Journal of Chromatography, 96 (1974) 223–228
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CHROM. 7507

THE CHROMATOGRAPHY OF A NUMBER OF INORGANIC IONS ON DEAE-CELLULOSE LAYERS IN FORMIC ACID MEDIA

A SELECTIVE SEPARATION OF SELENIUM(IV)

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(Received April 2nd, 1974)

SUMMARY

The adsorption behaviour of some 40 inorganic ions on layers of DEAE-cellulose (HCOO⁻) has been examined in aqueous formic acid media. The R_F values are measured as a function of formic acid concentration (1.0–6.0 *M*) and are compared with those obtained similarly on the microcrystalline cellulose Avicel SF. Of the species tested, selenium(IV) shows a useful chromatographic distribution, which has allowed the development of a very selective thin-layer chromatographic method for the separation of selenium(IV) from other species. Results are presented for the separation of selenium(IV) from 43 other inorganic species, including selenium(VI) and tellurium(VI). The use of Avicel SF layers also permits effective separation of tellurium(IV) from selenium(IV), selenium(VI) and tellurium(VI) by development with 1.0 *M* formic acid.

INTRODUCTION

Several studies on the adsorption characteristics and separation of inorganic ions on cation-exchange resins in aqueous formic acid[1–5] and mixed aqueous formic acid–organic solvent[5,6] media have been reported. However, there is little information about the adsorption and separation of inorganic ions on anion-exchange resins in formate media[7,8].

This work, part of a comprehensive study on the adsorption characteristics of a number of inorganic ions on a cellulosic anion exchanger (DEAE-cellulose) in aqueous formic acid media, has resulted in the development of a very selective method for the separation of selenium(IV) by thin-layer chromatography (TLC). With respect to the TLC separation of selenium, some information is available, but few selective separation methods have hitherto been developed[9–18].

EXPERIMENTAL

Metal solutions (0.1 *M*) were prepared as stock solutions that were 3 *M* in hydrochloric acid. Stock solutions of selenium(IV), selenium(VI), tellurium(IV), molybdenum(VI), tungsten(VI), rhenium(VII), fluoride, chloride, bromide and iodide were prepared by dissolving the sodium or ammonium salts in distilled water to yield the respective 0.1 *M* solutions; for tellurium(VI), sodium tellurate was dissolved in distilled water to give a 0.01 *M* solution because of the limited solubility of this salt. Solutions 0.1 *M* in silver(I), thallium(I) and lead(II) were prepared by dissolving the respective nitrates in 3 *M* nitric acid, and a stock solution of niobium(V) was prepared as described previously[19].

About 6 g of DEAE-cellulose (Cl^-) (Serva, Heidelberg, G.F.R.; for TLC use) was made into a slurry with water, placed in a conventional column and treated with 225 ml of 2 *M* formic acid; another 6-g portion of the DEAE-cellulose was treated similarly. The combined portions of DEAE-cellulose were washed with distilled water by centrifugation until the supernatant liquid was of pH 2.5, then the DEAE-cellulose ($HCOO^-$) was made into a slurry with 34 ml of distilled water and spread as a 250-μm layer on five 20 × 20 cm glass plates. The plates were air-dried for 1 h and then at 40° for 3 h, and were stored in a desiccator over saturated potassium bromide solution. Plates coated with DEAE-cellulose (Cl^-) or microcrystalline cellulose Avicel SF (F.M.C., Marcus Hook, Pa., U.S.A.), all with layers 250 μm thick, were similarly prepared and stored.

The inorganic ions (0.5 μl of solution) were applied to the layers and developed for 15 cm in rectangular glass tanks with ground-glass lids after equilibration for 1 h. The solvents used were aqueous formic acid (1.0, 3.0 or 6.0 *M*) and mixed solutions 1.0 *M* in formic acid and 0.0010–1.0 *M* in hydrochloric acid.

The metals were detected as described previously[20]; fluoride was detected by means of an alizarin–zirconium lake, and chloride, bromide and iodide were detected with silver nitrate solution[21].

RESULTS AND DISCUSSION

In Fig. 1, the R_F values of 40 inorganic ions on DEAE-cellulose ($HCOO^-$) are plotted as a function of formic acid concentration; the R_F values on Avicel SF are also given for purposes of comparison. It can be seen from Fig. 1 that vanadium(IV), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), gallium(III), tellurium(VI), cadmium(II), indium(III), antimony(III), thallium(I), lead(II), scandium(III), lanthanum(III), thorium(IV) and uranium(VI) were not adsorbed on the DEAE-cellulose ($HCOO^-$) to any great extent from the formic acid solutions tested. Although not illustrated, beryllium(II), magnesium(II), calcium(II), strontium(II), aluminium(III), samarium(III) and ytterbium(III) also were not adsorbed under the conditions used. However, selenium(IV), selenium(VI), molybdenum(VI), tungsten(VI), rhenium(VII), palladium(II), tin(IV), iridium(IV), platinum(IV), gold(III), mercury(II), chloride, bromide and iodide were strongly retained on DEAE-cellulose ($HCOO^-$) layers probably by ion exchange; selenium (IV) showed a chromatographic distribution particularly suitable for separations.

The adsorption behaviour of the inorganic ions was also examined on DEAE-cellulose (Cl^-) in the aqueous formic acid solutions. The results were almost the same as those illustrated in Fig. 1, but the R_F values of zinc(II), cadmium(II), indium(III), thallium(I) and lead(II) were lower, decreasing slightly with increasing concentration

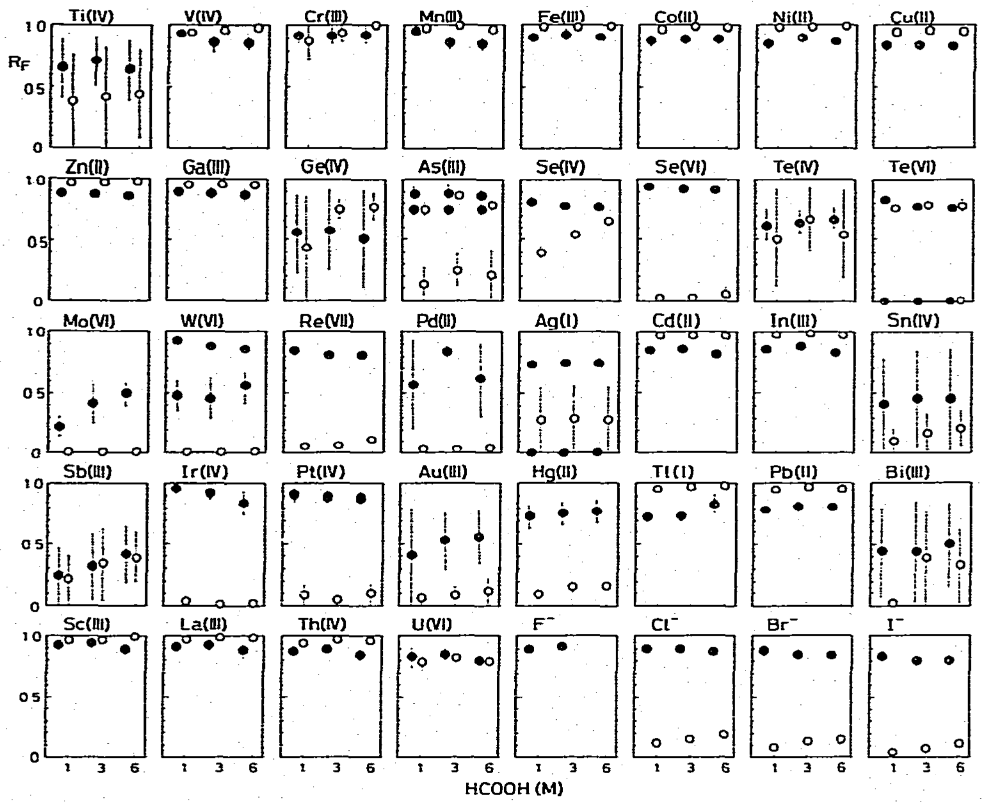

Fig. 1. R_F values of inorganic species on DEAE-cellulose (HCOO$^-$) and Avicel SF in formic acid media. ○, DEAE-cellulose; ●, Avicel SF. For convenience, the R_F values on Avicel SF have been arbitrarily displaced to the left along the abscissa.

of formic acid. The R_F values for zinc(II) on DEAE-cellulose (Cl$^-$) in 1.0, 3.0 and 6.0 M formic acid ranged from 0.87–0.98, 0.75–0.89 and 0.77–0.84 respectively; the corresponding values for cadmium(II) were 0.78–0.83, 0.70–0.77 and 0.61–0.69; those for indium(III) were 0.82–0.88, 0.77–0.83 and 0.74–0.81; those for thallium(I) were 0.66–0.81, 0.69–0.80 and 0.50–0.77; and those for lead(II) were 0.76–0.82, 0.69–0.76 and 0.69–0.76. For arsenic(III), the streaks from the starts (see Fig. 1) disappeared, and single-spot distribution resulted, the R_F values ranging from 0.85–0.90, 0.80–0.85 and 0.71–0.77 for 1.0, 3.0 and 6.0 M formic acid, respectively. The R_F values for selenium(IV) increased to some extent, ranging from 0.58–0.76, 0.67–0.78 and 0.70–0.89 for 1.0, 3.0 and 6.0 M formic acid, respectively. Silver(I) was retained strongly at the start, with no streaking over the range of formic acid concentrations tested. The metals that were retained strongly on DEAE-cellulose (HCOO$^-$) were also adsorbed more strongly on DEAE-cellulose (Cl$^-$), remaining at the start as small spots. The noble metals and mercury(II) appear to be retained on DEAE-cellulose (Cl$^-$) by ion exchange of their chloro-complexes stabilized by formic acid[20,22]. Lederer and Ossicini[23] have shown that palladium(II), osmium(IV), iridium(IV), platinum(IV), mercury(II), chloroaurate, etc., are retained on DEAE-cellulose paper in dilute hydrochloric acid solution. Both formation and adsorption of chloro-complexes are facilitated by formic acid, and it is immaterial whether the complex-forming chloride anions are introduced by the DEAE-cellulose (Cl^-), by the stock solution or by the solvent.

Halide ions are adsorbed rather strongly on DEAE-cellulose ($HCOO^-$) as is shown in Fig. 1, the sequence of adsorption decreasing in the order iodide, bromide, chloride: this is in accordance with their sequence of adsorption on strong-base resins[21].

TABLE I

R_F VALUES OF SOME INORGANIC SPECIES ON DEAE-CELLULOSE ($HCOO^-$)

Developing solvent, 1.0 *M* formic acid–hydrochloric acid.

Species	*HCl concn. (M)*				
	0.0010	*0.010*	*0.10*	*0.50*	*1.0*
Ti(IV)	0.00–0.90	0.00–0.86	0.00–0.92	0.85–0.90	0.93–0.94
Ge(IV)	0.70–0.89	0.73–0.88	0.66–0.89	0.75–0.89	0.79–0.91
As(III)	0.90–0.30	0.00–0.27	0.00–0.55	0.89–0.92	0.86–0.94
	0.82–0.93	0.79–0.88	0.81–0.91		
Se(IV)	0.38–0.47	0.35–0.45	0.45–0.50	0.73–0.77	0.81–0.86
Se(VI)	0.00–0.05	0.00–0.05	0.24–0.39	0.72–0.77	0.83–0.87
Te(IV)	0.04–0.93	0.06–0.92	0.30–0.94	0.69–0.91	0.76–0.96
Te(VI)	0.00		0.00	0.00	0.00
	0.77–0.85	0.74–0.83	0.77–0.85	0.76–0.83	0.83–0.89
Ag(I)	0.00–0.65	0.00–0.82	0.00–0.80	0.00–0.17	0.00–0.08
Sn(IV)	0.00–0.30	0.00–0.26	0.04–0.49	0.65–0.79	0.66–0.75

The influence of hydrochloric acid concentration on the R_F values of several species is shown in Table I, in which the R_F values on DEAE-cellulose ($HCOO^-$) in hydrochloric acid (of various concentrations) mixed with 1.0 *M* formic acid are listed as a function of hydrochloric acid concentration. With increasing concentration of hydrochloric acid, tailing is greatly reduced for titanium(IV), tellurium(IV), silver(I) and tin(IV). For selenium(IV) and selenium(VI), the R_F values increase with increasing concentration of hydrochloric acid, owing to competition between chloride ions and the ions of selenium for the ion-exchange sites.

It is interesting to note that streaking of arsenic(III) from the start disappears to leave single spots at the higher concentration range of hydrochloric acid (0.5–1.0 *M*): this is in accord with observations on adsorption on DEAE-cellulose (Cl^-) in pure formic acid media.

The separation of selenium(IV)

Selenium(IV) shows a chromatographic distribution on layers of DEAE-cellulose ($HCOO^-$) in formic acid media that is suitable for its separation from many other species. The R_F values of selenium(IV) on DEAE-cellulose (Cl^-) were somewhat higher than those on DEAE-cellulose ($HCOO^-$) over the range of formic acid concentrations tested. However, the behaviour of selenium(IV) on DEAE-cellulose (Cl^-) did not favour the separation of selenium(IV) from such ions as those of zinc (II), tellurium(VI), and cadmium(II). Thus, DEAE-cellulose ($HCOO^-$) was used throughout for the separations.

To judge from the chromatographic distribution of selenium(IV) and the somewhat extreme behaviour of many other species, it seems that sellenium(IV) can be selectively separated from a number of inorganic species by development with 1–3 *M* formic acid. Representative pairs were chosen and separated by TLC on DEAE-cellulose ($HCOO^-$) with 1 *M* formic acid as developing solvent: the results are shown

TABLE II

SEPARATION OF SELENIUM(IV) ON DEAE-CELLULOSE ($HCOO^-$)

R_F for Se(IV)	*R_F for other species*	*Concn. of HCOOH solvent (M)*
0.41–0.47	Be(II) (0.98–1.00)	1.0
0.43–0.49	Mg(II) (0.98–1.00)	1.0
0.41–0.47	Al(III) (0.94–0.99)	1.0
0.41–0.46	Ca(II) (0.96–1.00)	1.0
0.42–0.52	Sc(III) (0.96–1.00)	1.0
0.42–0.47	V(IV) (0.95–0.96)	1.0
0.41–0.47	Cr(III) (0.97–1.00)	1.0
0.41–0.47	Mn(II) (0.95–1.00)	1.0
0.41–0.48	Fe(III) (0.92–1.00)	1.0
0.38–0.45	Co(II) (0.94–1.00)	1.0
0.39–0.46	Ni(II) (0.94–1.00)	1.0
0.40–0.45	Cu(II) (0.90–0.92)	1.0
0.40–0.47	Zn(II) (0.94–0.99)	1.0
0.41–0.47	Ga(III) (0.93–0.94)	1.0
0.59–0.69	Ge(IV) (0.77–0.91)	3.0
0.41–0.48	As(III) (0.00–0.27, 0.79–0.88)	1.0
0.36–0.45	Se(VI) (0.00–0.05)	1.0
0.42–0.49	Sr(II) (0.96–1.00)	1.0
0.43–0.50	Y(III) (0.97–1.00)	1.0
0.36–0.43	Zr(IV) (0.94–1.00)	1.0
0.42–0.51	Nb(V) (0.00–0.11)	1.0
0.39–0.45	Mo(VI) (0.00–0.02)	1.0
0.40–0.47	Pd(II) (0.00–0.04)	1.0
0.40–0.47	Cd(II) (0.93–0.98)	1.0
0.43–0.48	In(III) (0.93–0.95)	1.0
0.46–0.52	Sn(IV) (0.00–0.26)	1.0
0.37–0.43	Te(VI) (0.74–0.82)	1.0
0.44–0.51	Ba(II) (0.97–1.00)	1.0
0.35–0.44	Hf(IV) (0.97–1.00)	1.0
0.39–0.45	W(VI) (0.00–0.02)	1.0
0.37–0.44	Re(VII) (0.01–0.05)	1.0
0.38–0.47	Ir(IV) (0.00–0.03)	1.0
0.39–0.47	Pt(IV) (0.00–0.11)	1.0
0.41–0.47	Au(III) (0.00–0.09)	1.0
0.39–0.46	Hg(II) (0.07–0.15)	1.0
0.40–0.47	Tl(I) (0.91–0.93)	1.0
0.39–0.46	Pb(II) (0.91–0.93)	1.0
0.37–0.45	Bi(III) (0.00–0.13)	1.0
0.40–0.45	La(III) (0.95–1.00)	1.0
0.41–0.46	Sm(III) (0.95–1.00)	1.0
0.41–0.47	Yb(III) (0.93–1.00)	1.0
0.43–0.53	Th(IV) (0.63–0.95)	1.0
0.38–0.44	U(VI) (0.68–0.87)	1.0

in Table II. Development took about 2.3 h, and the TLC system allowed effective separation of selenium(IV)–selenium(VI) and of selenium(IV)–tellurium(VI).

However, this system could not be used to separate selenium(IV) from tellurium(IV) because of the strong tailing of the tellurium. Use of DEAE-cellulose (Cl^-) resulted in appreciable reduction of the tailing, but separation was still not feasible. Chromatography on Avicel SF layers, however, gave effective separation of selenium (IV)–tellurium(IV) and of selenium(IV)–selenium(VI), tellurium(IV)–tellurium(VI), etc., in formic acid media. The following separations were accomplished on Avicel SF layers by development for 2 h with 1 *M* formic acid: tellurium(IV) (0.60–0.72) from selenium(IV) (0.76–0.82) and selenium(VI) (0.92–0.95); tellurium(IV) (0.58–0.72) from tellurium(VI) (0.00, 0.75–0.85) and selenium(VI) (0.94–0.98); and molybdenum(VI) (0.20–0.42) from rhenium(VII) (0.79–0.85). (The numerals in parentheses indicate the R_F range).

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