

## Selective separation of mercury from other heavy metal ions on bromophenol blue sorbed anion exchange resin

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Sorption of bromophenol blue (BPB) on Amberlite IRA-400 resin and its use in the separation of various metal ions have been studied. Distribution coefficients of a number of important metal ions have been determined in various solvent systems in order to explore the separation potentiality of these materials. Mercury has been selectively separated from various heavy metal ions using the bromophenol blue sorbed ion-exchange resin column.

Ion-exchange resins with large surface area and macroporous structure have been successfully used for the preparation of chelating sorbents. These chelating resins have been used effectively for the separation of metal ions<sup>1,2</sup>. The chelating agents which react selectively with metal ions are bound to the resin by ion exchange rather than by physical adsorption. These chelated ion-exchange resins are specific towards the separation of metal ions as well as anions.

In this note, we report the use of Amberlite IRA-400 as a substrate for the deposition of bromophenol blue and its application for the selective separation of  $Hg^{2+}$  from other heavy metal ions.

### Experimental

Bromophenol blue (BPB) and bromothymol blue (BTH) were used as chelating agents. Amberlite IRA-400 in  $Cl^-$  form (BDH) was used as the sorbent. All other chemicals used were of AR grade.

A Bausch and Lomb Spectronic-20 spectrophotometer and an Elico pH meter model LI-40 were used for spectrophotometric and pH measurements respectively.

Amberlite IRA-400 in the  $Cl^-$  form was treated with a solution of bromophenol blue (1000 ppm) for 24 h at pH 4.3. The resin was washed several times with demineralized water to remove excess

reagent. The modified resin was dried in an oven at  $60 \pm 2^\circ C$ .

To study the sorption of bromophenol blue under static condition, 0.25 g of Amberlite IRA-400 in  $Cl^-$  form was equilibrated with 40 ml of BPB solution (20-2000 ppm) for 24 h at constant pH 4.3 and at room temperature. The equilibrium concentration of bromophenol blue in the solution was determined spectrophotometrically at 570 nm.

### Distribution coefficients

To the metal ion solution (40 ml), modified Amberlite IRA-400 resin (0.4 g) was added and the contents were kept at  $26 \pm 4^\circ C$  for 24 h with intermittent shaking. The amount of metal ions left in the solution was determined titrimetrically using 0.01 M EDTA as titrant.  $K_d$  values were calculated as usual<sup>3</sup> and are presented in Table 1.

The modified resin (1.5 g) was packed into a column (i.d., 0.8 cm). 2.0 ml of mixture of metal ions was poured on the top of the column at a flow rate of 18-20 drops/min. The metal ions (except  $Hg^{2+}$ ) were eluted with acetate buffer of pH-3.7 and  $Hg^{2+}$  was then eluted with 2M HCl solution.

### Results and discussion

Silica gel Dowex 50-W $\times$ 8, Alumina, Amberlite IR-120 and Amberlite IRA-400 were tested for adsorption of various chelating agents. It was observed that only silica gel and Amberlite IRA-400 adsorb bromophenol blue (BPB) and bromothymol blue (BTB) irreversibly. After adsorption of BTB and BPB, the colour of the resin beads changed from yellow to dark green and dark blue respectively. However, the bromophenol blue sorbed resin was chosen for the separation of metal ions due to its high complex forming capability of BPB. Adsorption isotherm of bromophenol blue on Amberlite IRA-400 shows that the maximum sorption of BPB at pH 4.3 is  $1.6 \times 10^3$   $\mu mol/g$ . The  $\pi$ - $\pi$  dispersion forces arising from the aromatic nature of the resin and reagent seems to be responsible for the sorption of BPB on Amberlite IRA-400<sup>4</sup>. The hydrophobic nature of styrene divinylbenzene matrix of Amberlite IRA-400 resin appears to be an excellent support for the sorption of BPB.

Table 1—Distribution coefficients of metal ions in different buffer solutions on Amberlite IRA-400 sorbed with bromophenol blue

Metal ions	$K_d$					
	pH 2.5 <sup>1</sup>	pH 3.7 <sup>1</sup>	pH 4.6 <sup>1</sup>	pH 5.6 <sup>1</sup>	pH 8.0 <sup>1</sup>	pH 10 <sup>1</sup>
Mg <sup>2+</sup>	0.5	0.5	4.3	0.5	11.6	9.1
Zn <sup>2+</sup>	0.6	0.6	11.3	6.0	11.2	17.1
Cd <sup>2+</sup>	1.0	13.0	44.4	18.2	13.0	18.2
Sr <sup>2+</sup>	29.2	3.3	5.7	0.5	3.3	5.7
Ca <sup>2+</sup>	18.9	7.3	22.2	12.8	2.3	10.0
Pb <sup>2+</sup>	26.5	4.9	7.5	0.6	19.4	26.5
Ni <sup>2+</sup>	1.0	19.0	1.0	13.6	8.7	19.0
Co <sup>2+</sup>	1.1	5.8	11.0	1.1	0.6	8.3
Cr <sup>3+</sup>	4.0	4.0	15.2	7.5	4.0	19.4
Fe <sup>3+</sup>	2.3	10.0	25.7	46.7	37.5	29.4
Al <sup>3+</sup>	8.3	18.2	40.5	52.9	48.6	40.5
Cu <sup>2+</sup>	0.6	11.4	0.6	11.4	50.0	85.7
Mn <sup>2+</sup>	1.0	14.4	17.0	5.1	7.3	25.6
Ba <sup>2+</sup>	44.8	0.6	10.5	0.6	27.3	13.5
Hg <sup>2+</sup>	212.5	2525	2525	2525	2525	2525

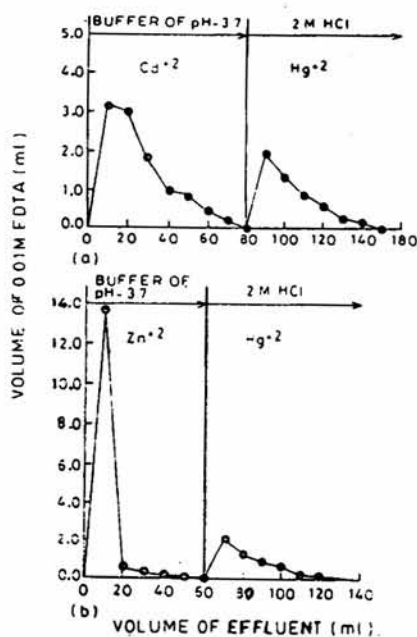
<sup>1</sup>1MCH<sub>3</sub>COOH<sup>1</sup>Acetate buffer

Fig. 1—Separations of (a) Cd<sup>2+</sup>-Hg<sup>2+</sup> and (b) Zn<sup>2+</sup>-Hg<sup>2+</sup> on Amberlite IRA-400 column sorbed with bromophenol blue. [Column height, 6.0/cm; Column diameter (i.d.), 0.8/cm; Mesh size, 20-50 mesh; Elution flow rate, 18-20 drops/min]

The distribution coefficients of metal ions in acetate buffer solutions of varying pH show that the uptake of Al<sup>3+</sup>, Fe<sup>3+</sup> and Hg<sup>3+</sup> increases with increase in pH of the buffer solutions. It is apparent from Table 1 that the  $K_d$  values are higher at pH 4.6 and 8.0 for most of the metal ions stud-

Table 2—Separation of mercury from other cations on Amberlite IRA-400 sorbed with bromophenol blue.

Mixture	Amount loaded (mg)	Amount found (mg)	Mean recovery <sup>1</sup> ± S.D. %	Vol. of eluent <sup>1</sup> used (ml)
Cd <sup>2+</sup>	11.69	11.58	99.04 ± 0.19	70
Hg <sup>2+</sup>	10.53	10.23	97.14 ± 0.21	60
Zn <sup>2+</sup>	11.64	9.81	84.27 ± 0.22	50
Hg <sup>2+</sup>	10.53	10.43	99.05 ± 0.207	60
Mg <sup>2+</sup>	2.33	2.31	98.96 ± 0.93	60
Hg <sup>2+</sup>	10.53	10.33	98.10 ± 0.209	70
Co <sup>2+</sup>	5.36	5.48	102.19 ± 0.391	40
Hg <sup>2+</sup>	10.53	9.93	94.29 ± 0.22	60
Mn <sup>2+</sup>	5.66	5.52	97.57 ± 0.39	90
Hg <sup>2+</sup>	10.53	10.12	96.19 ± 0.21	70
Fe <sup>3+</sup>	4.91	4.97	101.14 ± 0.45	70
Hg <sup>2+</sup>	10.53	10.13	96.19 ± 0.21	80
Al <sup>3+</sup>	2.81	2.71	96.63 ± 0.79	70
Hg <sup>2+</sup>	10.53	10.33	98.20 ± 0.20	60
Ni <sup>2+</sup>	5.87	5.84	99.50 ± 0.369	70
Hg <sup>2+</sup>	10.53	10.43	99.05 ± 0.207	70
Ba <sup>2+</sup>	11.54	12.36	107.14 ± 0.17	80
Hg <sup>2+</sup>	10.53	10.53	100.00 ± 0.20	60
Cu <sup>2+</sup>	9.91	7.75	78.21 ± 0.28	100
Hg <sup>2+</sup>	10.53	10.03	95.24 ± 0.22	70

<sup>1</sup>Average of five determinations.<sup>1</sup>2M HCl was used for elution of Hg<sup>2+</sup>, while acetate buffer of pH 3.7 was used for the other metal ions.

Table 3—Selective separation of  $\text{Hg}^{2+}$  from synthetic mixture of  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on Amberlite IRA-400 (bromophenol blue form) columns

Amount of $\text{Hg}^{2+}$ loaded (mg)	Amount of $\text{Hg}^{2+}$ found (mg)	Mean recovery $\pm$ S.D. %	Vol. of eluent <sup>†</sup> (ml)
3.01	3.01	100 $\pm$ 0.26	150
4.41	4.41	100 $\pm$ 0.29	175
5.61	5.52	98.57 $\pm$ 0.58	180
6.02	5.98	99.33 $\pm$ 0.30	185
6.82	6.80	99.71 $\pm$ 0.56	200

<sup>†</sup>Eluent: 2M HCl.

ied. The variation in  $K_d$  values may be due to the fact that metal-bromophenol blue complexes are most stable at pH 4.6 and 8.0: This is presumably because of specific interaction between the potential determining ion (BPB) retained on Amberlite IRA-400 resin (for BPB<sup>5</sup>;  $pK_1 = 4.00$ ,  $1.0 \times 10^{-4}$ ,  $pK_2 = 7.08$ ,  $8.4 \times 10^{-8}$ , ref. 5). If a complexing agent is adsorbed as a potential determining ion on the surface of the resin, metal ions are retained as counter ions on the resin, according to their specific interaction with the ligand.

The uptake of  $\text{Hg}^{2+}$  is exceptionally high. This may be due to the fact that mercury forms a relatively more stable complex with BPB. On the ba-

sis of this exceptional behaviour of  $\text{Hg}^{2+}$ , it has been possible to separate  $\text{Hg}^{2+}$  from a number of metal ions on a column of BPB-sorbed Amberlite IRA-400 resin. The results are summarized in Table 2 and a typical elution profile is shown in Fig. 1.

To check the selectivity and the reproducibility of the method, separation of different amounts of  $\text{Hg}^{2+}$  has been achieved from a synthetic mixture consisting of  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$  (2.79 mg),  $\text{Cr}^{3+}$  (2.60 mg),  $\text{Al}^{3+}$  (1.35 mg),  $\text{Cd}^{2+}$  (5.62 mg) or  $\text{Pb}^{2+}$  (10.36 mg) (Table 3). The results show that the method may be used for the removal of  $\text{Hg}^{2+}$  from industrial wastes and domestic water discharge.

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