

CHROM. 11,417

SYNTHESIS AND ION-EXCHANGE BEHAVIOUR OF NICKEL AND COBALT ANTIMONATES

QUANTITATIVE SEPARATION OF TERVALENT BISMUTH FROM FIFTEEN OTHER METAL IONS

MOHSIN QURESHI, K. G. VARSHNEY and NAIM FATIMA

Chemistry Section, Z. H. College of Engineering and Technology, Aligarh Muslim University, Aligarh, U.P. (India)

(First received April 11th, 1978; revised manuscript received July 26th, 1978)

SUMMARY

Various samples of nickel and cobalt antimonates have been synthesised under different conditions, and their ion-exchange capacities, solubilities and compositions have been determined. The most reproducible and chemically stable sample (NA-10) was prepared by adding 0.05 *M* nickel nitrate to 0.05 *M* antimononic acid at pH 11 and refluxing the resulting gel for 10 h in the mother liquor. The material was then filtered off, washed and dried at 100°. Its ion-exchange capacity was 0.89 mequiv./g with respect to K⁺. A column of NA-10 has been used to separate Bi³⁺ quantitatively from Cu²⁺, Cd²⁺, Al³⁺, Fe³⁺, Hg²⁺, Zn²⁺, Mn²⁺, VO²⁺, Mg²⁺, Ba²⁺, Ca²⁺, Sr²⁺, Co²⁺, Pb²⁺ and Y³⁺.

INTRODUCTION

The synthesis of inorganic ion exchangers is receiving considerable attention, as they are useful for the separation of metals and are also resistant to heat and radiation. Of the various salts hitherto synthesised for this purpose, antimonates show the most unusual selectivities¹. The antimonates of titanium², tin³, niobium⁴ and tantalum⁵ have already been studied, and here we describe the synthesis, ion-exchange properties and the separation potentials of the antimonates of nickel and cobalt.

EXPERIMENTAL

Reagents

All reagents and chemicals used in this study were of analytical grade.

Apparatus

Spectrophotometric, pH-metric, X-ray and infrared (IR) studies were carried out with a Bausch & Lomb Spectronic 20 colorimeter, an Elico pH meter (Model L1-10), a Philips X-ray unit and a Perkin-Elmer spectrophotometer (Model 621), respectively.

Preparation of antimononic acid

Antimononic acid ($H_4Sb_2O_7$) was prepared by passing 0.05 *M* potassium pyroantimonate through Dowex 50W-X8 (H^+).

Synthesis of various samples of nickel and cobalt antimonates

Ten samples each of nickel and cobalt antimonate were prepared by mixing 0.1 *M* $Ni(NO_3)_2$ or $Co(NO_3)_2$ with 0.1 *M* $SbCl_5$. The pH of the Ni- or Co-containing solution was 6, 8, 9, 10 or 11, and the ratio in which it was mixed with the Sb solution was 1:1, 1:2, 2:1 or 1:4. Of the various samples studied, one designated NA-10 was the most stable; the preparation, properties and synthesis of this material are described here.

Synthesis and properties of NA-10

The material was prepared by mixing 0.05 *M* $Ni(NO_3)_2$ and 0.05 *M* $H_4Sb_2O_7$ in the ratio 1:2 at pH 11. The precipitate so obtained was heated under reflux for 10 h in the mother liquor, filtered off, washed with distilled water and then dried at 100°. The dried material cracked into granules on immersion in water; these granules were placed in 1 *M* HNO_3 for several hours to convert them into the H^+ form and were then washed free from excess of acid and dried. The ratio of Ni to Sb in this material was 1.3:1. To determine the solubility, 500 mg of NA-10 was intermittently shaken for 24 h with 50 ml of H_2O , 0.1 *M*, 0.5 *M*, 2 *M* and 4 *M* HNO_3 , 0.05 *M*, 0.25 *M*, 1 *M* and 2 *M* H_2SO_4 and 0.1 *M*, 0.5 *M*, 2 *M* and 4 *M* HCl . The amounts (mg) of Ni dissolved were 0.00, 0.87, 12.43, 20.54, 16.80, 3.20, 7.30, 6.63, 10.35, 15.44, 20.02, 28.42 and 30.92, respectively; the amounts (mg) of Sb dissolved were 0.08, 2.32, 16.23, 15.93, 32.40, 2.83, 6.40, 12.42, 11.26, 34.30, 40.39, 51.34 and 60.32, respectively. The Sb was determined spectrophotometrically⁶, and Ni was determined complexometrically, with EDTA as titrant. The ion-exchange capacities of NA-10 for three monovalent and four divalent cations are shown in Table I.

TABLE I

ION-EXCHANGE CAPACITY OF NA-10 FOR CERTAIN CATIONS

<i>Ion</i>	<i>Ion-exchange capacity, mequiv./g</i>
Li^+	0.77
Na^+	0.87
K^+	0.90
Mg^{2+}	1.12
Ca^{2+}	1.23
Sr^{2+}	1.40
Ba^{2+}	1.52

pH-titration curves

A 500-mg portion of each sample in a 250-ml flask was shaken intermittently for 2 days with 100-ml portions of solutions containing different amounts of NaOH, then the pH of each solution was recorded. The experiment was repeated in the presence of a salt (NaCl) in order to maintain constant ionic strength; the results are summarised in Fig. 1.

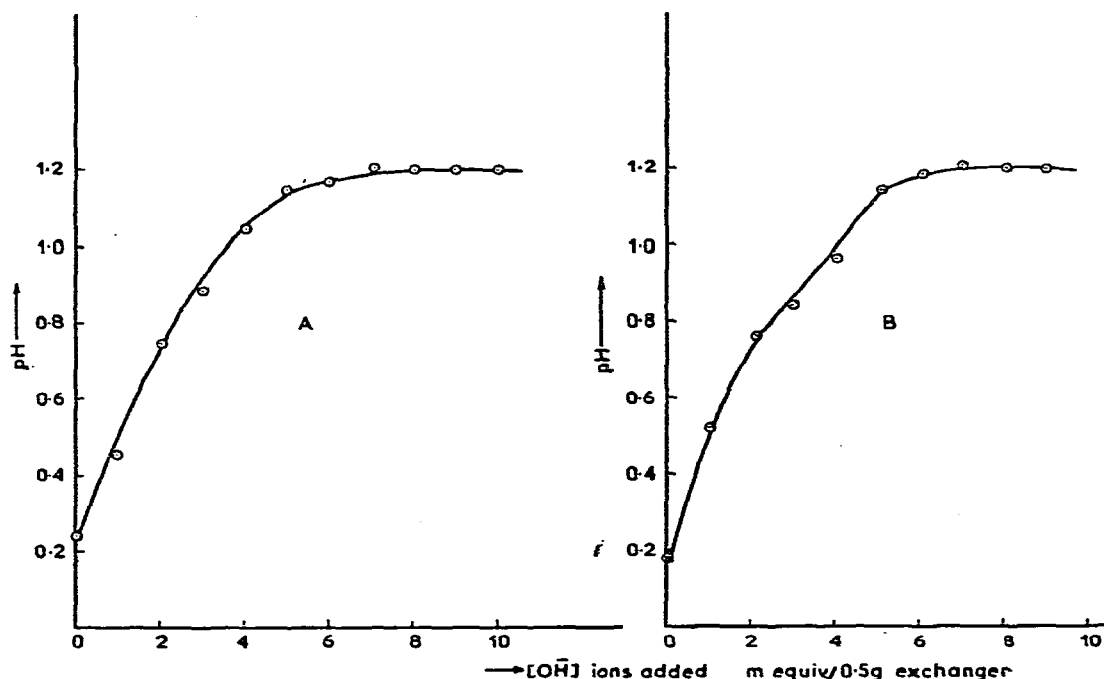


Fig. 1. pH-titration curves for NA-10 in the absence (A) and in the presence (B) of salt.

Concentration curve

A 500-mg portion of the sample was equilibrated with 50 ml of NaCl solution at various concentrations by intermittent shaking for 2 days, and the H^+ released were titrated with standard NaOH solution; a curve showing the ion-exchange capacities plotted against the concentration of the eluting solution is shown in Fig. 2.

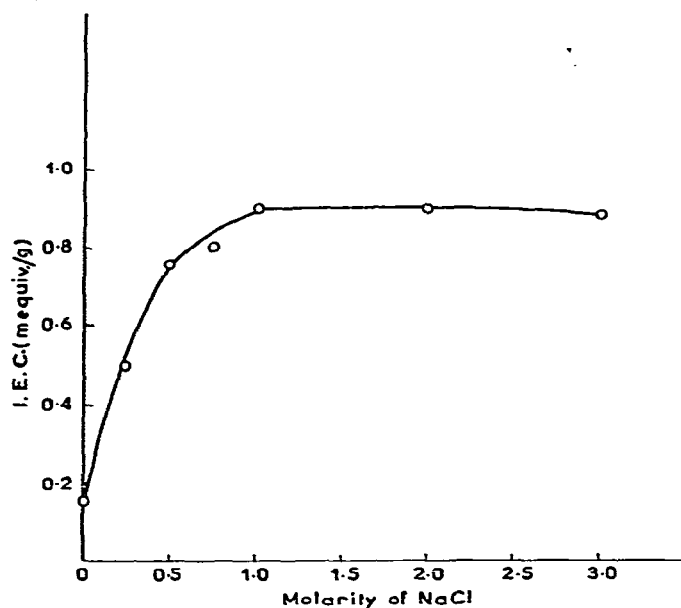


Fig. 2. Effect of eluent concentration on ion-exchange capacity (I.E.C.) of NA-10.

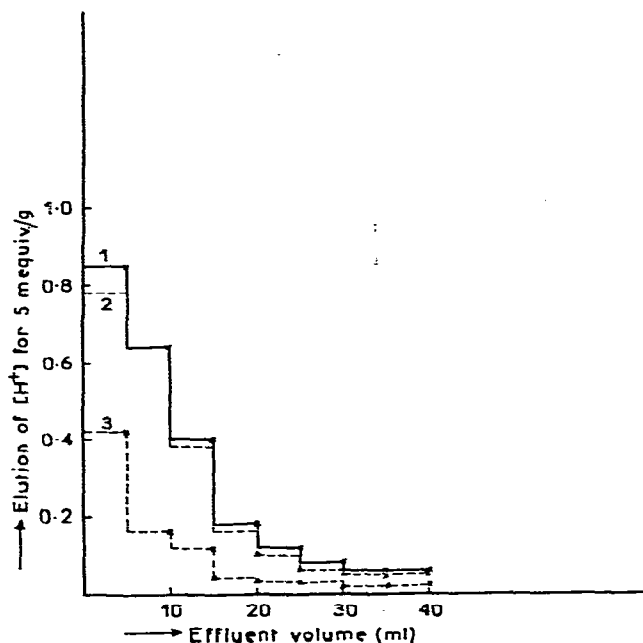


Fig. 3. Elution curve of NA-10 (H^+): 1, 3 M NaCl; 2, 2 M NaCl; 3, 1 M NaCl.

Elution curves

A column of 500 mg of NA-10 (H^+) was prepared, and the H^+ were eluted with 1 M, 2 M or 3 M NaCl. The H^+ in the eluate fractions were titrated, and the amount of H^+ was plotted against the volume of eluate to ascertain the volume of eluent necessary to remove H^+ completely from the column. The "curves" are shown in Fig. 3.

IR studies

The IR spectrum of NA-10 is shown in Fig. 4.

X-ray studies

X-ray studies on NA-10 revealed poorly crystalline behaviour; the d -values were as follows: 0.644, 0.634, 0.619, 0.608, 0.579, 0.558 and 0.532 Å.

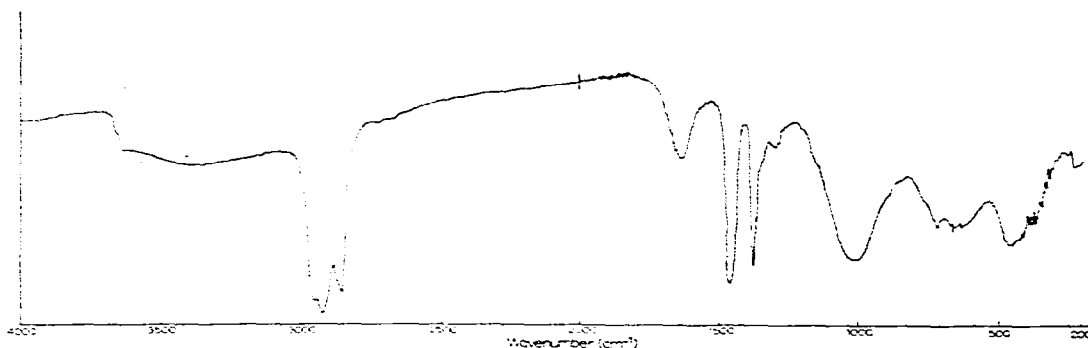


Fig. 4. IR spectrum of NA-10.

Separation studies

For separation studies, a glass tube was filled with 500 mg of NA-10 (H^+) supported on glass wool; the flow-rate in all separations was 0.6–0.8 ml/min. The species Cu^{2+} , Co^{2+} and Hg^{2+} were eluted with 3% NH_4Cl solution, Cd^{2+} , Fe^{3+} and Zn^{2+}

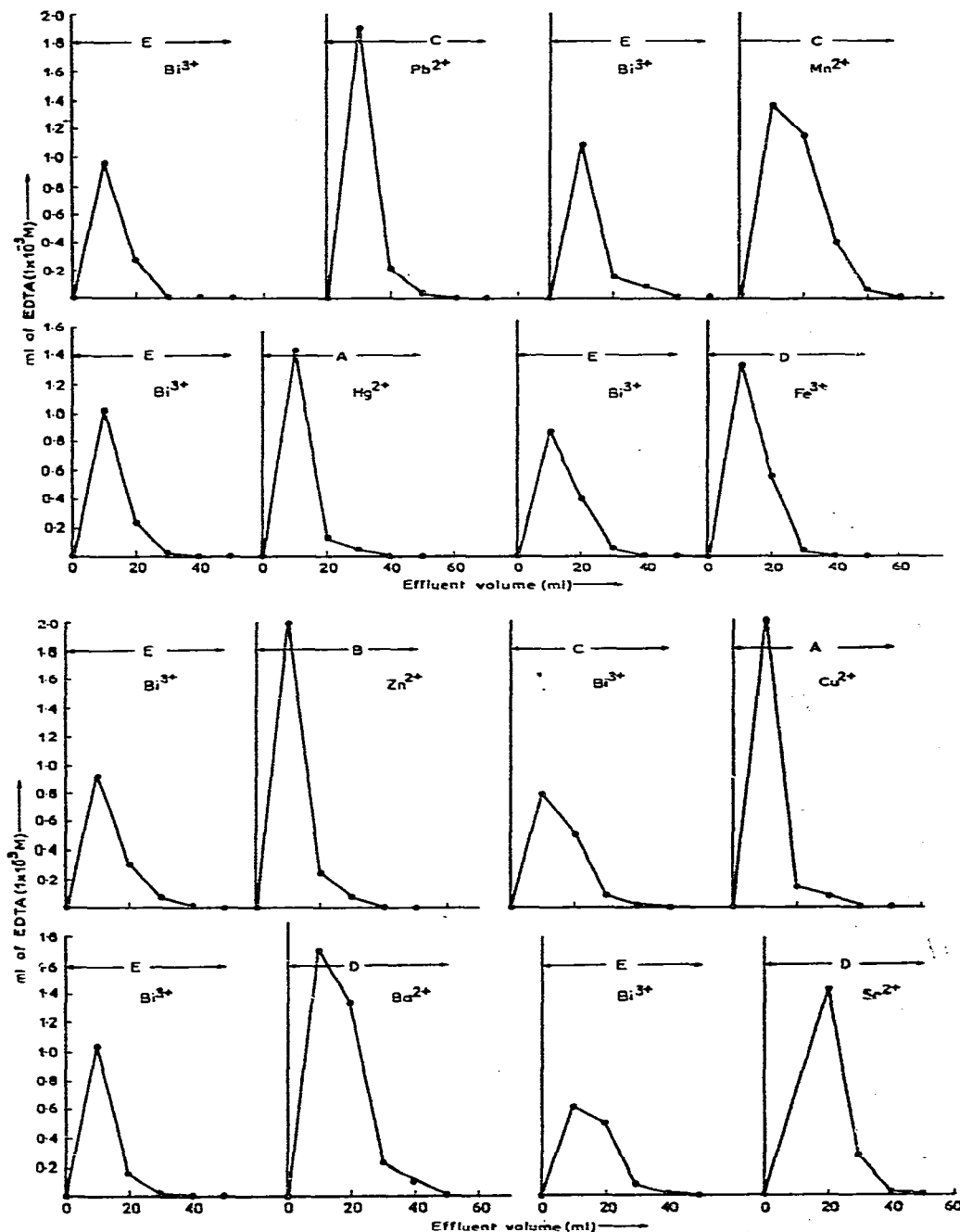


Fig. 5.

(Continued on p. 370)

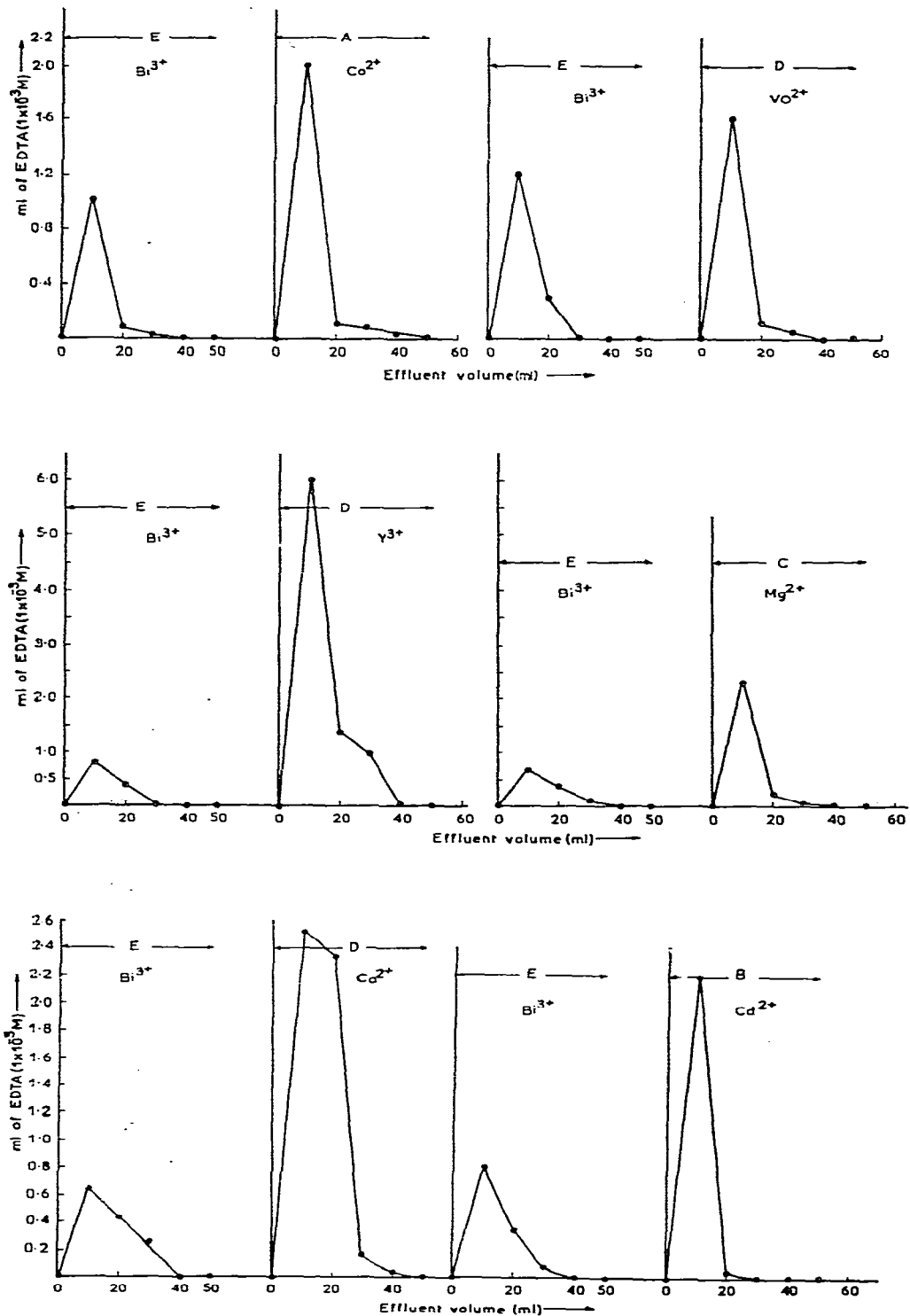


Fig. 5.

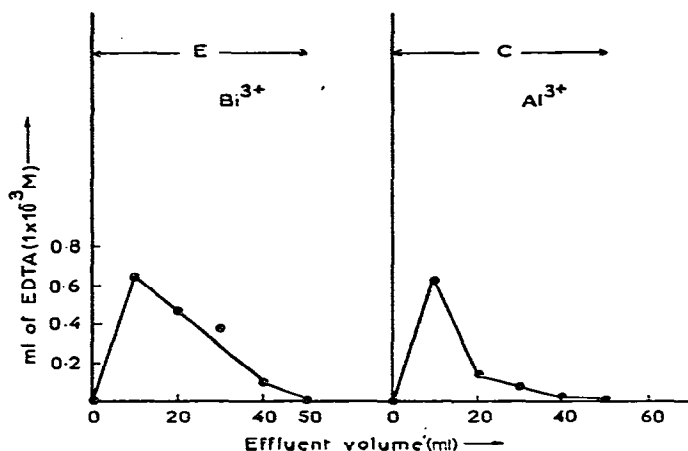


Fig. 5. Separation of Bi^{3+} from fifteen other metals on NA-10. Eluents: A, 3% NH_4Cl solution; B, demineralised water; C, 1 M NH_4NO_3 ; D, 1 M NH_4NO_3 -0.1 mM HNO_3 ; E, 1 M Na_2CO_3 .

with demineralised water, Pb^{2+} , Mg^{2+} , Mn^{2+} and VO^{2+} with 1 M NH_4NO_3 , Ba^{2+} , Sr^{2+} , Y^{3+} and Ca^{2+} with 1 M NH_4NO_3 -0.1 mM HNO_3 (1:1), and Bi^{3+} with 1 M Na_2CO_3 . The results are shown in Fig. 5.

DISCUSSION

The more important features of nickel and cobalt antimonates are outlined below:

The materials are highly resistant to mineral acids, especially HNO_3 ; even hot concentrated HNO_3 does not significantly affect the physical appearance of the samples. They are slightly soluble in cold HCl and dissolve completely in hot concentrated HCl . This is a general feature of most inorganic ion exchangers, which are dissolved in concentrated HCl for determination of their composition. The material with the best properties (NA-10) was prepared by adding $\text{Ni}(\text{NO}_3)_2$ solution to $\text{H}_4\text{Sb}_2\text{O}_7$ at pH 11 and heating the precipitate under reflux for 10 h in the mother liquor. Samples prepared in acidic media had slightly higher ion-exchange capacity than those prepared in basic media. With respect to other properties, such as stability and reproducibility, the higher pH is more suitable. The species present in the aqueous Sb-containing solution at pH 11 are anionic, e.g., $\text{Sb}(\text{OH})_6^-$; Ni and Co are not available as the nickelate(II) or cobaltate(II) species⁷. Thus, in alkaline medium Ni(II) or Co(II) antimonate may have the general formula $\text{M}(\text{OH})_2\text{M}_3(\text{HSb}_2\text{O}_7)$. The pH-titration curves (Fig. 1) indicate bifunctional behaviour of the acid salt. For elution of total H^+ from the column, the optimum concentration of NaCl is 1 M (Fig. 2); the elution curve in Fig. 3 was therefore obtained by using eluent of this concentration, and all the H^+ were eluted in 40 ml of eluate.

The IR spectrum of NA-10 exhibits the following characteristics: sharp intense peaks at 1000, 1375, 1460 and 2900 cm^{-1} ; weak peaks at 450 cm^{-1} and 1640 cm^{-1} ; broad and weak peaks at 720 cm^{-1} .

The peaks at 1375, 1460 and 2900 cm^{-1} are due to the Nujol used for pellet

formation, M–O bonding is represented by the peak at 450 cm^{-1} , and the presence of water molecules is indicated by the peak at 1640 cm^{-1} . The peak at 1000 cm^{-1} may be due to the presence of Sb_2O_3 .

The analytical utility of this exchanger has been established by the separations of Bi^{3+} from fifteen other metal ions (Fig. 5).

ACKNOWLEDGEMENT

We thank the University Grants Commission (India) for providing financial assistance.

REFERENCES

- 1 H. O. Phillips and K. A. Kraus, *J. Amer. Chem. Soc.*, 84 (1962) 2267.
- 2 M. Qureshi and V. Kumar, *J. Chem. Soc., London*, (1970) 1488.
- 3 M. Qureshi, V. Kumar and N. Zehra, *J. Chromatogr.*, 67 (1972) 351.
- 4 M. Qureshi, A. P. Gupta, T. Khan and J. P. Gupta, *J. Chromatogr.*, 144 (1977) 231.
- 5 M. Qureshi, J. P. Gupta and V. Sharma, *Anal. Chem.*, 45 (1973) 1901.
- 6 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience, London, 3rd ed., 1959, p. 423.
- 7 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, London, Sydney, 2nd ed., 1969, p. 880.