Indian Journal of Chemistry
Vol. 25A, April 1986, pp. 403-404

Studies on Polytungstoantimonate Ion Exchanger: Part II—Distribution Coefficient Measurement & Selective Ion Exchange Separation of Metal Ions

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Received 26 *July* 1985; *revised and accepted* 22 *October* 1985

Apparent distribution coefficients of metal ions on polytungstoantimonate (PTA) exchanger have been determined at *p*H 4-5, and in 0.1 *M* HNO_3, 1 *M* HNO_3, 0.1 *M* NaCl and 1 *M* NaCl media. On the basis of distribution coefficient values, some selective, ion exchange separations like Pb^{2+} from Mg^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and La^{3+}; Bi^{3+} from Mg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}; and Hg^{2+} from Mg^{2+}, Co^{2+} and La^{3+} have been achieved on PTA column.

In Part I of this series[1], the synthesis, physicochemical properties and ion exchange behaviour of five different polytungstoantimonate (PTA) ion exchanges were described. In this note the sample PTA (B1), having W: Sb ratio of 15.14 : 1 has been used in the measurement of the break-through capacities and the apparent distribution coefficients of various metal ions. On the basis of these measurements, selective ion exchange separations of Pb^{2+}, Bi^{3+} and Hg^{2+} from other metal ions have been achieved.

The apparatus used has been previously described[1]. For separation studies PTA (B1) (5 g) of mesh size 100-200 was inserted in a glass column (length 2.2 cm; int diam 1.2 cm) on glass-wool support and the column washed with demineralised water. The flow rate was maintained at ~0.6 ml/min. All chemicals used were of AR grade.

Break-through capacities of the PTA (B1) were determined for Mg^{2+}, Ca^{2+} and Pb^{2+} at *p*H 4-5 and for Bi^{3+} at *p*H 2.0. The concentrations of the metal ions used were: Mg^{2+}, 0.5 mg/ml; Ca^{2+}, 0.49 mg/ml; Pb^{2+}, 0.54 mg/ml; and Bi^{3+}, 0.49 mg/ml.

The distribution coefficients of metal ions were determined by batch operation as described in an earlier paper[2]. The concentration of the metal ion was initially 5×10^{-4} *M*. K_d values were determined at *p*H 4-5 and in 0.1 *M* HNO_3, 1 *M* HNO_3, 0.1 *M* NaCl and 1 *M* NaCl media. The distribution coefficients of various metal ions revealed that this material possessed marked selectivity and important separations could be achieved. Estimations were carried out by titration with standard EDTA solution[3,4].

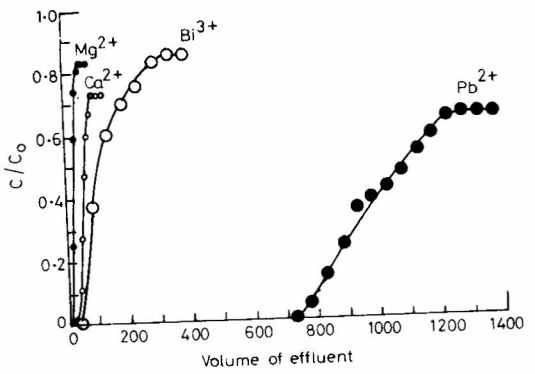

Fig. 1—Break through curves of Mg^{2+}, Ca^{2+} and Pb^{2+} at *p*H 4-5 and of Bi^{3+} at *p*H 2 on PTA (B1)

The probable composition of the material (B1) may be written as Sb_2O_5 $30WO_3.13H_2O$ after drying at 100°C. The break-through curve (Fig. 1) indicates the possibility of separation of Mg^{2+} and Ca^{2+} from Pb^{2+}. It is also evident from Fig. 1 that selective separation of Bi^{3+} from Mg^{2+} and Ca^{2+} can also be achieved. The break-through capacities for PTA (B1) at *p*H 4-5 are: Mg^{2+}, 1 mg/g; Ca^{2+}, 1.96 mg/g; and Pb^{2+}, 78.84 mg/g. For Bi^{3+} break-through capacity is 3.92 mg/g at *p*H 2.0.

The apparent distribution coefficients of metal ions on PTA (B1) and their ionic radii[5] are given in Table 1. The reproducibility of K_d values of metal ions has been checked and the average values of three determinations in each case are noted.

Table 1—Apparent Distribution Coefficients of Metal Ions on Polytungstoantimonate (B1) at 28 ± 2°C

Metal ion	Ionic radii (A)	*p*H 4-5	0.1 *M* HNO_3	1 *M* HNO_3	0.1 *M* NaCl	1 *M* NaCl
Mg^{2+}	0.65	87.5	59.7	9.6	17.1	0.8
Ca^{2+}	0.99	158.3	72.5	34.5	78.8	21.8
Zn^{2+}	0.74	239.9	74.0	1.1	69.0	3.6
Cd^{2+}	0.97	242.2	121.0	10.0	61.7	1.1
Hg^{2+}	1.10	218.5	199.7	93.0	23.9	1.9
Mn^{2+}	0.80	T.A.	109.3	3.8	79.1	6.3
Fe^{3+}	0.64	T.A.	129.8	70.9	58.2	45.4
Co^{2+}	0.72	180.6	29.26	0.8	16.6	0.8
Ni^{2+}	0.69	T.A.	102.5	1.25	75.0	15.0
Cu^{2+}	0.92	T.A.	129.8	69.7	114.7	19.6
Pb^{2+}	1.21	T.A.	244.8	173.4	—	—
Bi^{3+}	—	217.0 (at *p*H 2)	137.5	80.0	—	—
La^{3+}	1.15	231.2	67.8	1.9	86.7	37.5

T.A. = Total adsorption.

Table 2—Separation of Lead, Bismuth and Mercury from other Metals on PTA (B1) Column at 28±2°C

Mixture separated	Eluent	(ml)	Mixture separated	Eluent	(ml)
Mg^{2+}	1 *M* HNO_3	(40)	La^{3+}	1 *M* HNO_3	(45)
Pb^{2+}	4 *M* HCl	(45)	Pb^{2+}	4 *M* HCl	(40)
Ca^{2+}	1.5 *M* HNO_3	(40)	Mg^{2+}	0.25 *M* NH_4Cl	(35)
Pb^{2+}	4 *M* HCl	(40)	Bi^{3+}	4 *M* HNO_3	(30)
Zn^{2+}	1 *M* HCl	(45)	Ca^{2+}	0.5 *M* NH_4Cl	(30)
Pb^{2+}	4 *M* HCl	(40)	Bi^{3+}	4 *M* HNO_3	(30)
Cd^{2+}	1 *M* HCl	(25)	Co^{2+}	0.5 *M* NH_4Cl	(45)
Pb^{2+}	4 *M* HCl	(45)	Bi^{3+}	4 *M* HNO_3	(30)
Hg^{2+}	1 *M* NaCl	(30)	Zn^{2+}	0.5 *M* NH_4Cl	(25)
Pb^{2+}	4 *M* HCl	(40)	Bi^{3+}	4 *M* HNO_3	(30)
Mn^{2+}	1.5 *M* HNO_3	(40)	Cd^{2+}	0.5 *M* NH_4Cl	(25)
Pb^{2+}	4 *M* HCl	(45)	Bi^{3+}	4 *M* HNO_3	(30)
Fe^{3+}	1.5 *M* NH_4Cl	(30)	Hg^{2+}	0.5 *M* NH_4Cl	(20)
Pb^{2+}	4 *M* HCl	(25)	Bi^{3+}	4 *M* HNO_3	(40)
Co^{2+}	1 *M* HNO_3	(55)	Mg^{2+}	1 *M* HNO_3	(40)
Pb^{2+}	4 *M* HCl	(35)	Hg^{2+}	2 *M* HCl	(30)
Ni^{2+}	1.5 *M* HNO_3	(30)	Co^{2+}	1 *M* HNO_3	(40)
Pb^{2+}	4 *M* HCl	(45)	Hg^{2+}	2 *M* HCl	(35)
Cu^{2+}	1 *M* NH_4Cl	(40)	La^{3+}	1 *M* HNO_3	(40)
Pb^{2+}	4 *M* HCl	(30)	Hg^{2+}	2 *M* HCl	(35)

From Table 1 it is seen that the K_d values are higher for Pb^{2+}, Bi^{3+}, Fe^{3+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+} as compared to those of other metals, thereby, suggesting their possible separations from metal ions which have much lower distribution coefficients. It is also found that the K_d values of the metal ions decrease with the increase in $[H^+]$. In elution studies it is found that the decrease in hydrated ion size, e.g. $H^+ > Na^+ > NH_4^+$ favours the use of NH_4Cl as better eluting agent than other acids and salts. Satisfactory elution for Pb^{2+}, Bi^{3+} and Hg^{2+} have achieved with 4 *M* HCl, 4 *M* HNO_3 and 2 *M* HCl/1 *M* NaCl/0.5 *M* NH_4Cl respectively.

The data in Table 2 show that (i) Pb^{2+} can be quantitatively separated from Mg^{2+}, Ca^{2+}, La^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, and Cu^{2+}; (ii) Bi^{3+} from Mg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}; and (iii) Hg^{2+} from Mg^{2+}, Co^{2+} and La^{3+} The separation of Mg^{2+} from Ca^{2+}, Cu^{2+}, Fe^{3+}, and Ni^{2+} which was carried out in our laboratory using hydrous tungsten oxide column[6] could also be done using PTA (B1) (not shown in the text). The error of results are within the permissible range.

The authors are thankful to the UGC, New Delhi for sponsoring the project and to Prof A K De for constant encouragement.

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