

Anion exchange selectivities of Zn(II), Cd(II), Hg(II) and Ba(II) in KI solutions

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Potassium iodide provides a suitable medium for the anion exchange separation of a number of binary, ternary and quaternary metal ion mixtures. The procedure is rapid, convenient and is based on the quantitative formation of the anionic species $[MI_4]^{2-}$, in which Cd(II) and Hg(II) separations have been achieved from other metal ions. The separations are clear cut and the method can be applied for the removal and isolation of mercury by the conventional anion exchanger instead of using a chelating type where the elution process is rather difficult.

A large number of anions have been used as complexing agents for the separation of metal ions on ion exchange resin¹. Halides, (specially chloride) have been widely used for the ion exchange separations of metal ions², and some efforts have been made with solutions containing iodide^{3,4}. However, no attempt has been made to investigate systematically the anion exchange behaviour of the elements in aqueous potassium iodide solution. Therefore, an investigation of the anion exchange characterization of a number of cations has been undertaken. Moreover, anion exchange appeared to be quite promising, as zinc, cadmium and mercury are reported⁵⁻⁷ to form iodide complex of the type MI_4^- . The present work relates to separation of Mg(II), Ca(II), Sr(II), Ba(II), Al(III), Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), ZrO(II), and Th(IV) with the anion exchanger, Amberlite IRA-400 at thirteen different concentrations (0.16-2.08 MKI).

Experimental

Stock solutions (0.05-0.10 M) of various metals were prepared by dissolving their chlorides, sulphates or nitrates in doubly distilled water. The samples were either B.D.H. (AR) or E. Merck or S. Merck (G.R.) reagents, while zirconium solution was prepared using $ZrOCl_2 \cdot H_2O$ (Johnson Matthey, London) and thorium solution from its nitrate (Harrington Brothers, London). A little acid (HCl) was added to check the hydrolysis. Subsequently,

the solutions were standardized by the complexometric methods. An aqueous solution of 4.0 MKI (E. Merck, G.R.) was prepared and was standardized.

The anion exchange resin, Amberlite IRA-400 (8% cross-linking, 50-100 mesh, chloride-form, LOBA analytical grade) was pretreated, standardized and air-dried before use. The resin capacity and the moisture content were determined by the usual methods, and were found to be 1.14 meq/g and 22%, respectively.

Procedure

Determination of distribution coefficients (D) was carried out by the batch equilibration technique. Weighed amounts of the air-dried resin (1.000 g each) were added to the solution containing the metal ion and the iodide in 100 cm³ glass-stoppered flasks, which were agitated for 48 hr. It was ascertained previously that this time was adequate for the attainment of equilibrium. The resin was filtered off and the metal content was estimated in an aliquot of the filtrate employing the EDTA titration. The distribution coefficients were calculated using the relation,

$$D = \frac{\text{meq of the metal ion per g of resin}}{\text{meq of the metal ion per cm}^3 \text{ of solution}}$$

All the experiments were performed at the ratio of total amount of cation to total resin capacity ≈ 0.4 , using varying KI concentrations, and at room temperature ($30 \pm 2^\circ\text{C}$). The total volume of aqueous phase was 25 cm³. The result obtained are given in Table 1. Each set of experiments was carried out at least in duplicate and the average values were taken.

Accumulative experimental errors are estimated to be less than 2-5% of the results of D-values between 10 and 500, but are higher for very low D-values. The main sources of errors are inhomogeneity and the water content of the resin as the dry resin is a strong desiccant. Generally, D-values determined at relatively higher resin loadings, as in these experiments, provide more practical results than those determined at the tracer concentrations.

A slurry of 5 g air-dried resin (Cl⁻-form) in water was poured into a column (internal diameter 10 mm, bed height 9 cm). The column was saturated by the passage of 30 cm³ of 0.60 M KI. Then the mixture of Zn, Cd and Hg in 0.60 MKI (15 cm³) was poured into the column. The column was washed with 25 cm³ of 0.60 MKI solution to remove the ad-

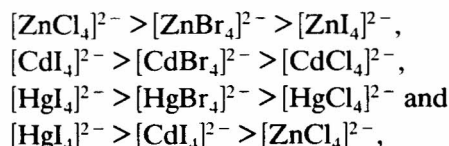
herent Zn completely as Zn exhibits almost no sorption by the resin at this concentration of KI. Cd and Hg were eluted successively by the eluants as reported in Table 2. After the elution of Cd, the resin column was washed with distilled water (40 cm³) and then Hg was eluted. The eluants were collected in 10 cm³ fractions, and the flow rate was 1.5 ± 0.2 cm³/min. Quaternary mixture of Mn, Zn, Cd and Hg in 2.08 M KI (feed volume = 20 cm³) was separated under similar conditions and sorbed metals were eluted as given in Table 2.

Results and discussion

The eluant, 1.5 M NH₄Cl-10% NH₃ (v/v), was found to be quite efficient and selective for the elution of Cd without disturbing Hg, leading to clearcut separation. Earlier workers¹⁰ have used nitric acid to elute Cd, which could affect Hg present in the same column. A comparison of elution results provided in Table 2 shows that a lesser volume of eluant was consumed to desorb Cd in 0.60 MKI compared

to that used in the case of 2.08 M KI. For Hg, 3M HNO₃ was used instead of 2M HNO₃. This deviation in the desorption with respect to KI concentration indicates that in dilute KI solutions Cd and Hg are weakly sorbed compared to their sorption in highly concentrated KI solutions. This behaviour has also been observed in the case of Zn sorption, which passed through the resin without being sorbed at 0.60 MKI, but was retained by the resin at 2.08 M KI. Moreover, at high concentrations of KI sorbable species probably occupy the upper part of the column due to strong tendency of exchange, while at lower [KI] the opposite happens and so lesser amount of the eluting agent is required. This is in agreement with the observations of Baggott and Willcocks¹⁰.

While Zn, Cd, Hg and Ba ions showed sorption on the resin in the investigated concentration range of iodide, no significant sorption was observed in the cases of Mg, Ca, Sr, Al, Mn, Co, Ni, Th and zirconyl cations (non-sorbable cations). At higher iodide concentrations, Zn, Cd and Hg showed strong tendency towards the resin. The loadings of these cations were selectively increased with the increase in KI concentration in the aqueous phase. This gradual enhancement is observed due to the formation of anionic iodato complexes¹¹, predominantly the species, [MI₄]²⁻. The reported⁵⁻⁷ comparative pattern of the orders of the metal halide stabilities for these anionic species is:



which clearly indicates and justifies the observed sorption trends in the iodide medium, i.e., DHg > DCd > DZn. In addition, because of the wider differences in the stability constants⁷ of iodide

Table 1—Distribution coefficients (D) of Zn, Cd, Hg and Ba at varying [KI] (M) with Amberlite IRA-400

[KI] (M)	Zn	Cd	Hg	Ba
0.16	NS	3.3	4.2	NS
0.32	NS	5.2	6.0	NS
0.48	NS	6.9	10.1	NS
0.64	0.6	10.5	14.6	0.4
0.80	2.0	12.6	21.0	1.2
0.96	3.3	15.7	27.8	2.0
1.12	4.5	19.2	35.5	2.9
1.28	5.9	22.6	45.7	3.9
1.44	7.9	28.1	57.1	3.2
1.60	11.5	35.0	81.9	2.5
1.76	20.1	49.2	110.0	1.1
1.92	34.8	65.1	174.9	0.1
2.08	51.1	101.2	486.0	NS

NS: Almost no sorption, i.e., D ≈ 0.

Table 2—Separation of Zn, Cd and Hg on Amberlite IRA-400 column

Mixture	Metal ion	Eluting agent	Vol. used (cm ³)	Introduced (mg)	Found (mg)	Error (%)
1	Zn	0.6 MKI	40	6.54	6.41	-1.98
	Cd	1.5 MNH ₄ Cl - 10% NH ₃ (v/v)	80	11.24	11.46	+1.95
	Hg	2.0 MHNO ₃	100	20.06	20.16	+0.49
2	Mn	2.08 MKI	30	5.15	5.15	0.0
	Zn	0.2 MNaCl	150	6.54	6.48	-0.90
	Cd	1.5 MNH ₄ Cl - 10% NH ₃ (v/v)	110	11.24	11.35	+0.97
	Hg	3.0 MHNO ₃	110	20.06	20.26	+0.99

complexes of these cations in comparison to the stability constant of chloride and bromide complexes, the iodide is found to be a superior and an advantageous medium to obtain the successful separation of Zn, Cd, Hg and other metal ions. So at higher concentrations of iodide (1.90-2.10 M) a number of separations of Zn, Cd and Hg from other metal ions can be achieved. At lower KI concentrations (0.50-0.60 M), Zn also passes through resin bed unadsorbed due to its weak tendency to form anionic iodide complexes^{5,6}, while Cd and Hg are retained by the resin and eluted by suitable eluants as shown in Table 2. In addition to the ternary and quaternary separations shown in Table 2, a number of binary separations can be achieved using selective KI concentrations.

At lower KI concentrations, the formation of the mononegatively charged species $[MI_3]^-$ appears less quantitative though Cyr¹² and Soe *et al.*¹³ reported the existence of $[CdI_3]^-$ in aqueous and mixed methanol-KI solutions, respectively. Also, the iodide ion, being mononegatively charged as well as smaller in size compared to the complex species, exchanges in preference to $[MI_3]^-$ leading to low metal ion uptake by the resin. Marcus *et al.*¹⁴ have reported that the complex species $[MI_3]^-$ is not preferred by the resin and this contributes towards the decrease in the metal ion sorption.

The relatively low metal ion sorption, at low KI concentrations is also due to the poor formation of divalent negatively charged species though the molar ratio of the metal ion to the iodide was 1:8 at lowest KI concentration taken, i.e., 0.16 M. Therefore, it appears that the iodide is not able to replace the coordinated water of the metal ion completely at these low KI concentrations to facilitate the greater formation of higher negatively charged complex

species. The formation of neutral species MI_2 cannot be ruled out, but as HgI_2 is insoluble in water its existence is almost nil in the chosen range of KI concentrations.

In case of Ba(II), it seems that above 1.28 M KI, the iodide anion starts competing with or replacing the barium iodide complex species in the resin. Other non-sorbed metal ions have poor tendency to form the anionic species to be taken up by the resin as in case of Mn¹⁵.

The study of the effect of pH on D-values is not possible as KI decomposes in acid. The observation that is general D-values decrease with the decrease of pH and vice-versa¹⁶, is not applicable in the case of present iodide system.

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