Anion Exchange Studies of Indium(III) in Malonate and Ascorbate Solutions Separation from Mixtures

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Summary

Systematic studies are presented on the anion-exchange behaviour of indium on Dowex 21K in malonic acid and ascorbic acid solutions. Hydrochloric, sulphuric, nitric and perchloric acids, also sodium and ammonium nitrate at different concentrations were tested as eluants in the two systems. Their efficiency was evaluated in terms of elution constants. Methods have been developed for the separation of indium from several elements in malonate as well as ascorbate media with the technique of selective sorption, selective elution or by gradient elution.

The separation and determination of Indium has attracted great attention, and a number of methods for its separation by cation-exchange chromatography are known but very few by anion exchange.

Indium has been separated in chloride media [1, 2] from aluminium, gallium and thallium on Dowex-1 by anion-exchange chromatography. It has also been separated from several elements in bromide media [3] employing 90 % methanol – 10 % 4.5 M HBr. Indium has been separated from zinc in sulphate media [4] on EDE-10P resin, being selectively retained by the resin. A similar separation was also achieved in carbonate media [5]. Some attempts have been made to use thiocyanate media [6] for its separation from iron and aluminium. The separation of gallium from indium [7] was achieved on Dowex 1 x 8 resin in iodide media where, after eluting gallium with 0.5 M KI; indium was eluted with 1 M NH_4Cl. An effort was made to study various negatively charged complexes of indium in acetate, formate and propionate [8] solutions. However systematic studies of indium in organic acid media are lacking.

This paper describes systematic studies of indium in malonate and ascorbate media using Dowex 21K resin. Various mineral acids and their salts were used as the eluants. It was possible to separate indium from large number elements such as thallium, aluminium, iron antimony, lead and cadmium which are usually associated with indium.

Experimental

Apparatus and Reagents

The ion exchange column used (1.4 x 18 cm) was similar to one described earlier [9] with automatic fraction collector, 10 ml syphon and Cambridge pH meter.

A stock solution of indium was prepared by dissolving 1.78 g $InCl_3.3H_2O$ (B.D.H., AnalaR) in 250 ml distilled water. The solution on standardization volumetrically [10] with EDTA contained 3.04 mg ml^{-1} indium.

Dowex 21K (Dow Chemical Company, 50–100 mesh, Cl^- form) was used in both cases.

For ion-exchange runs for malonate or ascorbate media the resin was converted to the appropriate form by passing a 5 % solution of malonic acid buffered at pH 4.5 or ascorbic acid buffered between pH 4 and 5. Later the resin was washed free of malonic or ascorbic acid solution.

Results and Discussion

Ion-Exchange Studies in Malonate Medium

An anionic malonate complex of indium was prepared by the addition of 2 g malonic acid and adjusting the pH to 4.6 by the addition of ammonia and malonic acid. The solution was sorbed on the column at the rate of 1 ml min^{-1}. After washing the column with 25 ml water, indium was eluted with various eluants (Table 1, Fig. 1). The effluent was collected in 10 ml fractions each being analysed for the indium content by EDTA.

The various parameters namely V_{max}, peak elution volume, V_t the total volume of the eluant used and hence the elution constant and volume distribution coefficients were calcuated as usual [11]. On the basis of the results, the eluants can be arranged in the order of decreasing efficiency:

$$HCl > HNO_3 > H_2SO_4 > NaNO_3 > NH_4NO_3$$

Ammonium sulphate, chloride and acetate were found to be poor eluants between 0.1 M and M.

Ion-Exchange Studies in Ascorbate Medium

An anionic ascorbato complex of indium was prepared by the addition of about 2 g of ascorbic acid and adjusting the pH to 4.5 by 0.1 M NH_4OH or dilute ascorbic acid. As before, the solution was sorbed on the column at the rate of 1 ml min^{-1}. The column was washed with 25 ml water and indium eluted (Table 2, Fig. 2). Study of V_{max}, the peak elution volume and the elution constant shows that the eluants can be arranged in order of decreasing efficiency:

$$HNO_3 > H_2SO_4 > HClO_4 > HCl > NH_4NO_3$$

Other eluants such as sodium chloride and nitrate, ammonium sulphate, acetate and chloride were found to be inefficient between 0.1 M and M.

Table 1. Anion-exchange studies of Indium in malonate media In = 15.2 mg, resin = 8.51 gm

No.	Eluant, (M)		Peak elution volume, V_{max}, ml	Total volume of eluant, V_t, ml	Total recovery of Indium, %	Elution constant (E)	Volume dist. coefficient D_V
1	HCl	0.10	150	200	99.97	0.209	4.78
		0.25	100	160	99.97	0.335	2.98
		0.50	60	120	100.00	0.650	1.54
		1.0	60	100	100.10	0.650	1.54
2	H_2SO_4	0.10	–	200	79.47	–	–
		0.25	150	170	99.19	0.209	4.79
		0.50	100	120	100.00	0.335	2.98
		1.0	50	110	100.10	0.849	1.18
3	HNO_3	0.10	–	200	80.73	–	–
		0.25	180	190	100.00	0.182	5.51
		0.50	65	90	100.11	0.526	1.90
		1.0	50	90	100.80	0.849	1.18
4	NH_4NO_3	0.25	–	200	59.72	–	–
		0.50	–	110	69.59	–	–
		1.0	55	100	99.60	0.650	1.54
5	$NaNO_3$	0.25	–	200	–	–	–
		0.50	145	200	94.12	0.209	4.79
		1.0	60	120	97.60	0.650	1.54

Table 2. Anion-exchange studies in ascorbate media In = 15.2 mg, resin = 8.51 gm

No.	Eluant, (M)		Peak Elution volume, V_{max}, ml	Total volume of eluant, V_t, ml	Total recovery of Indium, %	Elution constant (E)	Volume dist. coefficient D_V
1	HNO_3	0.10	120	160	99.32	0.270	3.70
		0.25	80	100	99.61	0.442	2.26
		0.50	50	90	99.87	0 848	1.18
		1.00	40	70	100.40	1.224	0.82
2	HCl	0.10	140	170	100.00	0.226	4.43
		0.25	70	100	100.00	0.326	1.90
		0.50	70	90	100.00	0.326	1.90
		1.00	40	60	100.10	1.224	0.82
3	H_2SO_4	0.10	140	190	99.33	0.226	4.43
		0.25	80	110	99.92	0.442	2.26
		0.50	60	90	99.96	0.650	9.54
		1.00	40	70	99.99	1.224	0.82
4	$HClO_4$	0.25	80	130	99.20	0.442	2.26
		0.50	60	120	99.37	0.650	1.54
		1.00	40	80	99.64	1.224	0.82
5	NH_4NO_3	0.25	–	200	6.08	–	–
		0.50	–	200	51.99	–	–
		1.00	80	120	97.37	0.650	1.54

Separations in Malonate Medium

These separation were based upon processes such as selective sorption, selective elution with specific eluants and gradient elution.

Separation from Alkali and Alkaline Earths, Thallium(I), Mercury(II), Iron(II), Bismuth(III)

These metals do not form malonate complexes at pH 4.6 and are therefore not retained on the column when sorbed along with indium. Indium was later eluted with M HCl. Separation of indium from the above mentioned metals is thus possible by selective sorption.

Separation from Zinc, Cadmium, Manganese, Cobalt, Nickel, Palladium and Antimony(III)

These metals form weak malonate complexes compared with indium. Hence after sorption they can be desorbed first [13] very easily with water, followed by elution of indium with 200 ml of M HCl.

Table 3. Separation of Indium in malonate and ascorbate media, In = 15.2 mg, Column 1.4 x 18 cm

Foreign ion	Amt. added	Malonate medium		Ascorbate medium	
		Indium recovered mg	% Indium recovered	Indium recovered mg	% Indium recovered
Li	60.2	15.20	100.00	15.20	100.00
Rb	60.2	15.20	100.00	15.20	100.00
Cs	60.2	15.20	100.00	15.20	100.00
Be	60.2	15.20	100.00	15.20	100.00
Mg	60.2	15.19	99.97	15.20	100.00
Ca	42.1	15.10	99.35	15.20	100.00
Sr	45.0	15.18	99.86	15.20	100.00
Ba	50.7	15.16	99.70	15.18	99.86
Tl(I)	30.5	15.10	99.35	15.10	99.35
Hg(II)	27.9	15.16	99.70	15.20	100.00
Bi(III)	25.5	15.20	100.00	15.20	100.00
Fe(II)	43.1	15.19	99.97	15.18	99.86
Zn	62.8	15.19	99.97	15.20	100.00
Cd	62.8	15.19	99.97	15.20	100.00
Mn	30.40	15.18	99.86	15.19	99.97
CO	30.40	15.18	99.86	15.20	100.00
Ni	30.40	15.18	99.86	15.20	100.00
Pd	32.7	15.10	99.36	15.22	100.01
Sb(III)	35.16	15.14	99.59	15.16	99.70
Al	45.06	15.15	99.68	15.18	99.86
V(IV)	52.17	15.18	99.86	–	–
Fe(III)	53.56	15.18	99.86	–	–
Cu	45.72	15.20	100.00	–	–
Pb(II)	25.2	15.16	99.70	15.16	99.70
Zr(IV)	47.61	15.20	100.00	15.14	99.59
Th(IV)	42.12	15.14	99.59	–	–
U(VI)	43.45	15.10	99.36	–	–
CrO_4^{2-}	25.3	15.20	100.00	15.15	99.68
ReO_4^-	15.9	15.10	99.70	15.10	99.36
VO_3^-	17.62	15.13	99.54	15.10	99.36
AsO_3^{3-}	30.9	15.20	100.00	15.16	99.70
MO_7O_{24}	32.6	15.20	100.00	15.13	99.54
PO_4^{3-}	32.6	15.10	99.36	15.19	99.97

Separation from Aluminium, Vanadium(IV), Iron(III), Copper(II), Lead, Zirconium, Thorium(IV) and Uranium(VI)

It was observed that these elements also form reasonably strong complexes with malonic acid [13, 14] under the experimental conditions for the complexation of indium, but such complexes can be eluted before indium with specific eluants. Thus aluminum can be eluted with 0.25M $NaNO_3$, vanadium(IV) and iron(III) with M NaCl, copper(II) with 0.25M NaCl, lead and zirconium with 1M CH_3COONH_4 followed by the elution of indium with 0.25M HNO_3.

However, uranium(VI) and thorium(IV) forms strong complexes with malonic acid as compared to that of indium. In this case indium was first eluted with 0.1M HCl followed by the gradient elution of uranium(VI) or thorium(IV) with M HCl.

Separation from Oxyanions

In the case of separation of indium from chromate, rhenate and vanadate, indium was first eluted with 0.25M HNO_3 followed by the elution of chromate with 2M NH_4Cl, rhenate with 2M KCl and vanadate with 2M NH_4OH. While in the case of separation of indium from arsenate, molybdate and phosphate, all these anions were first eluted with 0.5M NaCl followed by indium with 1M NH_4NO_3.

Separations in Ascorbate Medium

Separation by Selective Sorption

It is possible to separate indium from a number of other elements in ascorbate media. These include alkali and alkaline earths, thallium(I), mercury(II), bismuth(III), zinc, cadmium, manganese, cobalt, nickel, palladium, antimony(III) and aluminium, by the process of selective sorption as these metals do not form ascorbate complexes [15] at pH 4.2 and are therefore not retained on the column, whereas indium which is retained can be eluted with M HNO_3.

Separation from Zirconium and Molybdenum by Gradient Elution

It is possible to elute selectively indium first with 0.1M HCl followed by zirconium and molybdenum with 2M HCl.

Efforts to separate indium from uranium(V,I), thorium(IV), vanadium(IV) and titanium(IV) were unsuccessful as they also formed ascorbate complexes along with indium.

From 10 runs with 15.2 mg of indium in malonate and ascorbate media 15.2 ± 0.1 mg indium was recovered. The results show an accuracy of 2.5 %, the proposed method is very rapid, simple and selective for the separation of indium from various other elements.

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