Ion exchange properties of bismuth antimonate

Anita Bhargava & C Janardanan*
Department of Chemistry, Sree Narayana Post-Graduate College, Kannur, Kerala 670 007, India
Received 16 January 1996; revised 15 January 1997

Studies on the synthesis, composition and ion exchange properties of bismuth antimonate have been carried out. The exchanger is stable in water, alcohol, acetic acid, 1 M H2SO4, 1 M HNO3, and in aqueous solutions of LiCl, NaCl, KCl, MgCl2 and BaCl2. The empirical formula of bismuth antimonate is proposed as Bi3O3Sb2O5.H2O. Bismuth-antimony ratio has been calculated from gravimetric analysis to be 1:1. The exchange capacity for various alkali and alkaline earth metal ions have been determined by batch method. Distribution coefficients of various metal ions indicate that bismuth antimonate has a high affinity for Ag+, Cu2+, Mg2+, Hg2+, Pb2+, Ce4+, Th4+ and Zr4+.

The resurgence of interest in synthetic inorganic ion exchangers has largely stemmed from the fact that these materials can be used under conditions unfavourable towards organic resins. Their resistance towards heat and ionising radiation makes them attractive alternative to organic resins in the field of radiochemical technology. Since some of these ion exchangers show selectivity towards certain ions a number of separations can be conveniently carried out.

Among the acidic salts of multivalent metals the antimonates of quadrivalent metal ions show promising ion exchange properties. In the present note we report the ion exchange characteristics of trivalent bismuth antimonate.

Experimental

Bismuth nitrate, potassium pyroantimonate obtained from Loba Chemie (India) were used as such. All other reagents used were of AR grade.

Bismuth antimonate was prepared by adding 500 ml of 0.05 M bismuth nitrate to 500 ml of potassium pyroantimonate (0.05 M) with constant stirring. Dil. nitric acid and dil. NaOH were used to be maintain pH at 1. On standing for 24 h the precipitate settled. It was filtered, washed first with dil. HNO3 (pH = 1), then with demineralised water and dried at room temperature. The material was then converted into H+ form by treatment with 1.0 M HNO3 for 24 h with occasional shaking and intermittent changing of the acid. The exchanger obtained was a white amorphous substance.

The exchanger (100 ml)ground to fine powder, was dissolved in 10 ml of conc. HNO3. Bismuth was estimated as oxyiodide and antimony as pyrogallate.

The ion exchange capacity of the sample was determined by the column operation. The ion exchanger (1.0 g) in the H+ form was placed in the column with glass wool support. Sodium chloride (1.0 M) was used as the eluent, and 250 ml of eluate was collected in every case. The hydrogen ions eluted from the column were determined titrimetrically with standard NaOH. The exchanger could be regenerated twice without any appreciable loss of exchange capacity.

Beyond this 50% of the exchange capacity was lost. This loss may be due to the hydrolysis of the exchanger. The distribution studies were carried out for several metal ions by batch process by equilibrating the metal ion solution with the exchanger beads for 6 h at room temperature (30±1°C). The Kd values were calculated using the expression,

\[ K_d = \frac{(1-F) \times F}{(20/0.1)} \]

where I is the volume of EDTA consumed by the original solution and F is the volume of EDTA consumed at equilibrium. The total volume of the solution was 20 ml and the amount of exchanger used was 0.1 g. The concentration of the metal ions was determined by EDTA titrations.

For separation studies of binary mixtures, 5 g of the exchanger in the H+ form was taken in a glass column (30 cm x 1.1 cm dia). The rate of flow in all separations was 0.5 ml/min. The separation was carried out for metal ions for which the separation factor was greater than 5. In all separations 5 ml of 0.005 M metal ion solutions were used.

Results and discussion

Bismuth antimonate was obtained in the form of white amorphous substance. It was stable in water, alcohol, acetic acid, 1.0 M H2SO4, 1.0 M HNO3 and in aqueous solutions of LiCl, NaCl, KCl, MgCl2,
NOTES

Table 1—Distribution coefficients of some metal ions on bismuth antimonate ion exchange

<table>
<thead>
<tr>
<th>Cation</th>
<th>Taken as</th>
<th>$K_a$ (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>Nitrate</td>
<td>350</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Sulphate</td>
<td>110</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Sulphate</td>
<td>210</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Nitrate</td>
<td>160</td>
</tr>
<tr>
<td>Co³⁺</td>
<td>Nitrate</td>
<td>0.00</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Chloride</td>
<td>280</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Sulphate</td>
<td>10</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Chloride</td>
<td>35</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Nitrate</td>
<td>15</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>Chloride</td>
<td>180</td>
</tr>
<tr>
<td>Th⁴⁺</td>
<td>Nitrate</td>
<td>85</td>
</tr>
<tr>
<td>Ce⁴⁺</td>
<td>Nitrate</td>
<td>70</td>
</tr>
<tr>
<td>Zr⁴⁺O</td>
<td>Chloride</td>
<td>80</td>
</tr>
</tbody>
</table>

CaCl₂ and BaCl₂. The maximum ion exchange capacity was found to be 0.93 meq/g. The chemical composition was found to be 1:1 (Bi:Sb) with a variation of ±0.01% for successive determinations. The empirical formula of bismuth antimonate is proposed as Bi₂O₃.Sb₂O₅.12H₂O.

The effect of size and charge of the metal ion on the capacity of the exchanger was studied for all the alkali and alkaline earth metal ions. The order of the exchange capacities on bismuth antimonate is as follows:

Li⁺(0.30) < Na⁺(0.93) < K⁺(0.98)
Ba²⁺(0.71) > Sr²⁺(0.68) > Ca²⁺(0.64) > Mg²⁺(0.60)

The exchange capacities are given in parentheses. The ion exchange capacity increases with decrease in hydrated ionic radii. This trend in the exchange capacities confirms that the exchange takes place in the hydrated forms.

A study of the effect of temperature on the exchange capacities revealed that ion exchange capacity decreases with increase in temperature and a complete loss of exchange takes place at > 200°C.

The distribution studies of thirteen metal ions have revealed that bismuth antimonate shows affinity for the metal ion in the order:

Ag⁺ > Ca²⁺ > Mg²⁺ > Hg²⁺ > Pb²⁺ > Zn²⁺ > Th⁴⁺ > Zr⁴⁺O

Ce⁴⁺ > Cu²⁺ > Cd²⁺ > Ni²⁺ > Co²⁺ (Table 1)

The effect of electrolyte (HNO₃, NH₄NO₃) concentration on the distribution coefficient of some metal ions was also studied. The sorption of cation on exchanger was found to be decrease with increase in electrolyte concentration.

Separation of Cd²⁺-Hg²⁺, Cu²⁺-Hg²⁺, Co²⁺-Ni²⁺, Cu²⁺-Pb²⁺ and Co²⁺-Cu²⁺ were achieved on a column of bismuth antimonate. The eluents used were HNO₃, NH₄NO₃ and HCl. The recovery range from 97-100% with a variation of 1% for repetitive determinations (Table 2). The exchanger is suitable for the quantitative separation of Hg²⁺ from Cd²⁺, Cu²⁺ and Cu²⁺ from Pb²⁺, Co²⁺.

References
7 Qureshi M, Varshney K B & Israili A H, Chromatogr, 50 (1972) 141.