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Chromatography of Inorganic Ions on TEAE-cellulose Layers in Hydrochloric Acid Media

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Synopsis. The ion-exchange behavior of inorganic ions on TEAE-cellulose was investigated in hydrochloric acid media with and without methanol. Adsorbabilities are low relative to those on strongly basic ion-exchange resin, varying with acid concentration in line with gradual building-up of chlorocomplexes.

Only fragmentary information is available on paper-[1-8] and thin-layer[9]-chromatography of inorganic ions on a strongly basic anion-exchange cellulose with a quarternary ammonium group. Recently we have investigated the adsorption behavior of about 15 metal ions on TEAE-cellulose columns[10] in hydrochloric acid media, revealing markedly weak preference of metal ions to TEAE-cellulose relative to a strongly basic ion-exchange resin. The work was extended in order to obtain individual adsorption characteristics of a number of metal ions on TEAE-cellulose in hydrochloric acid as well as methanol–hydrochloric acid media. The thin-layer-chromatographic method was used throughout, which served to distinguish small differences in weak adsorption among metal ions.

Experimental

Triethylaminoethylcellulose (Serva, Heidelberg, G. F. R., 0.68 meq/g, for column use), a strong base anion-exchange cellulose, was used in the chloride form. Twenty g of swollen TEAE-cellulose was made into a slurry with 65 ml of deionized water, and spread over five 20×20 cm glass plates 500 μm thick. After being dried at 40 °C for several hr it was stored in a desiccator over a saturated potassium bromide solution. Metal ions[11] (1 μl of solution) were developed by the ascending technique for a distance of 15 cm in a rectangular glass tank with ground glass lid, after 1 hr equilibration. They were detected as described previously.[12]

Results and Discussion

In Fig. 1 are illustrated the R_f values of 43 metal ions as a function of hydrochloric acid concentration. The R_f trends against hydrochloric acid concentration are similar to those reported by Lederer and Ossicini[13] for DEAE- and AE-cellulose papers. Chlorocomplexes of noble metals and oxyacids including V(V), Se(IV), Cr(VI), Mo(VI), W(VI), and Re(VII) are adsorbed on a TEAE-cellulose column to a great extent from 0.001 M HCl, showing that K_d(weight distribution coefficient)$>$100.[10] However, because of the strong preference of chloride ions to ion-exchange sites, the adsorbabilities decreased rapidly with increasing concentration of hydrochloric acid; K_d values for several ions in 0.1 M HCl were Se(IV)$<$2, Mo(VI) 20, Pd(II) 160, Re(VII) 20, Ir(IV)$>$100, Pt(IV)$>$100 and 25 (two bands appeared), Au(III) 80, Hg(II) 90, being mostly insufficient to allow effective column separation. From 6 M HCl these metals were adsorbed with $K_d \leq$ 10, being eluted from a 1 g TEAE-cellulose column actually with no adsorption. The column elution study based on the 1 g TEAE-cellulose column[10] did not distinguish the difference in adsorption among *e.g.* Ni(II), Se(IV), Zn(II), and Te(IV) over the 0.10—6 M HCl concentration range, but the tlc chromatograms clearly demonstrate their differences (Fig. 1).

The adsorption of Zn(II), Ga(III), Cd(II), In(III), Sn(IV), and Te(IV) increases with increasing concentration of hydrochloric acid. These metals exhibit a maximum adsorption on a strongly basic resin in the range ~2 to ~8 M HCl.[14] On the other hand, Pd(II), Ag(I), Re(VII), Pt(IV), Au(III), Hg(II), and Bi(III) are adsorbed tightly on the strongly basic resin,

TABLE 1. R_f VALUES OF METAL IONS IN METHANOL–HCl (1:1) ON TEAE-CELLULOSE LAYER (500 μm)

HCl (M)	1.0	6.0	11.2
Be (II)	1.00	0.99	0.85
Mg (II)	0.96	0.91	0.79
Al (III)	0.99	0.99	0.76
Ca (II)	0.91	0.69	0.52
Sc (III)	0.94	0.82	0.65
Ti (IV)	0.94	0.89	0.68
V (IV)	0.94	0.88	0.66
Cr (III)	0.95	0.98	0.65
Mn (II)	0.93	0.86	0.65
Fe (III)	0.91	0.79	0.51
Co (II)	0.94	0.85	0.50
Ni (II)	0.94	0.84	0.68
Cu (II)	0.87	0.65	0.53
Zn (II)	0.37	0.42	0.48
Ga (III)	0.98	0.57	0.55
Se (IV)	0.77	0.84	0.85
Y (III)	0.93	0.68	0.49
Zr (IV)	0.0—0.44	0.0—0.67	0.0—0.38
Mo (VI)	0.0, 0.56	0.50	0.53
Pd (II)	0.08	0.32	0.40
Ag (I)	0.00	0.0—0.53	0.18—0.64
Cd (II)	0.20	0.40	0.49
In (III)	0.67	0.56	0.54
Sn (IV)	0.52	0.32	0.25
Sb (III)	0.38	0.47	0.51
Te (IV)	0.63	0.34	0.24
Ba (II)	0.78	0.34	0.00
La (III)	0.92	0.64	0.44
Sm (III)	0.92	0.62	0.43
Yb (III)	0.92	0.64	0.44
Hf (IV)	trail	trail	trail
W (VI)	0.00	0.00	trail
Re (VII)	0.33	0.54	0.59
Ir (IV)	0.08, 0.34	0.0—0.51	0.0, 0.57
Pt (IV)	0.05	0.21	0.30
Au (III)	0.23	0.37	0.42
Hg (II)	0.09	0.32	0.38
Pb (II)	0.0—0.39	0.06—0.46	0.46
Bi (III)	0.09	0.27	0.38
Th (IV)	0.92	0.33—0.73	0.29
U (VI)	0.94	0.54	0.33

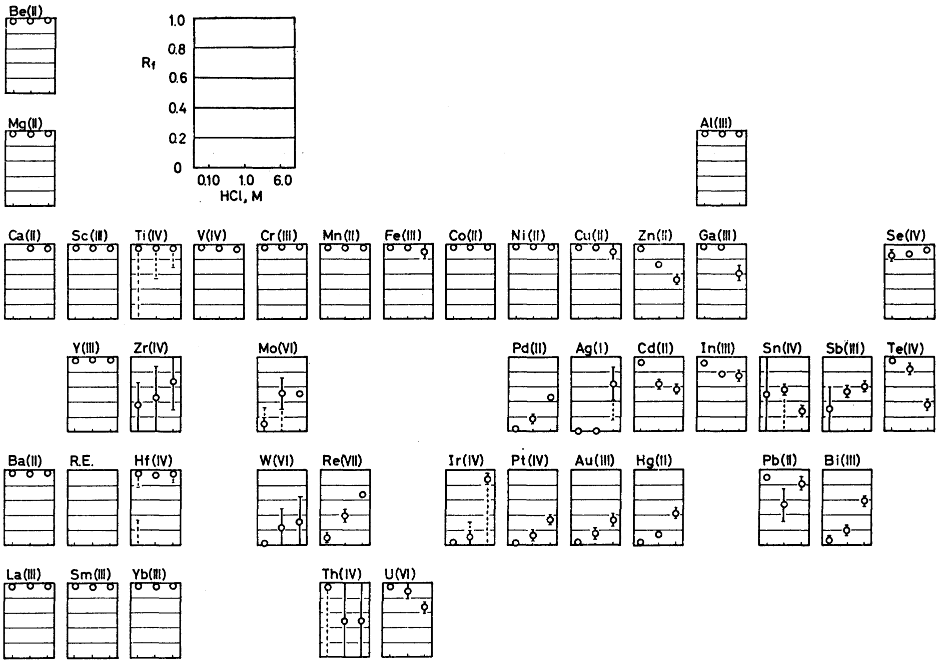

Fig. 1. R_f values of metals on TEAE-cellulose layer (500 μm) in hydrochloric acid media.

showing decreasing adsorption with increasing hydrochloric acid concentration.[14] All these metals show a similar decrease in their adsorption on TEAE-cellulose with increasing hydrochloric acid concentration. In hydrochloric acid media the distribution curve of metals on the strongly basic resin can be described in terms of the gradual building-up of cationic, neutral, and anionic chlorocomplexes with increasing hydrochloric acid concentration, corresponding to positive, zero, and negative slopes of the adsorption curve (log distribution coefficient *vs.* HCl concentration), respectively.[15,16] Closely related adsorption trends, observed in the TEAE-cellulose–hydrochloric acid system, suggest that the dominant factor controlling the R_f values is ion-exchange, but not the partition, which sometimes dominates to control the distribution of metals in chromatography involving the ion-exchange cellulose.[17]

We have also examined the adsorption behavior of metals in methanol–hydrochloric acid media (1 : 1) as a function of hydrochloric acid concentration (1.0, 6.0, and 11.2 M). The R_f values of the metals are summarized in Table 1. Adsorption trends do not change except for Zn(II) and Cd(II), which indicate the decrease in adsorption with increasing concentration of hydrochloric acid. Actually, polar methanol considerably enhances the formation of anionic chlorocomplexes of these metals.

Analytical separation in aqueous hydrochloric acid and mixed methanol–hydrochloric acid media is quite feasible. With 1 M HCl the following separation was accomplished: Hg(8—17)-Cd(58—64)-Zn(69—75); Bi(15—24)-Sb(52—59)-In(72—81)/or Se(77—92); Au(11—16)-Cd(55—65)-Cu(90—100). With 6 M HCl elution the separations Te(35—43)-Cd(56—63)-In(69—78); Sn(26—33)-Cd(57—67)/or Sb(53—63)-In(76—79); Pt(31—43)-Mo(45—51)-Re(65—71); U(57—70)-La(90—100)/or Hf(94—100) were successful. By elution with methanol–6 M HCl (1:1) Ba(30—41)-Ca(64—79)-Be(100); Pd(16—27)-Cu(57—66)-Ni(72—100); Pt(12—21)-Au(28—34)-Cu(57—64)-Ni(72—100); Hg(21—28)-Zn(31—40)-Cu(58—66)-Ni(74—100) were separated, respectively. Pt(15—32)-Au(35—43)-Co(46—55)-Ni(69—83); Zr(7—33)-Y(45—58)-Sc(58—71); U(20—30)-Y(43—58)-Ti(58—76); Zr(7—31)/or Th(17—46)-Ti(48—77); Co(46—57)-Mn(69—86) were separated by elution with methanol–11.2 M HCl (1: 1). The oxidation states of metals separated are the same as listed in Table 1. The values in parentheses indicates the range of R_f (×100).

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