Cation exchange chromatographic separation of a number of metal ions in ammonium iodide media

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The cation exchange behaviour of 11 metal ions in NH_4I at various concentrations (0.096-2.08 M) has been studied with Dowex 50W-X4 resin (200-400 Mesh, NH_4^+-form). The distribution coefficients are determined by batch technique to evaluate the conditions for column chromatographic separation. A number of binary, ternary and quaternary separation of synthetic mixtures have been reported.

While anion exchange resin in iodide media provides a clear-cut separation of some elements[1,2], procedures based on the use of cation exchange resin have been found to be more convenient. Except the separation of cadmium from zinc reported by Kallmann et al.[3], no work has been published so far on the cation exchange in iodide media. The present note reports a systematic investigation of cation exchange behaviour of 11 metal ions in ammonium iodide media in eight different concentrations in the range 0.096-2.08 M.

Experimental

Stock solutions (0.05-0.10 M) of various metal ions were prepared as reported elsewhere[4]. The solutions were standardized by the complexometric methods[5,6]. An aqueous solution of ammonium iodide (4.0 M) (Sisco chem) was prepared and standardised for the iodide content. The cation exchange resin Dowex 50W-X4 (200-400 Mesh, H^+-form, Fluka AG) was pretreated and converted to NH_4^+ form, standardised and air-dried before use. The resin capacity and moisture content was determined by the usual methods and were 3.16 meq/g and 24% respectively.

The distribution coefficients (D) were determined by the batch equilibration technique as described elsewhere[4]. In achieving the various separations by column chromatography, the general procedure previously described[4] has been followed unless otherwise stated. In order to facilitate the flow of the
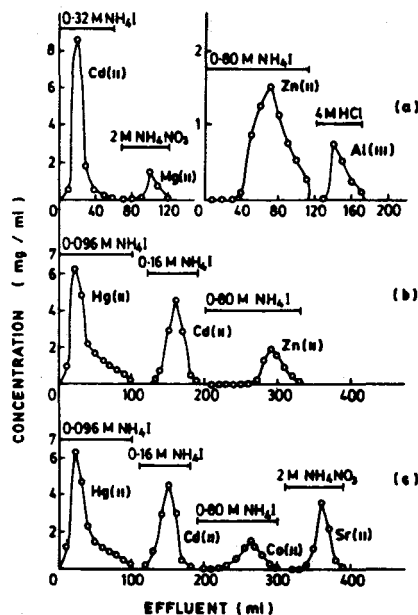

Fig. 1—Separation curves of binary, ternary and quaternary mixtures of metal ions on Dowex 50W-X4

eluting agents, the porcelain pieces were placed alongwith the resin bed. The resolution of the synthetic binary, ternary and quaternary mixtures are shown in Fig. 1. Both the ternary and quaternary mixtures were prepared in 0.096 M ammonium iodide solution, while the binary mixtures of Cd-Mg and Zn-Al were prepared in 0.32 M and 0.80 M ammonium iodide solution respectively. The metal ions eluted are shown in Fig. 1.

Results and discussion

The affinity of a metal ion towards a cation exchange resin can be described by binding the metal ion in a complex. The sorption will be less, if the complex formed has a little positive, zero or a negative charge. The sorption of the cations investigated initially decreases as the iodide concentration increases, as shown in Table 1.

The Hg(II) and Cd(II) ions are weakly sorbed due to strong complex formation of negatively charged species mainly, MI_4^{2-} (refs 7-9). The moderate sorbed metal ions, Zn(II), Co(II), Ni(II), Mn(II) and Mg(II), have poor tendencies to form negatively charged species, and that too only at high concentrations of iodide[7,10]. The strongly sorbed cations, Al(III), Ca(II), Sr(II) and Th(IV) are retained by the resin due to their poor complexing nature and high positive charge. At higher concentrations of ammonium

Table 1—Distribution coefficients (D) and separation factors $\alpha(\alpha_{Hg}^M)$ of metal ions in 0.096-2.08 M aqueous ammonium iodide on Dowex 50W-X4

Metal ion	Ammonium iodide concentration (M)									
	0.096		0.16		0.80		1.44		2.08	
	D	α	D	α	D	α	D	α	D	α
Mg(II)	150.79	23.50	128.12	22.00	13.58	3.60	7.23	3.10	4.87	3.00
Al(III)	1982.10	309.70	1628.96	280.60	40.02	10.80	13.15	5.70	6.61	4.10
Ca(II)	268.15	41.90	235.71	40.60	26.40	7.10	9.43	4.10	7.88	4.90
Mn(II)	172.90	27.10	148.21	25.50	17.54	4.70	7.55	3.20	7.33	4.60
Co(II)	60.80	9.50	53.12	9.20	16.32	4.40	11.23	4.80	5.12	3.20
Ni(II)	160.51	25.10	137.50	23.70	18.52	5.00	9.33	4.00	7.28	4.60
Zn(II)	72.22	1130	59.58	10.20	15.92	4.30	9.29	4.00	8.83	5.50
Sr(II)	T.S.	V.V.H.	T.S.	V.V.H.	562.52	152.00	402.27	174.90	336.68	213.00
Cd(II)	36.60	5.70	27.87	4.80	6.98	1.80	3.78	1.60	2.56	1.60
Hg(II)	6.40		5.80		3.70		2.30		1.58	
Th(IV)	1455.20	227.30	1201.23	207.10	50.51	13.60	25.00	10.80	23.68	14.90

T.S.: Shows almost total sorption.
V H.: Indicates very high α value.

Table 2—Expected metal ion complexes in ammonium iodide solution (0.096-2.08 M)

Metal ion	Complex formed	Complex nature	References
Hg(II)	HgI_4^{2-}	Very strong	8
Cd(II)	CdI_4^{2-}	Strong	
	CdI_3^-	less stable	8,9,12
	CdI_4^{2-}	less stable	13
Zn(II)	ZnI_4^{2-}	weak	1,3
Mn(II)	MnI_4^{2-}	unstable	10
	MI_6^{2-}	unstable	

All the metal ions investigated except Hg(II) form neutral complexes in the above iodide solution.

iodide solutions, these metal ions form a neutral species, and therefore, have not been taken by cation exchange resin[11]. The metal ions and their complexes formed with ammonium iodide are presented in Table 2. The ammonium iodide solution (0.096 M) was found most suitable for the chromatographic separation of Hg(II) and Cd(II) ions. This concentration was found to be appropriate since no precipitate of HgI_2 took place and also at this concentration, the separation factors ($\alpha = D_i/D_j$, where i and j are two different metal ions) are the highest, as shown in Table 1. In addition, at such a low concentration, the iodide do not interfere in metal ions estimations. Moreover higher α values predict a more quantitative separation. The very high α values for Sr(II) which shows a lower trend at low concentrations of ammonium iodide solution are due to total sorption of Sr(II) by the resin as shown in Table 1. The separation of Zn from Ni in 0. 0 M NH_4I could not be achieved as both Zn and Ni pass together in the effluent of 0. 0 M ammonium iodide solution.

As ammonium is the secondary cation in the present case, it causes no difference at low salt concentrations. However, at higher concentrations, the association of the secondary cation with a resin invasion is strong. Such associated complexes are too large to enter the resin[14].

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