Chromatography on ion exchange papers

The behaviour of some metal ions on carboxylic exchangers

Ion exchange data for metal ions are available for many aqueous systems, both for strong cation and anion exchangers, however, relatively little work has been done with carboxylic resins as their adsorption from strongly acid solutions is poor. Ion exchange papers with carboxylic exchangers have been used to our knowledge only in one separation, that of Ag–Pb–Bi–Hg by WIELAND AND BERG[1], who worked with a laboratory-made carboxylic paper and developed with ammonium acetate (0.1 *M* at pH 3.).

We thus thought it interesting to extend our survey of the chromatographic behaviour of metal ions on ion exchange papers to two carboxylic ion exchange papers, the carboxymethyl-cellulose paper (Whatman CM-50) and the Amberlite WA-2 paper (containing about 45 % of Amberlite IRC-50). As eluant we used buffers with equal molarities of sodium acetate and acetic acid and hoped to avoid pH gradients by working on the "plateau" of the buffer. This proved adequate for the Whatman CM-50 paper which could be employed unwashed as supplied by the manufacturers.

TABLE I

R_F VALUES OF METAL IONS ON WHATMAN CM-50 PAPER

Eluents: 1 = 1 *N* sodium acetate–1 *N* acetic acid;
2 = 0.5 *N* sodium acetate–0.5 *N* acetic acid;
3 = 0.1 *N* sodium acetate–0.1 *N* acetic acid.

Ion	*Eluent*		
	1	*2*	*3*
Ag^+	0.5	0.36	0.17
Te^+	0.48	0.46	0.25
Bi^{+++}	0.88	0.6	0.05
Cd^{++}	0.72	0.44	0.08
Pb^{++}	0.53	0.27	0.04
Hg^{++}	0.78	0.56	0.09
Cu^{++}	0.63	0.34	0.04
Fe^{+++}	elongated comet		0.03
Co^{++}	0.70	0.52	0.10
Ni^{++}	0.68	0.52	0.10
Mn^{++}	0.75	0.52	0.13
Zn^{++}	0.72	0.45	0.09
Al^{+++}	0.78	0.36	0.04
Sc^{+++}	0.75	0.44	0.04
Y^{+++}	0.79	0.50	0.04
La^{+++}	0.66	0.32	0.02
Ce^{+++}	0.69	0.29	0.03
Zr^{++++}	comet to LF	comet → 0.39	comet → 0.08
Be^{++}	0.85	0.71	0.12
Mg^{++}	0.84	0.62	0.17
Ca^{++}	0.65	0.45	0.08
Sr^{++}	0.62	0.48	0.11
Ba^{++}	0.52	0.35	0.05
$Co(NH_3)_6^{+++}$	0.55	0.27	0.02
$Co(en)_3^{+++}$	0.66	0.29	0.03
ReO_4^-	0.72	0.76	0.94

The Amberlite WA-2 paper required washing with HCl and distilled water as well as placing the spots 3 cm behind the liquid front to avoid the formation of double spots. The ions to be chromatographed were dissolved in the acetate buffer as their nitrates. Metal ions which are usually stable as anionic complexes (*e.g.* $AuCl_4^-$) were not studied. Uranyl ions precipitated in the buffer. The R_F values obtained with various molarities of sodium acetate–acetic acid are shown in Tables I and II.

TABLE II

R_F VALUES OF METAL IONS ON AMBERLITE WA-2 PAPER

Eluents: 1 = 3 *N* sodium acetate–3 *N* acetic acid;
2 = 2 *N* sodium acetate–2 *N* acetic acid;
3 = 1 *N* sodium acetate–1 *N* acetic acid.

Ion	*Eluent*		
	1	*2*	*3*
Ag^+	0.17	0.13	0.06
Tl^+	0.33	0.24	0.20
Bi^{+++}	0.02	0.00	0.00
Cd^{++}	0.21	0.14	0.06
Pb^{++}	0.15	0.06	0.02
Hg^{++}	0.05	0.03	0.00
Cu^{++}	0.21	0.15	0.04
Fe^{+++}	0.00	0.00	0.00
Co^{++}	0.58	0.48	0.25
Ni^{++}	0.57	0.46	0.27
Mn^{++}	0.64	0.50	0.31
Zn^{++}	0.35	0.23	0.13
Al^{+++}	0.00, 0.52	0.00, 0.41	0.00, 0.41
Sc^{+++}	0.04	0.02	0.00
Y^{+++}	0.23	0.11	0.03
La^{+++}	0.14	0.07	0.03
Ce^{+++}	0.16	0.08	0.02
Zr^{++++}	0.03	0.03	0.03
Be^{++}	0.18, 0.46	0.10, 0.33	0.05, 0.18
Mg^{++}	0.79	0.64	0.48
Ca^{++}	0.49	0.38	0.23
Sr^{++}	0.48	0.37	0.27
Ba^{++}	0.32	0.26	0.15
$Co(NH_3)_6^{+++}$	0.04	0.02	0.02
$Co(en)_3^{+++}$	0.01	0.01	0.00
ReO_4^-	0.75	0.68	0.55

Fe(III) and Zr(IV) yield diffuse comets on Whatman CM-50 paper. Beryllium and aluminium give double spots on the Amberlite WA-2 paper. Most other ions give elongated spots on the Whatman CM-50 paper and very compact sharp spots on the Amberlite WA-2 paper. Perrhenate was chromatographed as it is a monovalent anion which is strongly adsorbed on neutral surfaces and gives thus an indication of the adsorption effect. $Co(NH_3)_6^{+++}$ and $Co(en)_3^{+++}$ were examined to see whether there are great differences between trivalent ions which could complex with the carboxylic groups and those (*i.e.* the complexes) which could not.

As shown in the tables the cobalt complexes have R_F values of the same order as the trivalent metal ions and hence there seems to be little indication that complex formation is predominant.

TABLE III

R_F VALUES OF METAL IONS ON AMBERLITE WA-2 PAPER

Eluents: 1 = 1 *N* sodium acetate–1 *N* acetic acid in 20 % aqueous methanol;
2 = 1 *N* sodium acetate–1 *N* acetic acid in 40 % aqueous methanol;
3 = 1 *N* sodium acetate–1 *N* acetic acid in 60 % aqueous methanol;
4 = 1 *N* sodium acetate–1 *N* acetic acid in 80 % aqueous methanol.

Ion	*Eluent*			
	1	*2*	*3*	*4*
Fe^{+++}	0.00	0.00	0.00*	0.00*
Co^{++}	0.29	0.26	0.16*	0.13*
Ni^{++}	0.27	0.24	0.14	0.12
Zn^{++}	0.10	0.08	0.07	0.03
Mg^{++}	0.46	0.45	0.44	0.39
Ca^{++}	0.24	0.20	0.16	0.10
Sr^{++}	0.24	0.18	0.12	0.05
ReO_4^-	0.54	0.60	0.54	0.51

* Placed 4 cm behind the liquid front to avoid double spotting.

In all there are few interesting separations, (except perhaps with Ag^+–Tl^+–Pb^{++}) most ions adsorbing with similar R_F values and there is good agreement with what can be expected from the law of mass action. The only interesting results concern the alkaline earths where there is the usual difference between Ba and Sr but not between Sr and Ca. Sr and Ca are inseparable on both papers with if anything slightly higher R_F values for Sr than for Ca. Similarly in group 3, yttrium has higher R_F values than Sc inverting the order to La–Sc–Y.

We would like to suggest that the lack of separation of Ca–Sr is due to a number of equilibria involving hydration, complex formation with acetate as well as with the carboxylic groups of the papers. Table III shows some data with methanol–water mixtures. In 60 % methanol the difference between Sr and Ca is already sufficient to permit a separation into adjacent spots.

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