CHROM. 5093

Chromatographic techniques using liquid anion exchangers

IV. HF systems*

Reversed-phase extraction chromatography on supports impregnated with liquid anion exchangers is used with solutions of many inorganic acids as eluants. Most frequently, paper and thin-layer techniques are employed, but with HF systems only paper chromatographic (PC) results have been published[1]. In the present communication, we report on thin-layer chromatography (TLC) with HF-containing eluants. Four exchangers were selected to represent primary (Primene), secondary (Amberlite LA-2) and tertiary (Alamine) amines, and quaternary ammonium salts (Aliquat). Elution was performed with 0.1–20 N aq. HF solutions.

For reversed-phase TLC, glass plates are normally covered with silica gel impregnated with a liquid exchanger, but silica gel and glass are unsuitable for fluoride systems. It was found that cellulose powder on polyvinyl chloride sheets is a very useful support for this class of separations.

Materials and methods

Aliquat 336 is a methyl-tri-*n*-alkylammonium chloride with an average of 27–33 carbon atoms and a mean mol. wt. of 475; Alamine 336 is a C_8–C_{10} straight-chain alkylamine with a tertiary amine content of minimal 90% and a mean mol.wt. of 392. Both exchangers are manufactured by General Mills (Kankakee, Ill., U.S.A.). Amberlite LA-2 is a dodecyltrialkylmethylamine with a mean mol. wt. of 374; Primene JM-T is a mixture of a relatively large number of trialkylmethylamines (18–24 carbon atoms); the middle fractions having a mean mol. wt. of 300–310 were isolated by repeated vacuum distillation[2]. The latter two amines are supplied by Rohm and Haas (Philadelphia, Pa., U.S.A.).

A 0.1 M solution of the amines in chloroform is equilibrated with an equal volume of 1 N HF; Aliquat is converted into the fluoride salt by shaking its (0.1 M) solution with an equal volume of a 0.3 M AgF + 0.7 N HF solution. It is of interest to note that repeated equilibration with 1 N HF does not lead to quantitative conversion of the Aliquat chloride. Use of an Aliquat (F, Cl) mixture so obtained in chromatography causes the occurrence of too high R_F values and streaking of the spots, especially at low HF normalities. 100 ml of the solution containing liquid anion exchanger are thoroughly mixed with 30 g of cellulose powder (Avicel TG 104, F. M. C., Marcus Hooke, Pa., U.S.A.). PVC sheets (0.5 mm thickness) are cut into plates of appropriate size (7 × 2.5 cm) and these are dipped into the cellulose slurry. Superfluous material is wiped off the back and a small margin is made along the edges. 2–6 spots are applied to each plate. Sample solutions are prepared by dissolving commercially available oxides or salts in 1 N HF. (With the metal ions, care was taken to avoid the presence of strongly complexing foreign anions.)

Ascending chromatography is carried out for a 3.0-cm run, in perspex jars. Developing times as a rule are between 3 and 5 min. The (impregnated) cellulose adheres well to the PVC carrier material. As the only exception, Primene-treated cel-

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* For part III of this series, see ref. 3.

lulose sometimes flakes off when developing with 0–2 N HF. Details regarding the experimental technique and the visualisation procedures may be found in refs. 3 and 4.

Results and discussion

Of the 28 ions studied, Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and In(III) show slight sorption ($R_F > 0.8$) over the whole HF concentration range investigated. These results agree with those obtained by PRZESZLAKOWSKI[1] on paper impregnated with anion exchanger and by FARIS[5] in a study of the adsorption of elements from aqueous HF solutions by a strong base resin exchanger. It may be assumed, therefore, that the ions in question do not form anionic metal–fluoro complexes or only form very weak ones.

For all other ions, R_F vs. N HF plots are presented in Fig. 1. Streaking of the spots occasionally occurs at low HF concentrations; Ti(IV) always forms streaking spots below 1 N HF. The combined data, which generally show good agreement with

TABLE I

QUALITATIVE SEPARATIONS IN LIQUID ANION EXCHANGER–HF SYSTEMS

Ions to be separated				Exchangers	N HF
Mo	As	Ge		Primene	4
B	Ti	Al		LA-2	3
Nb	W	Fe		LA-2	12
Re	W	Mo		·LA-2	6–8
U	V	Fe		LA-2; Alamine	4
Ta	W	V		LA-2; Alamine; Aliquat	8–12
Re	Te	V	Se	LA-2; Alamine; Aliquat	4–6

the paper chromatographic results of PRZESZLAKOWSKI[1], indicate that all four exchanger–HF systems investigated may well be employed in practice. Several interesting separations may be read from the figure. Examples are given in Table I.

It is interesting to note that for all ions investigated, sorption decreases with an increase of the aqueous HF concentration. The conclusion holds for both liquid and resin anion exchangers. This characteristic sorption *vs.* concentration curve has been explained by the formation of extractable anionic fluoro complexes at relatively low aqueous HF concentrations and non-extractable higher metal–fluoro complexes at higher acid concentrations (*cf.* ref. 6). However, for a more plausible explanation, we can point to the competitive extraction of hydrofluoric acid itself.

As is well known from several liquid–liquid extraction studies with tertiary amines[7,8], HF is easily extracted beyond the amount of acid necessary to neutralise the amine; ratios of R_3N:HF = 1:2–4 are obtained for 1–10 N HF. The extraction of excess acid may be interpreted in terms of the formation of HF_2^-, and subsequently higher hydrogen-bonded anions. Research in our laboratory has demonstrated that the same phenomenon occurs with primary and secondary amines, and also with quaternary ammonium salts; *i.e.*, we may write (R = alkyl; R' = alkyl or H):

$$RR'_2N_{org.} + HF_{aq.} \rightleftharpoons RR'_2NH^+F^-_{org.} \tag{1}$$
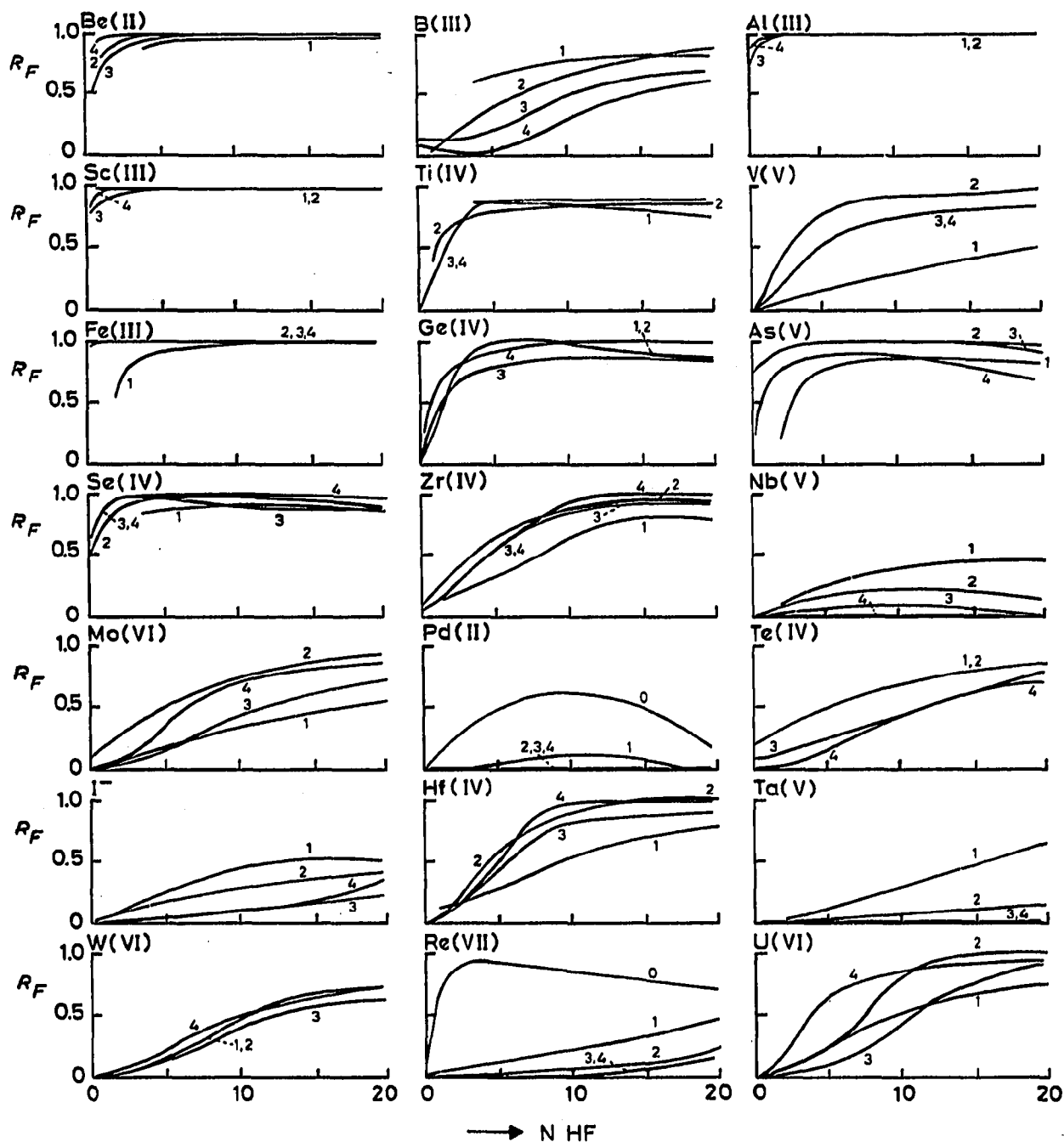
for the neutralisation of the amines, and

Fig. 1. R_F vs. N HF spectra for 21 ions, using cellulose impregnated with Primene (1), Amberlite LA-2 (2), Alamine 336 (3) or Aliquat 336 (4), and cellulose not treated with an anion-exchanger (0).
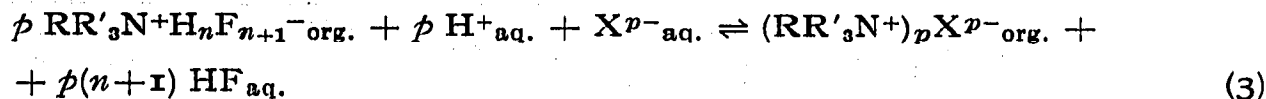
$$RR'_3N^+F^-_{org.} + n\ HF_{aq.} \rightleftharpoons RR'_3N^+H_nF_{n+1}^-{}_{org.} \tag{2}$$

for the uptake of excess HF by both alkylamine·HF and quaternary ammonium fluoride salts.

The $H_nF_{n+1}^-$ entity is more readily extractable than the relatively small, simple F^- anion, and so competes much better than the latter with the extraction of the metal–fluoro, etc. anions. The formation of $H_nF_{n+1}^-$ will thus considerably decrease the sorption of the elements investigated.

An analogous phenomenon, though to a much lesser extent, occurs in chloride systems. Here, the formation and preferential extraction of HCl_2^- at high aqueous HCl concentrations also causes the desorption of many metal ions, as is well known from both chromatography and extraction[9].

In order to determine the effect of phenomena such as hydrolysis and adsorption to the support, chromatography is also carried out on non-impregnated cellulose powder. R_F values of 0.7–0.8 or higher, consistently found for all ions with the exception of Pd(II) and Re(VII) (see Fig. 1), show that the above-mentioned effects hardly play a role. In conclusion, for the elements collected in Fig. 1, sorption is predominantly determined by anion exchange. Thus, the equilibria governing the reversed-phase extraction chromatography in fluoride systems may be represented by:

$$p\ RR'_3N^+H_nF_{n+1}^-{}_{org.} + p\ H^+_{aq.} + X^{p-}_{aq.} \rightleftharpoons (RR'_3N^+)_pX^{p-}_{org.} +$$
$$+ p(n+1)\ HF_{aq.} \tag{3}$$

with $n \geqslant 0$; X^{p-} represents metal–fluoro anions such as FeF_6^{3-} and TaF_7^{2-}, and anions of various other types such as e.g. I^- and ReO_4^-.

As a last point of interest, we may discuss the sorption strength of the four liquid anion exchangers. For all ions tested the sorption on Alamine-treated cellulose is higher than on Amberlite-impregnated cellulose, although the differences are sometimes very small. This observation confirms the results of PRZESZLAKOWSKI[1], who finds the order of sorption tertiary (TnOA) > secondary (Amberlite LA-2). However, somewhat surprisingly, with the quaternary exchanger Aliquat and the primary amine Primene, controversial results are obtained. As can be observed from the figures for some ions, e.g. B(III), Nb(V), Te(IV), Ta(V), Re(VII) and I^-, the order tertiary $\simeq$ quaternary > secondary > primary, commonly found with monobasic inorganic acids[3,10], is obtained. However, with others, e.g. V(V), Fe(III), Mo(VI), Zr(IV) and Hf(IV), the order of increasing sorption is properly speaking reversed: primary > secondary $\simeq$ tertiary $\simeq$ quaternary. Lastly, for a few ions, e.g. Ti(IV), Ge(IV), W(VI) and U(VI), a distinct sorption sequence of the exchangers cannot be given at all.

Since only a few systematic investigations have been carried out on the extraction of metal ions from fluoride solutions, it is not easy to draw parallels, if existent, between chromatography and extraction. It can be noted, however, that in the case of Fe(III), SHEVCHUK et al.[11] have observed that the extraction efficiency of primary amines clearly surpasses that of all other exchangers tested. This is possibly due to steric factors; since three amine·H^+ cations must be attached to the FeF_6^{3-} anion, the sorption/extraction by means of primary amines will be favoured over that involving more bulky, i.e. secondary, tertiary or quaternary, exchangers. This hypo-

thesis has been stated earlier to explain the good extractability of highly charged complex anions by primary amines in *e.g.* cyanide and oxalate[12,13], sulphate[14], and phosphate[15] systems, and found valid for both extraction and chromatography. The present chromatographic experiments confirm the hypothesis both by yielding the "normal" sorption sequence for the mononegative anions BF_4^-, ReO_4^- and I^-, and the reversed order for FeF_6^{3-}. However, in the absence of further data on the nature of the extracted species and in lack of a complete understanding of the factors causing the occurrence of the normal sorption sequence with singly and doubly charged anions, it cannot be concluded yet that steric effects are the only cause of the (partial) reversal of the normal order of sorption strength.

Free Reformed University,   U. A. TH. BRINKMAN
Chemistry Laboratory,   P. J. J. STERRENBURG
Amsterdam (The Netherlands)   G. DE VRIES

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