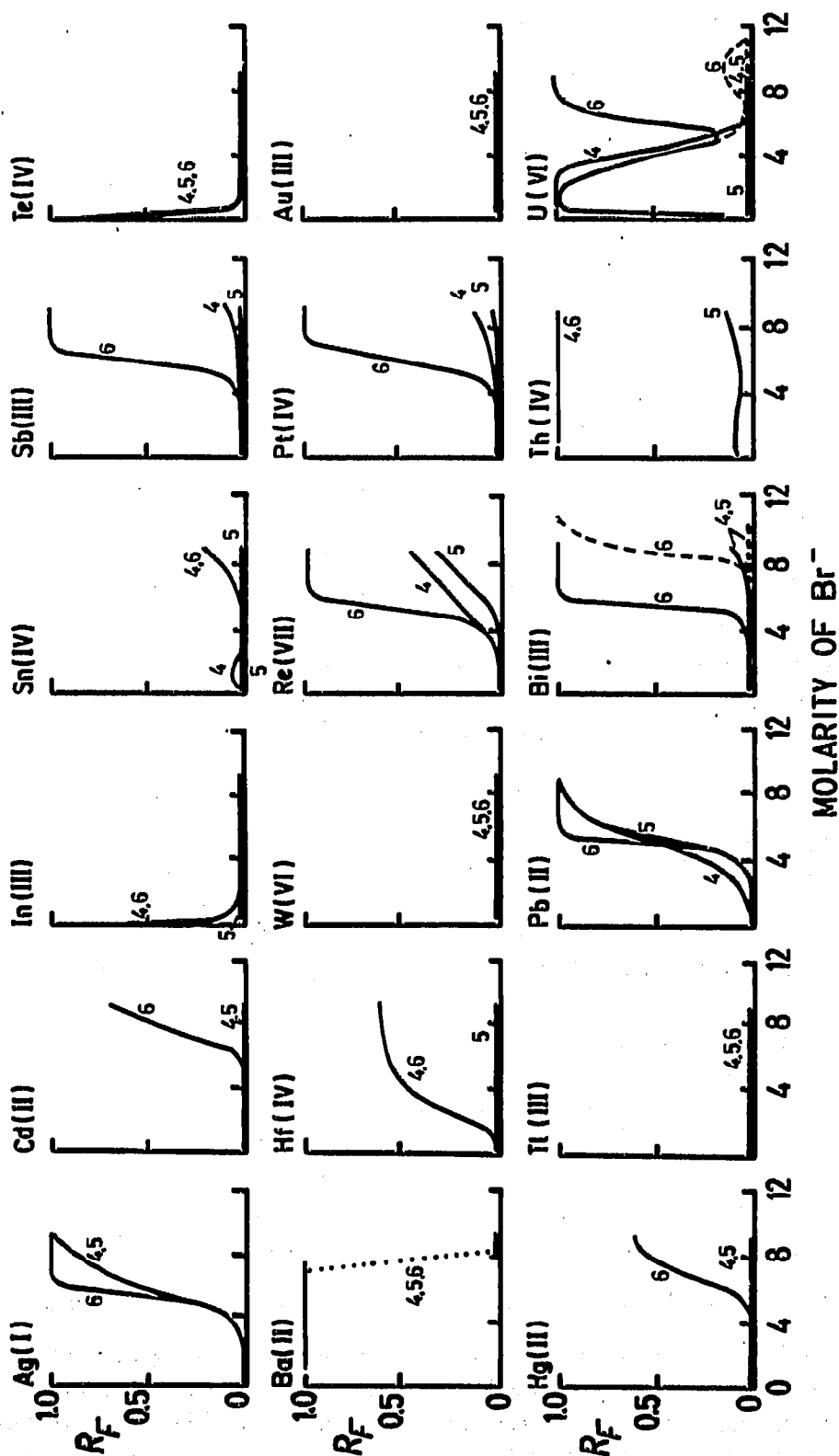Be(II), Mg(II), Al(III), Ca(II), V(IV),
Cr(III), Ni(II), Y(III), R.E.(III).

Fig. 3. $R_F$ versus $M$ Br⁻ spectra in thin-layer chromatography using silica gel impregnated with AlamO (4), TOPO (5) or TOAsO (6). Eluants: ———, HBr; ----, acidified LiBr. Diffuse spots are indicated by dots.

### Reversed-phase chromatography

$R_F$ versus $N$ HBr spectra for about 40 ions are shown in Figs. 2 (amines) and 3 (oxides). Chromatography on non-impregnated silica gel (Fig. 2) has been carried out in order to determine the effect of phenomena such as hydrolysis, precipitation

and adsorption to the support. $R_F$ spectra for 7 selected ions in extractant–LiBr systems are included in Figs. 2 and 3.

*Amines*

Only a few workers have devoted attention to the use of $Br^-$-containing eluants in reversed-phase extraction chromatography. Paper chromatography has been carried out for about 40 ions with up to 6 $M$ $Br^-$ (HBr and acidified NaBr)[11,12]; two exchangers were selected, *viz.* tri-*n*-octylamine and Amberlite LA-2. Secondary (Amberlite LA-1), tertiary (tri-*i*-octylamine and Adogen 368) and quaternary (Aliquat 336 and Adogen 464) exchangers have been employed in thin-layer chromatography on silica gel[13,14]; $R_F$ spectra for 9 ions are reported*.

The $R_F$ spectra in Fig. 2 indicate that the sorption strength of the amines increases in the order primary $<$ secondary $<$ tertiary, the sequence commonly observed in liquid anion-exchanger–monobasic strong acid systems[13,16]. Our results show a close agreement with the quoted literature data on liquid anion exchangers, and also with the $R_F$ spectra reported by BAGLIANO *et al.*[17] for some metal ions on the strong-base resin paper Amberlite SB-2. As the only major discrepancy we note that Ga(III) shows strong sorption in the liquid anion exchanger–HBr systems — which parallels data observed for liquid[4,12] and resin[18] exchanger–HCl systems — whereas $R_F = 1.0$ is reported for the Amberlite SB-2 paper. The differences occurring with Ti(IV) and Zr(IV) may be attributed to the role played by the support: no sorption is observed in *e.g.* the Alamine–HBr system when cellulose powder is used instead of silica gel.

Up to 9 $M$ $Br^-$ substitution of HBr by its lithium salt leads to a slight increase in sorption only with *e.g.* Mn(II) and Co(II) (see also Fig. 5). This result comes up to expectations, since the formation, and competitive extraction, of $HX_2^-$ (X = Br or Cl), which occurs readily with HCl, is much less pronounced with HBr (Fig. 1 and ref. 8). On the other hand, it must be admitted that the distinct increase in sorption observed for Pd(II) and Bi(III) cannot easily be explained using the $HBr_2^-$ hypothesis.

A survey of the $R_F$ spectra in Fig. 2 shows that the ions may be divided into three groups as regards their sorption behaviour (Table I): (*a*) $R_F > 0.9$ *in all amine–HBr systems* — with the ions in the group, formation of negative metal–bromo complexes is negligible and no anion exchange occurs; (*b*) $0.9 > R_F \geqslant 0.0$, *sorption increasing in the order primary $<$ secondary $<$ tertiary* — negatively charged complexes are formed and extracted in at least part of the HBr concentration range investigated and the anion-exchange process may be represented by:

$$[n\mathrm{RR'}_3\mathrm{N}^+\mathrm{Br}^-]_{org.} + [\mathrm{MBr}_p^{n-}]_{aq.} \rightleftharpoons [(\mathrm{RR'}_3\mathrm{N}^+)_n\mathrm{MBr}_p^{n-}]_{org.} + [n\mathrm{Br}^-]_{aq.} \qquad (1)$$

where R = alkyl; R' = alkyl or H. The behaviour of the ions on untreated silica gel shows that complicating factors are hardly present. Two types of exceptions may be noted, *viz.* hydrolysis and/or precipitation at low aqueous HBr concentrations (Ag, Sn and Sb) and, probably, the formation of polyanions and cationic species (Mo; refs. 14 and 19); (*c*) $0.9 > R_F \geqslant 0.0$ — *equal sorption in all three amine–HBr systems*.

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* When preparing this manuscript, a further paper[15] came to our notice which includes $R_F$ spectra for 18 ions in TnOA–Br⁻ and Amberlite LA-1–Br⁻ systems (support, $SiO_2$; eluant, NaBr acidified with $HClO_4$). Agreement with our data is good.

TABLE I

PROVISIONAL CLASSIFICATION OF IONS ACCORDING TO THEIR BEHAVIOUR ON CHROMATOGRAPHY IN AMINE (OXIDE)–HBr SYSTEMS

| Grouping by predominant phenomena | | | | | |
|---|---|---|---|---|---|
| Group a<br>No anion exchange<br>No complications | | Group b<br>Anion exchange | | | Group c<br>Precipitation,<br>hydrolysis, etc. |
| Be | Mg | Cr(VI) | Mn | Fe | Ti |
| Al | Ca | Co | Cu | Zn | As |
| Sc | V(IV) | Ga | Se(?) | Mo | Zr |
| V(V) | Cr(III) | Pd | Ag | Cd | Ba |
| Ni | Y | In | Sn | Sb | Hf |
| Ce | Yb | Te | Re | Pt | W |
| Th | | Au | Hg | Tl | |
| | | Pb | Bi | U | |

The role of the anion exchanger is negligible and the shape of the $R_F$ spectra is mainly determined by phenomena such as precipitation of insoluble salts (Ba) and adsorption to the support and/or hydrolysis (Ti, Zr, Hf and W). This hypothesis is confirmed by the fact that the shape of the $R_F$ spectra does not alter when chromatography is carried out on non-impregnated silica gel.

Comparison of the classification in Table I with the one previously reported[14] for $Cl^-$ systems reveals that there are minor differences only: V(V) (Group a), and As(III) and W(VI) (both Group c) all belong to Group b in the amine–HCl system.

*Oxides*

No data have been reported in the literature on chromatography in any of the three oxide–$Br^-$ systems.

The $R_F$ spectra for the AlamO–$Br^-$ system show a very close analogy with those reported for the corresponding amine systems (Figs. 2 and 3). The sorption strength of AlamO varies between that of Amberlite and Alamine, depending on the ion selected for comparison (ref. 1*). The data strongly suggest an identical mechanism of extraction for the two types of compounds; *i.e.*, the classification given in Table I applies for AlamO too, and the sorption of ions in Group b may be represented by:

$$[nR_3NOH^+Br^-]_{org.} + [MBr_p^{n-}]_{aq.} \rightleftharpoons [(R_3NOH^+)_n MBr_p^{n-}]_{org.} + [nBr^-]_{aq.} \quad (2)$$

However, minor deviations such as encountered with Cu(II) in the $Cl^-$ system (extraction of $CuCl_3^-$ and $CuCl_4^{2-}$ with AlamO, and of $CuCl_4^{2-}$ only with amines[1]) may also occur here. The chromatographic data do not allow us to reach any conclusions regarding this aspect.

With TOPO, identical $R_F$ spectra are obtained for each ion over the whole HBr concentration range investigated, whether the extractant is equilibrated or not. Besides, the quality of the chromatograms is the same in both cases. Therefore, the equilibration step may safely be omitted.

A comparison of the data presented for TOPO and AlamO, or the amines, reveals that the shape of the $R_F$ spectra generally is the same. For the majority of the ions investigated the sorption strength of TOPO is approximately equal to that of

* Note that in ref. 1 the figures, but not the legends, on pages 174 and 176 should be interchanged.

Alamine. However, Sc(III), Ti(IV), V(V), Zr(IV), Mo(VI), Hf(IV), Th(IV) and U(VI) all show strong sorption on TOPO-impregnated silica gel, whereas sorption is rather weak — or even completely absent (Sc and Th) — with AlamO- or amine-impregnated silica gel. The effect of the substitution of HBr by LiBr can be observed with Mn(II) and Bi(III) only, since the other five ions tested show $R_F = 0$ even at high HBr normalities.

The differences noted when comparing TOPO and amines or amine oxides, may be explained as follows. The latter two types of extractants are present as the respective bromide salts over the whole Br⁻ concentration range investigated in the present study and in consequence, ions such as Sc(III) and Th(IV), which do not form anionic metal–bromo complexes, show $R_F = 1.0$ at all Br⁻ concentrations with both AlamO and amines. However, with TOPO, at low acid concentrations, a considerable proportion of the extractant is present in its free form (Fig. 1). This strongly suggests that the sorption occurring on TOPO-impregnated supports is due to the formation of compounds such as ScBr$_3$·$n$TOPO and ThBr$_4$·$m$TOPO (refs. 20 and 21). Solvation of neutral metal(oxy)bromides probably also explains the high extraction efficiency of TOPO towards Zr(IV), Hf(IV), Mo(VI) and U(VI).

The explanation of the extraction of Sc(III), Th(IV), etc., through solvation may lead one to propose a similar extraction mechanism in the case of ions such as Co(II), Cu(II), Fe(III), Zn(II), In(III) and Bi(III), despite the closely analogous sorption behaviour of these ions on TOPO and amine-impregnated silica gel. Oppositely, however, the very fact of this analogous behaviour suggests that Co(II), Cu(II), etc., are extracted by TOPO as complex metal–bromo anions, even though Sc(III) and Th(IV) are extracted as neutral metal bromides. Neither of these two viewpoints can be defended on the basis of the qualitative similarity, or dissimilarity, of $R_F$ *versus* $M$ Br⁻ spectra only. Evidence for the occurrence of a mixed solvation–anion-exchange mechanism with Co(II) will be presented in the next section.

The $R_F$ spectra obtained for the TOAsO–HBr system show a superficial analogy with those recorded for the other extractant–HBr systems only. Admittedly, up to 5–6 $N$ HBr the resemblance is fair, but the sharp increase of the $R_F$ values occurring with TOAsO at the stated normality is never observed with any of the other extractants. The sharp increase of the $R_F$ values in the TOAsO–Br⁻ systems has a parallel in the strong desorption occurring for many metal ions in the TOAsO–Cl⁻ system[1]. Therefore, it lies at hand again to ascribe the rapidly decreasing extractability of the ions to the preferential extraction of a second molecule of acid: in the present case HBr (Fig. 1). The distinct shift of the ascending branches of both the $R_F$ and the acid-extraction curves to higher aqueous Br⁻ concentrations upon substitution of the HBr by LiBr supports this suggestion. The hypothesis explains the experimental data very satisfactorily, even though the break in the $R_F$ and the acid-extraction curves occurs at rather widely divergent acid concentrations; the presence (extraction) or absence (chromatography) of a diluent probably plays a role here. No explanation can as yet be offered for the rapid and stoichiometric uptake of the second molecule of HBr (HCl), which appears to be a rather unique property of the arsine oxide.

*Separations*

Several interesting separations are recorded in Fig. 4. As is apparent from this figure, and even more so from a detailed study of the $R_F$ spectra in Figs. 2 and 3, the
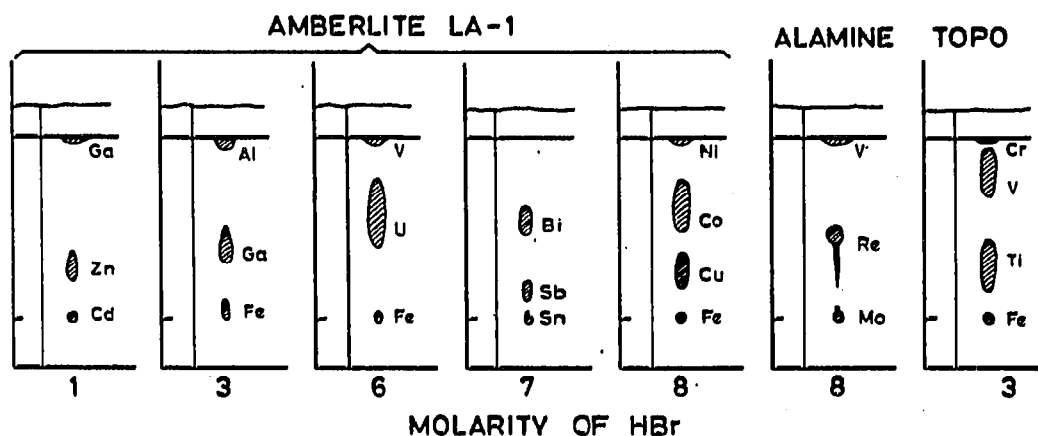
Fig. 4. Examples of separations carried out in various extractant–HBr systems. V = V (V); Cr = Cr(III).

moderately sorbing Amberlite LA-1 offers the best opportunities in analysis. One may add that for special purposes, *e.g.* the separation of Sc(III), Zr(IV) or Th(IV) ($R_F$ = 0.0) from a rather large number of elements ($R_F$ = 1.0), TOPO will come in useful.

*Liquid–liquid extraction*

Data on liquid–liquid extraction of metal ions from aqueous bromide solutions are comparatively sparse. Reference may be made here to studies by SUZUKI AND SOTOBAYASHI[22], ALIAN[23] and BRINKMAN[14] on extraction by amines. As an illustration, some data from refs. 14 and 22 are summarized in Table II. Bearing in mind that the results of reversed-phase chromatography may be compared with data obtained in liquid–liquid extraction on the basis of the well-known relationship

$$D = k(1/R_F - 1) \tag{3}$$

where $D$ is distribution coefficient and $k$ is constant, we may conclude that a good qualitative agreement exists. The same conclusion is reached when considering the results reported by ALIAN.

A study has been made of the systems extractant–Co(II)–Br⁻. Percentage extraction *versus* $M$ Br⁻ curves are shown in Fig. 5. The organic phases obtained in the three amine–Co(II)–Br⁻ and the AlamO–Co(II)–Br⁻ systems have identical

TABLE II

COMPARISON OF PERCENTAGE EXTRACTION AND $R_F$ VALUES FOR NINE ELEMENTS IN THE AMBERLITE LA-1–HBr SYSTEM

Percentage extraction and $R_F$ values correspond to refs. 22 and 14, respectively.

| Ion | | *Percentage extraction* | | | $R_F$ | | |
|---|---|---|---|---|---|---|---|
| | *N HBr* | *0.3* | *0.5* | *7.0* | *0.3* | *0.5* | *7.0* |
| Mn(II) | | 0.0 | 0.0 | | 1.0 | 1.0 | |
| Ni(II) | | 0.0 | 0.0 | 0.8 | 1.0 | 1.0 | 1.0 |
| Co(II) | | 0.0 | 0.0 | 1.4 | 1.0 | 1.0 | 0.7 |
| Fe(III) | | 0.4 | 0.5 | 99.7 | 0.9 | 0.8 | 0.0 |
| Cu(II) | | 0.5 | 0.5 | 39.4 | 0.9 | 0.9 | 0.3 |
| Zn(II) | | 1.9 | 3.4 | | 0.6 | 0.2 | |
| Pb(II) | | 87.8 | 89.4 | | 0.02 | 0.01 | |
| Bi(III) | | 100.0 | 100.0 | | 0.0 | 0.0 | |
| Cd(II) | | 100.0 | 100.0 | | 0.0 | 0.0 | |
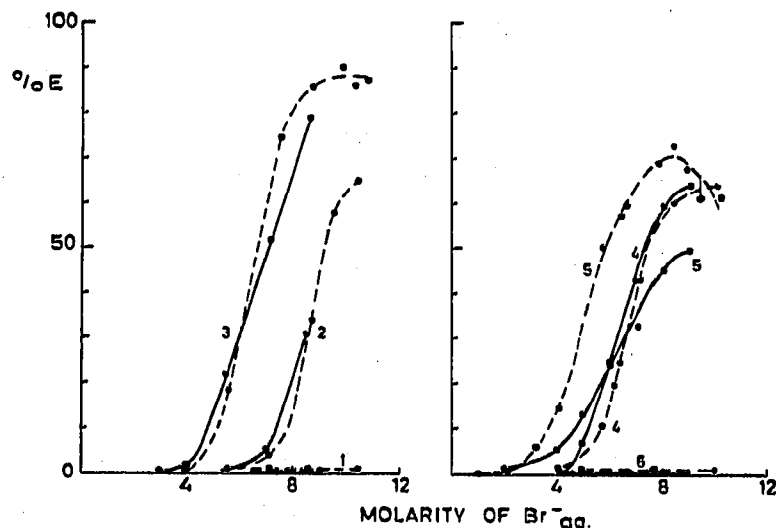
Fig. 5. Percentage extraction *versus* $M$ Br$^-$ curves for various o.1 $M$ extractant–o.o4 $M$ CoBr$_2$–Br$^-$ systems. ————, HBr; – – – –, LiBr acidified with o.4 $N$ HBr. Diluent: toluene. $V_{aq.} = V_{org.}$. For explanation of symbols, see Figs. 2 and 3.

visible absorption spectra (absorption maxima at 726, 699, 664 and 640 nm), irrespective of the extractant used, the molarity of the aqueous bromide solution and the use of either HBr or LiBr. The spectra indicate that CoBr$_4$$^{2-}$ is the sole Co(II)-containing species present in the organic extracts[14,24,25].

With TOPO, a slightly different situation arises. Again the percentage extraction and sorption vary in a qualitatively similar way. Spectra recorded for organic TOPO phases that have been contacted with CoBr$_2$ dissolved in conc. HBr, are identical with those recorded for amines and AlamO. This indicates that the sorption/extraction proceeds through an anion-exchange mechanism; the complex anion probably constitutes part of an associated electrolyte of the type (TOPOH$^+$)$_2$CoBr$_4$$^{2-}$*. However, spectra recorded for organic phases contacted with solutions of CoBr$_2$ in o.1–2 $N$ HBr, are virtually identical with the spectrum of CoBr$_2$ dissolved in a solution of TOPO in toluene (absorption maxima at 677, 647, 618 and 597 (sh.) nm; *cf.* ref. 27). This suggests that, at low aqueous HBr concentrations, cobalt is present in the organic phase as CoBr$_2$·$n$TOPO. If HBr is substituted by (acidified) LiBr, the organic extracts show the spectrum attributed to solvated CoBr$_2$ even up to 4 $M$ Br$^-$. This is presumably due to the fact that the use of LiBr strongly retards the formation of TOPOH$^+$Br$^-$ (Fig. 1b): a larger proportion of TOPO remains in its free form, and the extraction of CoBr$_2$ is preferred to that of CoBr$_4$$^{2-}$.

Even though a complete analysis of the absorption spectra as a function of the aqueous Br$^-$ concentration has not been made as yet, the present data allow us to conclude that the sorption/extraction of Co(II) follows a mixed solvation/anion-exchange mechanism. In the literature, similar "mixed" mechanisms have been reported for *e.g.* the systems tri-$n$-butyl phosphate–Co(II)–Cl$^-$ and amine oxide–U(VI)–Cl$^-$ (refs. 28 and 29). In the former case, extraction through solvation occurs up to approx. 2 $N$ HCl; with uranium, extraction through solvation is reported for virtually acid-free (< o.035 $N$) aqueous solutions only. This is according to expecta-

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* The presence of additional TOPO and/or water molecules in the complex is not excluded[10,26].

tions: only in this acid concentration range (which is well outside the one used in our present study) a large proportion of the amine oxide will be present in its free form.

The percentage extraction of Co(II) by TOAsO is very low ($< 3\%$) up to 9 $M$ Br⁻ (both HBr and LiBr). This result is not too surprising in view of the hypothesis outlined when discussing the $R_F$ spectra. Assuming the extraction efficiency of TOAsO at low aqueous bromide concentrations to be about equal to that of AlamO, as is suggested by the $R_F$ spectra in Fig. 3, one may expect that the extraction of Co(II) by TOAsO starts at an aqueous concentration of 3–5 $M$ Br⁻. However, from this concentration, the preferential uptake of a second molecule of HBr (Fig. 1b) effectively prevents the extraction of cobalt, which, therefore, remains virtually negligible.

A single concluding remark may be made here. The data presented above clearly show that the resemblance of the $R_F$ spectra for a few, or a specified group of, ions in different extractant–HBr systems does not guarantee that the underlying mechanism is identical in both cases (TOPO *versus* amines). On the other hand, good agreement between the $R_F$ spectra for, properly speaking, *all* ions in two extractant–HBr systems strongly suggests that the mechanism of extraction for these systems indeed is the same (amines and amine oxides). To put it differently, with the amines and amine oxides, extraction proceeds through anion-exchange, while with TOPO both solvation and anion-exchange play a role.

REFERENCES

1 H. R. LEENE, G. DE VRIES AND U. A. TH. BRINKMAN, *J. Chromatogr.*, 57 (1971) 173.
2 J. KENNEDY AND R. PERKINS, *J. Inorg. Nucl. Chem.*, 26 (1964) 2601.
3 A. J. F. BLAIR AND H. MICHAEL, *Rept. 434-PC*, Jülich (BRD), 1966.
4 U. A. TH. BRINKMAN, G. DE VRIES AND E. VAN DALEN, *J. Chromatogr.*, 25 (1966) 447.
5 G. DE VRIES, H. R. LEENE AND U. A. TH. BRINKMAN, in preparation.
6 G. DE VRIES AND U. A. TH. BRINKMAN, *J. Chromatogr.*, 64 (1972) 374.
7 E. CERRAI AND C. TESTA, *J. Chromatogr.*, 5 (1961) 442.
8 J. I. BULLOCK, S. S. CHOI, D. A. GOODRICK, D. G. TUCK AND E. J. WOODHOUSE, *J. Phys. Chem.*, 68 (1964) 2687.
9 D. E. LINDER, R. A. ZINGARO AND K. IRGOLIC, *J. Inorg. Nucl. Chem.*, 29 (1967) 1999.
10 A. I. MIHAILICHENKO, *Radiokhimiya*, 12 (1970) 594.
11 S. PRZESZLAKOWSKI AND E. SOCZEWINSKI, *Chem. Anal. Warsaw*, 11 (1966) 895.
12 S. PRZESZLAKOWSKI, *Chem. Anal. Warsaw*, 12 (1967) 1071.
13 U. A. TH. BRINKMAN, G. DE VRIES AND E. VAN DALEN, *J. Chromatogr.*, 23 (1966) 287.
14 U. A. TH. BRINKMAN, *Thesis*, Amsterdam, 1968.
15 A. MUCHOVÁ AND V. JOKL, *Chem. Zvesti*, 25 (1971) 280.
16 U. A. TH. BRINKMAN, in E. S. PERRY AND C. J. VAN OSS (Editors), *Progress in Separation and Purification*, Vol. IV, Wiley-Interscience, New York, 1971, p. 241.
17 G. BAGLIANO, G. GRASSINI, M. LEDERER AND L. OSSICINI, *J. Chromatogr.*, 14 (1964) 238.
18 M. LEDERER AND L. OSSICINI, *J. Chromatogr.*, 13 (1964) 188.
19 S. KAMIYA, M. TOKUTOMI AND Y. MATSUDA, *Bull. Chem. Soc. Japan*, 40 (1967) 407.
20 D. F. C. MORRIS AND K. J. SUTTON, *Bull. Chem. Soc. Japan*, 40 (1967) 786.
21 T. SATO AND M. YAMATAKE, *J. Inorg. Nucl. Chem.*, 31 (1969) 3633.
22 T. SUZUKI AND T. SOTOBAYASHI, *Bunseki Kagaku*, 12 (1963) 910; 13 (1964) 1103.
23 A. ALIAN, *Mikrochim. Acta*, (1968) 981.
24 D. A. FINE, *J. Amer. Chem. Soc.*, 84 (1962) 1139.
25 D. F. C. MORRIS, E. L. SHORT AND D. N. SLATER, *J. Inorg. Nucl. Chem.*, 26 (1964) 627.
26 T. J. CONOCCHIOLI, M. I. TOCHER AND R. M. DIAMOND, *J. Phys. Chem.*, 69 (1965) 1106.
27 F. A. COTTON, D. M. L. GOODGAME, M. GOODGAME AND A. SACCO, *J. Amer. Chem. Soc.*, 83 (1961) 4157.
28 D. F. C. MORRIS AND E. L. SHORT, *Electrochim. Acta*, 7 (1962) 385.
29 R. G. PUZIĆ, *J. Inorg. Nucl. Chem.*, 34 (1972) 1031.