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THIN-LAYER CHROMATOGRAPHIC BEHAVIOUR OF METALS ON DEAE-CELLULOSE IN OXALIC ACID AND MIXED OXALIC ACID–HYDROCHLORIC ACID MEDIA

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SUMMARY

The adsorption behaviour of 46 metals on layers of DEAE-cellulose has been examined in aqueous oxalic acid media. R_F values are given as a function of oxalic acid concentration over the range 0.010–0.30 *M* and are compared with those obtained in a similar manner with Avicel SF. R_F data are also presented for 48 metals in oxalic acid–hydrochloric acid mixtures, where the oxalic acid concentration was kept constant at either 0.030 or 0.25 *M* and that of hydrochloric acid was varied from 0.010 to 3.0 *M*. Pronounced ion exchange takes place in oxalic acid media for many metals, but a limited number of metals are adsorbed on DEAE-cellulose from the mixed acid media. The versatility of the chromatographic system investigated is demonstrated by many multi-component separations conducted without marked tailing.

INTRODUCTION

There have been few systematic studies on the behaviour and separation of metals on anion-exchange resins in oxalic acid, oxalate and oxalic acid–mineral acid mixtures. De Corte *et al.*[1] determined the distribution coefficients of 12 elements on Dowex 1 in oxalic acid medium (0.001–0.98 *M*) and developed a scheme for the chromatographic separations of As(III), Mn(II), Co(II), Zn(II) and Cu(II); Na(I), Mn(II) and Zn(II); and Ce(III) and Lu(III). Strelow *et al.*[2] measured the anion-exchange distribution coefficients with Bio-Rad AG-1 for 36 elements in oxalic acid–hydrochloric acid mixtures and presented elution curves for multi-component systems. Scattered information on the ion-exchange separation of metals in oxalic acid, oxalate and oxalic acid–mineral acid mixtures is also available[3–12].

This work was undertaken in order to investigate the adsorption characteristics of metals on the anion exchanger DEAE-cellulose (henceforth abbreviated to DEAE) in aqueous oxalic acid and oxalic acid–hydrochloric acid mixtures by thin-layer chromatography. The chromatographic systems investigated permit many useful separations of analytical interest to be conducted effectively on DEAE.

EXPERIMENTAL

Stock solutions of metals

Metal stock solutions (0.1 *M*) were prepared as described previously[13]. The solutions of platinum metals (3 *M* hydrochloric acid) except for Pt(IV) were aged for 2 years after their preparation. The stock solution of Pt(IV) was allowed to stand for 2 months before use. The aged stock solutions of Ru(III) and Rh(III) were chromatographed on a DEAE(Cl^-) layer with 3 *M* hydrochloric acid, each yielding two spots: R_F 0.52 and 0.76 for Ru(III) and R_F 0.00 and 0.78 for Rh(III).

Preparation of thin-layer plates

DEAE (Serva, Heidelberg, G.F.R., for TLC) was used as adsorbent. For comparison purposes the microcrystalline cellulose Avicel SF (F.M.C., Marcus Fook, Pa., U.S.A.) was also used as adsorbent.

DEAE (oxalate form) plates. About 13 g of DEAE were washed with 500-ml portions of 0.002 *M* sodium hydroxide solution by centrifugation until the supernatant liquid was free from chloride ions. DEAE was then washed once with deionized water. The DEAE was mixed with 200 ml of 0.2 *M* oxalic acid and stirred for 5 min, and finally washed with deionized water by centrifugation until the pH of the supernatant liquid was 3. The DEAE (oxalate form) thus prepared was slurried with 28 ml of deionized water and spread in 250-μm thick layers on five 20 × 20 cm glass plates. The plates were dried in air for 1 h and then at 40° for about 3 h, and were stored in a desiccator over saturated potassium bromide solution.

DEAE (chloride form) plates. About 13 g of DEAE were slurried with 200 ml of 1 *M* ammonium chloride solution, adjusted to pH 1 with hydrochloric acid, and stirred mechanically for 5 min. The DEAE then was washed with 200 ml of 0.1 *M* hydrochloric acid, and finally with deionized water until the pH of the supernatant liquid was 3; after each wash the aqueous phase was removed by centrifugation. DEAE in the chloride form was slurried with 28 ml of deionized water and spread in 250-μm thick layers on five 20 × 20 cm glass plates. The plates were dried and stored as above.

Avicel SF plates. After being washed with deionized water by centrifugation, about 18 g of Avicel SF was slurried with 30 ml of deionized water and spread in 250-μm thick layers on five 20 × 20 cm glass plates. The plates were dried and stored as for the DEAE plates.

Development

The metals (0.5 μl of stock solution) were applied to the layers and developed in rectangular glass tanks with ground-glass lids after equilibration for 1 h. The solvent front was allowed to rise 15 cm from the start. The solvents used were aqueous oxalic acid (0.010, 0.030, 0.10 and 0.30 *M*) and mixed solutions (0.030 or 0.25 *M* in oxalic acid and 0.010–3.0 *M* in hydrochloric acid). The DEAE (oxalate form) layers were used in the oxalic acid system and the DEAE (chloride form) layers in the mixed oxalic acid–hydrochloric acid system.

The metals were detected as described previously[14]. The R_F values reported are the averages of duplicate or triplicate determinations.

RESULTS AND DISCUSSION

In the oxalic acid and oxalic acid–hydrochloric acid media the acid fronts generally do not move to the liquid front. In Table I(A) are summarized the locations of the oxalic acid fronts on DEAE and Avisel SF in oxalic acid media. In addition to the oxalic acid front a hydrochloric acid front appeared in dilute mixed acid media and is indicated for each mixture in Table I(B).

TABLE I

OXALIC ACID AND HYDROCHLORIC ACID FRONTS ON DEAE AND AVICEL SF

(A) Oxalic acid (HOx) media

Solvent system	*Location of HOx front (R_F)*	
	DEAE	*Avicel SF*
0.01 *M* HOx	0.25	0.63
0.03 *M* HOx	0.40 (0.48)*	0.79
0.10 *M* HOx	0.63 (0.64)*	0.81
0.30 *M* HOx	0.78 (0.80)*	0.83

(B) Oxalic acid (HOx)–HCl media

Solvent system	*Location of fronts on DEAE (R_F)*	
	HOx	*HCl*
0.03 *M* HOx–0.01 *M* HCl	0.38	0.89
–0.1 *M* HCl	0.67	0.95
–0.5 *M* HCl	0.80	1.00
–1.0 *M* HCl	0.81	1.00
–3.0 *M* HCl	0.90	1.00
0.25 *M* HOx–0.01 *M* HCl	0.78	1.00
–0.1 *M* HCl	0.80	1.00
–0.5 *M* HCl	0.83	1.00
–1.0 *M* HCl	0.83	1.00
–3.0 *M* HCl	0.90	1.00

* Values in parentheses indicate average R_F values of the fronts which appeared when acidic sample solutions (mostly 0.5 μl of 3 *M* HCl) had been applied.

In Fig. 1, R_F values of 46 metals on DEAE (oxalate) are given as a function of oxalic acid concentration. R_F values on Avicel SF are also illustrated for comparison. It can be seen that most metals are not retained on Avicel SF to an appreciable extent from oxalic acid solutions, with some exceptions such as Te(IV), which is adsorbed to a lesser extent from oxalic acid solutions of lower concentration. On the other hand, pronounced adsorption of many metals takes place on DEAE from oxalic acid solutions. Over the tested concentration range, very strong retention ($R_F = 0$) was noted for Ti(IV), Cu (II), Mo(VI), Pd(II), W(VI), Ir(IV), Pt(IV), Au(III) and Bi(III). For other metals strong adsorption is exhibited, except for Cr(III), As(III) and Tl(I) at oxalate concentrations in the range 0.01–0.3 *M*. There are distinct differences in adsorbability between DEAE and Avicel SF for the metals including Be(II), Al(III), Sc(III), Ti(IV), V(IV), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Ge(IV), Se(IV), Y(III), Zr(IV), Nb(V), Mo(VI), [Ru(III)], [Rh(III)], [Pd(II)], Cd(II), In(III), Sn(IV), Sb(III), La(III), Sm(III), Yb(III), Hf(IV), W(VI), Re(VII), Ir(IV), Pt(IV), Au(III), Hg(II), [Pb(II)], [Bi(III)], [Th(IV)] and U(VI) (for the metals in square brackets tailing takes place on either adsorbent, but general differences in absorbability are apparent).

These metals were located on the DEAE layer either along or below the oxalate

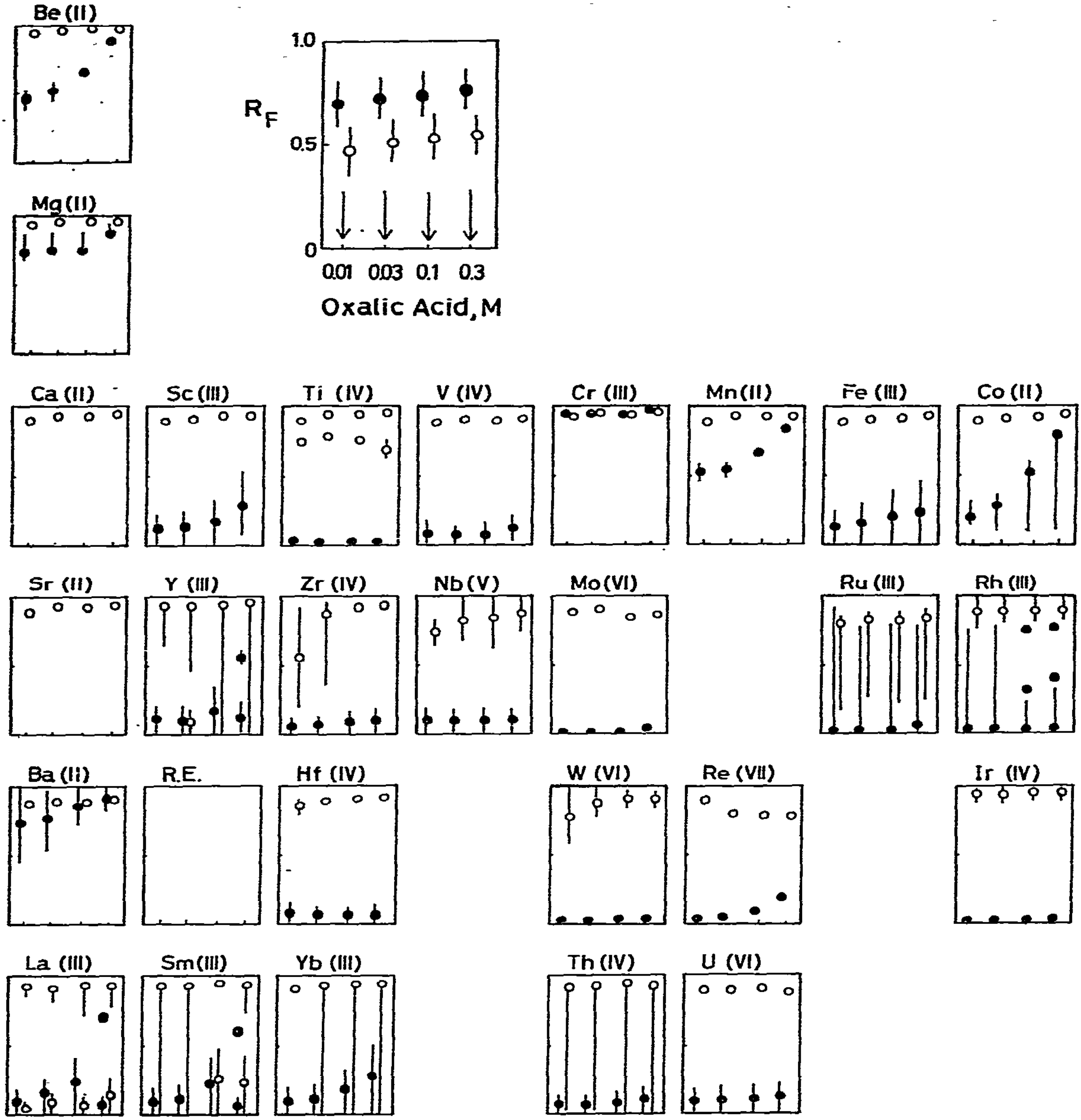
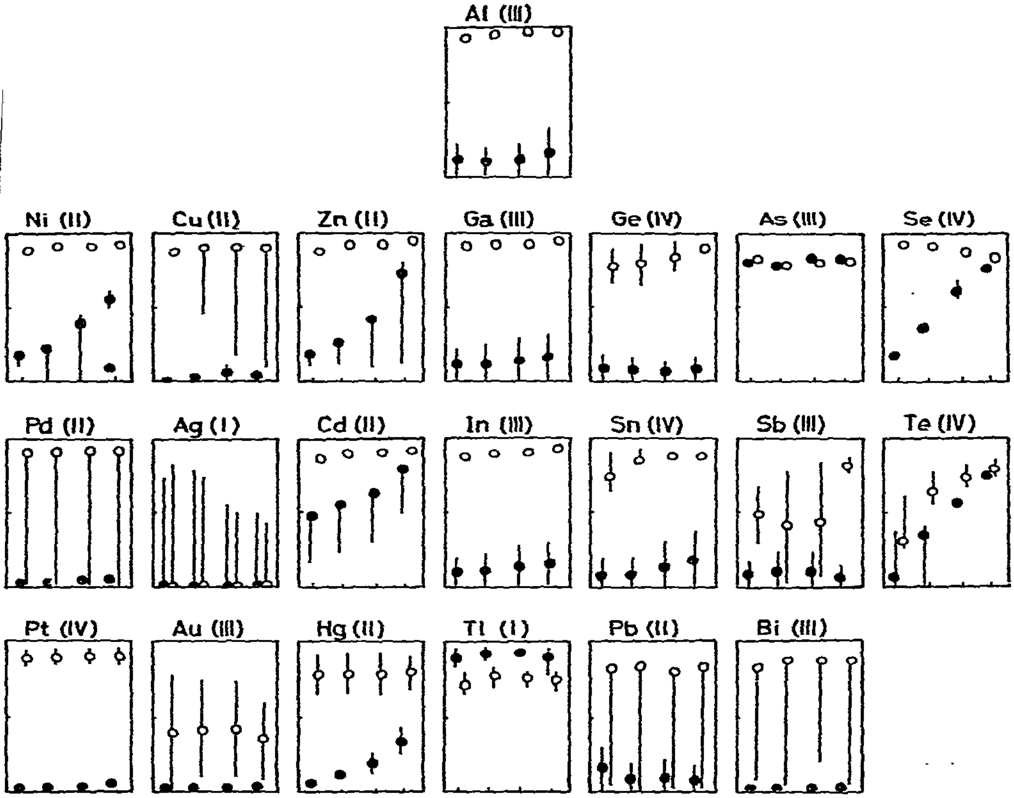


Fig. 1. R_F values of metals on DEAE (●) and Avicel SF (○) in oxalic acid solutions. For convenience, R_F values on Avicel SF are shifted arbitrarily to the right on the abscissa.

front over the oxalic acid concentration range tested; Be(II), Mn(II), Cd(II) and perhaps Se(IV) moved just along the oxalate front.

The different behaviours of the metals towards DEAE and Avicel SF can be understood by assuming the formation and subsequent anion-exchange adsorption



of oxalato complexes of these metals in oxalate media. Regarding the retention of the precious metals, their retention can probably be ascribed to ion exchange of their chloro complexes, because of their application to the DEAE layer from hydrochloric acid solution[13–15] and of their low oxalato complex formation tendencies.

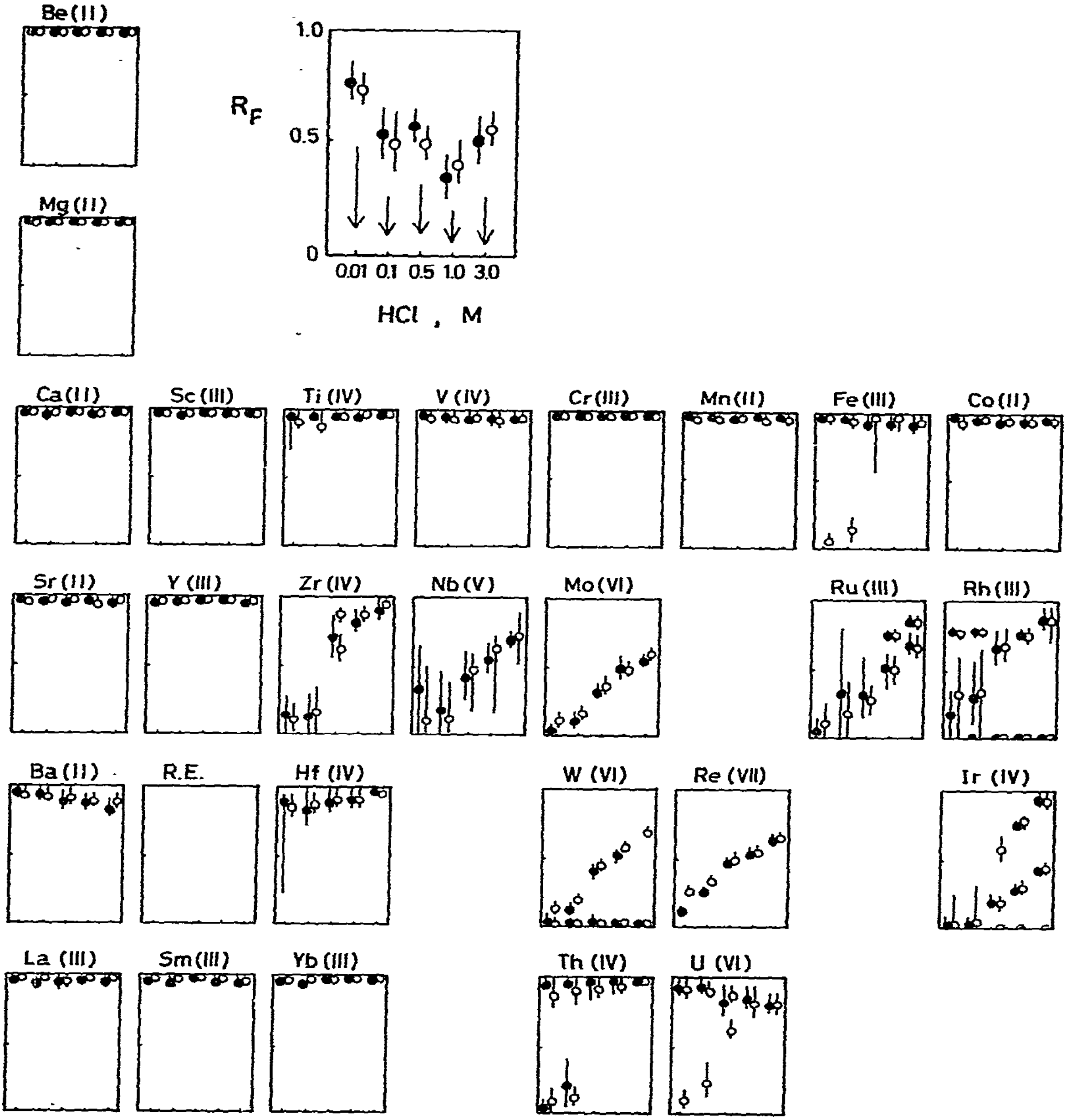
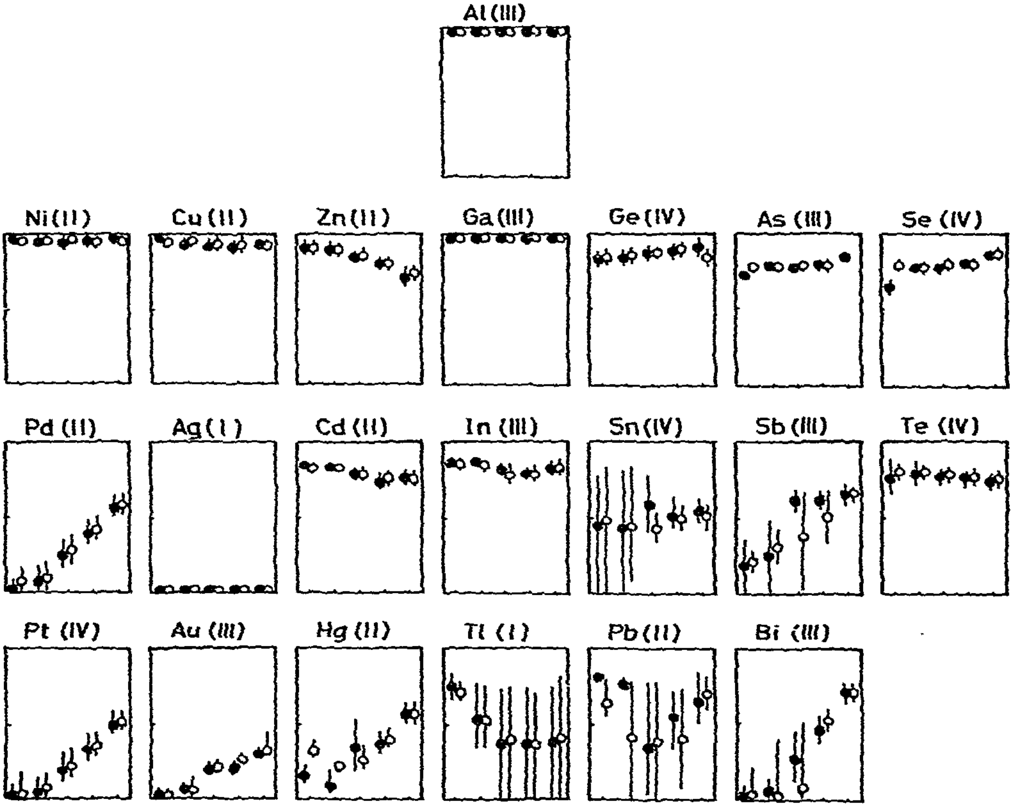


Fig. 2. R_F values of metals on DEAE in oxalic acid–HCl mixtures. The concentration of oxalic acid was kept constant at either 0.030 *M* (●) or 0.25 (○) *M*.

It is worth noting the difference in the adsorption sequences of the metals toward DEAE and a strongly basic anion-exchange resin in oxalic acid media. Fortunately, distribution coefficients for twelve metals on Dowex 1 are now available[1] for oxalic acid solutions of concentration 0.001–0.98 *M* (saturated solution).



The adsorption sequence of metals from 0.01 *M* oxalic acid solution is Mo(VI)[$>10^5$] $>$In(III), Lu(III), Sc(III) [$>10^4$] $>$Cu(II) [*ca.* 10^4] $>$Ce(III) [*ca.* 5000] $>$Zn(II) [*ca.* 3500] $>$Hg(II) [2000] $>$Co(II) [400] $>$Mn(II) [*ca.* 20] $>$As(III) [1.7], where the values in square brackets are the distribution coefficients, mostly obtained by interpolation from the original data. In our 0.01 *M* oxalic acid–DEAE system, the sequence is Mo(VI) >Cu(II), Hg(II) >Sc(III), In(III), REE >Zn(II) >Co(II) >Mn(II) >As(III) (REE represents rare-earth elements). Metals which are adsorbed weakly on Dowex 1 are not retained on DEAE to any significant extent. However, the selectivity sequences of metals on the two exchangers do not always coincide.

In Fig. 2 are illustrated the R_F values of 48 metals on DEAE(Cl^-) in mixed oxalic acid–hydrochloric acid media. The concentration of oxalic acid is kept constant at either 0.030 or 0.25 *M* and the concentration of hydrochloric acid is varied over the range 0.010–3.0 *M*. The addition of hydrochloric acid resulted in a rapid decrease in adsorption for nearly all of the metals tested, regardless of the concentration of oxalic acid. Even the presence of 0.01 *M* hydrochloric acid renders many metals virtually non-adsorbable on DEAE; thus Sc(III), Ti(IV), V(IV), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Ge(IV), Se(IV), Y(III), Cd(II), In(III), Te(IV), REE, U(VI), etc., exhibit R_F values of unity or near unity in spite of the presence of oxalic acid (0.030 and 0.25 *M*). Some metals are still retained on DEAE from hydrochloric acid of lower concentrations, as is found, for example for Zr (IV), Mo(VI), Pd(II), Sb(III), W(VI), Re(VII), Ir(IV), Pt(IV), Au(III), Hg(II) and Bi(III). These metals move well below the oxalic acid front. For some of these metals Lederer and Ossicini[16] have reported similar trends in R_F values on DEAE-paper as a function of hydrochloric acid concentration, although the comparison is possible only for a limited range of hydrochloric acid concentrations. The similar behaviour of metals on DEAE in both hydrochloric acid and mixed hydrochloric acid–oxalic acid does not exclude the role of oxalato and chloro-oxalato complexes on the retention mechanism. However, it is true that the apparent role of oxalic acid is not significant in mixed oxalic acid–hydrochloric acid media.

Strelow *et al.*[2] determined anion-exchange distribution coefficients (K_d) with AG 1-X8, a strongly basic anion-exchange resin, for 36 elements in oxalic acid–hydrochloric acid mixtures. The adsorption behaviour of metals in AG 1 appears to be almost independent of those on DEAE in the mixed acid media. Some examples can be mentioned. Sn(IV) is retained on AG 1 the most strongly of the 36 elements studied from the mixtures, with $K_d > 10^4$ for 0.05 *M* oxalic acid + 0.01–2.0 *M* hydrochloric acid and also $K_d > 10^4$ for 0.25 *M* oxalic acid + 0.01–1.0 *M* hydrochloric acid mixtures. In our system the corresponding R_F values are near 0.5, although tailing is marked at lower concentrations of hydrochloric acid. The R_F values of Ti(IV) on DEAE actually remain unchanged (*ca.* 1.0), but the corresponding K_d on AG 1 decreases rapidly with increasing concentration of hydrochloric acid: $>10^4$ for 0.01 *M* HCl, 7800 for 0.1 *M* HCl, 1450 for 0.5 *M* HCl, 213 for 1 *M* HCl and 1.3 for 3 *M* HCl (0.25 *M* oxalic acid present), Mo(VI) has K_d values on AG 1 very similar to those of Ti(IV), but the R_F values vary from 0 to 0.6 (see Fig. 2). It is likely that oxalato complexes dominate and control the R_F values on DEAE in oxalic acid media (Fig. 1), but chloride ions compete with the complexes for ion-exchange sites and release them easily even at lower concentrations of hydrochloric acid in the mixed acid media. DEAE strongly favours chloride ions.

A knowledge of the R_F values for metal ions chromatographed on DEAE in oxalic acid and the mixed acid media will permit many separations of analytical interest to be conducted easily. We accomplished separations involving La(III)–Ba(II), Be(II)–Mg(II), Ni(II)–Mn(II), Co(II)–Mn(II), Hg(II)–Cd(II), V(IV)–Cr(III), Ti(IV)–Cr(III), Sb(III)–As(III), Bi(III)–As(III), Pb(II)–Tl(I), etc., in oxalic acid media and Hg(II)–Zn(II), Hg(II)–Cd(II), Zr(IV)–Ti(IV), Zr(IV)–V(IV), Ir(IV)–Co(II), In(III)–Ga(III), In(III)–Al(III), W(VI)–Mo(VI), U(VI)–Mn(II), Fe(III)–In(III)–Se(IV) Hg(II)–Au(III), Mn(II)–Cd(II)–Hg(II)–Au(III), Cu(II)–Zn(II)–Sn(IV)–Au(III), Ni (II)–Cd(II)–Hg(II)–Au(III), Mn(II)–U(VI)–Sn(IV)–Au(III), Ni(II)–Pd(II)–Au(III), Cu (II)–Pt(IV)–Au(III), etc., in oxalic acid–hydrochloric acid mixtures, confirming the validity of the R_F values shown in Figs. 1 and 2.

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