Solvent extraction separation of antimony(III) with
2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A)

Sunita V Bandekar & PM Dhadke
Inorganic Chemistry Laboratory, Department of Chemical Technology,
University of Mumbai, Matunga, Mumbai 400 019, India

Received 9 September 1999; revised 24 February 2000

Solvent extraction of antimony(III) from aqueous chloride with 2-ethylhexyl phosphonic acid mono-2-ethyl hexyl ester (PC-88A) in toluene has been investigated. The optimum conditions required for quantitative extraction have been determined by studying the effect of various parameters such as acid concentration, reagent concentration, diluent effect, stripping agent, equilibrium time and diverse ions. Antimony(III) is quantitatively extracted from 0.1 M HCl with 1.5x10^-4 M PC-88A in toluene as well as xylene when equilibrated for 2 min. Antimony(III) from the loaded organic phase is stripped with 8.5 M H_2SO_4 and determined spectrophotometrically by iodide method. The method has been successfully applied for the separation of antimony(III) from commonly associated metals and its determination in real samples.

Antimony and its compounds are industrially important because of their usefulness in the manufacture of alloys, paints, paper, plastic, textiles, glass, clay products and rubber. It has also been used as medicine, e.g., the drug sodium stibogluconate is used for the treatment of kala azar also known as black fever (Leishmaniasis).

Various organic reagents have been reported in the literature for the solvent extraction of antimony while the chemistry of organophosphorus compounds have been described by Lobana. However some of these extraction methods suffer from limitations as given below. The extraction of antimony was incomplete with SRS-100 in benzene and thionaphthenic acid in carbon tetrachloride. N-Hydroxy-N-nitroso cyclohexyl amine and hexahydrocupferron in chloroform suffered from the limitations of critical pH conditions: Amberlite LA-1 in ethyl acetate and iso-octylmercapto acetate extracts it in carbon tetrachloride but in the presence of tin, extraction of antimony(III) was observed to be incomplete. 18-Crown-6(ref. 8) and bis-(2-ethylhexyl) hydrogen phosphorodithioate from perchlorate, bromide and sulphate medium have also been used for the extraction of antimony. In case of bis(2,4,4-trimethylpentyl) dithiophosphinic acid, i.e., Cyanex 301 (ref.10), the stripping of antimony(III) from the organic phase was not given. Triphenyl phosphine oxide (TPPO) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) have been widely used for the extraction of various transition and rare earth metals.

In the present investigation, antimony(III) has been quantitatively extracted with PC-88A in toluene from hydrochloric acid media. The proposed method is successfully applied for the separation of antimony(III) from commonly associated metals and its determination in real samples.

Experimental

UV-visible spectrophotometer (GBC Scientific Equipments Pvt. Ltd., Australia, model GBC 911A) with 10 mm matched quartz cells was used for absorbance measurement and a digital pH meter (Elico Pvt. Ltd., India, model LI-120) was used for measuring pH of the solution.

The stock solution of antimony(III) was prepared by dissolving antimony oxide in doubly distilled water containing concentrated HCl and was standardized gravimetrically. The required concentration of antimony(III) was prepared by appropriate dilution of the stock solution with doubly distilled water containing concentrated HCl. The extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A Structure I) kindly supplied by Daihachi Chemical Industries Ltd., Japan was used without further purification. The structure of PC-88A is as given below:

\[
\begin{align*}
\text{C}_2\text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{C}_3\text{H}_7\text{CH}_2\text{CH}_2\text{CH}_3\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{C}_2\text{H}_5
\end{align*}
\]

The acidity of the aqueous phase containing 60 μg of Sb(III) was adjusted to appropriate values with HCl (such that the concentration of HCl on dilution would be 0.1 M), diluted to 10 ml and transferred to a separating
Table 1 - Separation of antimony(III) from multicomponent mixtures

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Conc. (μg)</th>
<th>pH/ Acidity</th>
<th>PC-88A Conc. (M)</th>
<th>Stripping agent</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(III)</td>
<td>50</td>
<td>0.1 M HCl</td>
<td>1.5x10⁻¹ 1.5x10⁻¹</td>
<td>8.5 M H₂SO₄</td>
<td>99.1</td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>50</td>
<td>unextracted</td>
<td></td>
<td>4.0 M HCl</td>
<td>99.2</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>100.0</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>50</td>
<td>0.1 M HCl</td>
<td>1.5x10⁻¹ 6x10⁻³</td>
<td>8.5 M H₂SO₄</td>
<td>99.4</td>
</tr>
<tr>
<td>Bi(III)</td>
<td>200</td>
<td>pH 1.5, 0.1 M NH₄NO₃</td>
<td>unextracted</td>
<td>2.0 M HNO₃</td>
<td>99.6</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>98.7</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>100</td>
<td>0.1 M HCl</td>
<td>1.5x10⁻¹ 1.5x10⁻¹</td>
<td>8.5 M H₂SO₄</td>
<td>98.9</td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>50</td>
<td>0.1 M HCl</td>
<td>6x10⁻³</td>
<td>4.0 M HCl</td>
<td>99.2</td>
</tr>
<tr>
<td>Bi(III)</td>
<td>150</td>
<td>pH 1.5, 0.1 M NH₄NO₃</td>
<td>unextracted</td>
<td>2.0 M HNO₃</td>
<td>99.6</td>
</tr>
<tr>
<td>Tl(I)</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>98.5</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>100</td>
<td>0.1 M HCl</td>
<td>1.5x10⁻¹ 1.5x10⁻¹</td>
<td>8.5 M H₂SO₄</td>
<td>99.1</td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>50</td>
<td>0.1 M HCl</td>
<td>6x10⁻³</td>
<td>4.0 M HCl</td>
<td>99.2</td>
</tr>
<tr>
<td>Bi(III)</td>
<td>150</td>
<td>pH 1.5, 0.1 M NH₄NO₃</td>
<td>unextracted</td>
<td>2.0 M HNO₃</td>
<td>100.0</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 2 - Analysis of antimony in alloy and pharmaceutical samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Antimony (mg)</th>
<th>Mean Value</th>
<th>Found %</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>Sn(82.2), Zn(0.04), Sb(9.45), Cu(4.58)</td>
<td>9.43</td>
<td>9.35</td>
<td>9.40</td>
<td>99.50</td>
</tr>
<tr>
<td></td>
<td>Pb(3.18), As(0.15), Bi(0.11), Cd(0.14), Fe(0.024), Ni(0.17)</td>
<td>9.43</td>
<td>9.35</td>
<td>9.40</td>
<td>99.50</td>
</tr>
<tr>
<td>Drug</td>
<td>Sodium stibogluconate containing Sb(V) (equivalent to 330 mg)</td>
<td>100</td>
<td>100.51</td>
<td>99.45</td>
<td>99.45</td>
</tr>
<tr>
<td></td>
<td>(Albert David Ltd., Calcutta, India) Phenol I.P. = 0.15 w/v</td>
<td>100</td>
<td>100.51</td>
<td>99.45</td>
<td>99.45</td>
</tr>
</tbody>
</table>

* Average of three determinations
funnel. Then 10 ml of $1.5 \times 10^4 M$ PC-88A in toluene was added to it and shaken for 3 minutes. The two phases were allowed to settle and separate. Sb(III) from the organic phase was stripped with $8.5 M H_2SO_4$ and determined spectrophotometrically by iodide method\textsuperscript{14}.

Results and discussion

The effect of acid concentration on the extraction of antimony was studied by varying the hydrochloric acid concentration of the aqueous phase from 0.05-2.0 $M$. The extraction was found to be quantitative with 0.1 $M$ HCl and with further increase in concentration of hydrochloric acid, the percentage extraction of antimony was found to decrease.

Antimony was extracted with varying concentrations of the reagent, PC-88A ranging from $1.0 \times 10^{-1}-2.0 \times 10^{-1} M$ dissolved in toluene. The minimum concentration of PC-88A required for quantitative extraction was found to be $1.5 \times 10^{-1} M$. A graph of log D vs log [PC-88A] was plotted and the slope was found to be 0.96 which is nearly equal to 1. Hence the metal to reagent ratio was equal to 1:1. Antimony(III) was extracted with $1.5 \times 10^{-1} M$ PC-88A in various diluents. The extraction of antimony(III) was found to be quantitative with toluene and xylene whereas with cyclohexane (87.18%), benzene (77.22%), hexane (83.76%), chloroform (72.28%), carbon tetrachloride (72.28%) and dichloromethane (65.35%) it was found to be incomplete. Toluene was preferred as the diluent as it provided better phase separation.

The effect of stripping agent was studied. Antimony(III) from the loaded organic phase was stripped with different concentrations of acids such as HCl, $H_2SO_4$, HNO\textsubscript{3} and HClO\textsubscript{4}. The quantitative stripping was observed with $8.5-10.0 M H_2SO_4$ whereas with HCl, HNO\textsubscript{3} and HClO\textsubscript{4} it was found to be incomplete. Hence $8.5 M H_2SO_4$ was used as a stripping agent. The aqueous phase containing Sb(III) was shaken with $1.5 \times 10^{-1} M$ PC-88A in toluene for different periods of equilibration time from 0.5-20 minutes and the minimum equilibrium time required was found to be 1.0 min. It was observed that there was no adverse effect on the extraction of Sb(III) when equilibrated for a longer time.

The effect of various diverse ions on the extraction of Sb(III) with PC-88A in toluene was tested. The tolerance limit of the individual diverse ions was determined. Alkali and alkaline earth metal ions (Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+}, Cs\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Ba\textsuperscript{2+}, Sr\textsuperscript{2+}) were tolerated in the ratio of 1:20 while transition metal ions (V\textsuperscript{3+}, Mn\textsuperscript{2+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+}, Fe\textsuperscript{3+}, Hg\textsuperscript{2+}) and In\textsuperscript{3+} were tolerated in the ratio of 1:10. Noble metal ions (Ru\textsuperscript{3+}, Rh\textsuperscript{3+}, Pd\textsuperscript{2+}, Pt\textsuperscript{2+}, Au\textsuperscript{3+}), some main group metal ions (Al\textsuperscript{3+}, Be\textsuperscript{2+}, Ti\textsuperscript{4+}, Pb\textsuperscript{2+}) and Cr\textsuperscript{3+} were tolerated in the ratio of 1:5. Sn\textsuperscript{4+} and Bi\textsuperscript{3+} were tolerated in the ratio of 1:1 while As\textsuperscript{3+} interfered. Anions like SO\textsubscript{4}\textsuperscript{2-}, SO\textsubscript{3}\textsuperscript{2-} were tolerated in the ratio of 1:50 whereas NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-}, citrate, oxalate and tartrate were tolerated in the ratio of 1:20. The anions like Br\textsuperscript{-}, I\textsuperscript{-}, EDTA, thiourea and SCN\textsuperscript{-} were tolerated in the ratio of 1:10.

Separation of antimony from multicomponent mixtures

Antimony(III) was separated from various multicomponent mixtures of commonly associated metals with PC-88A (Table I). It was separated from the binary mixtures with tin(IV), bismuth(III), lead(II), thallium(I), copper(II) and nickel(II). Antimony(III) was extracted with $1.5 \times 10^{-1} M$ PC-88A in toluene from 0.1 $M$ HCl. It was observed that under these conditions, tin(IV) was coextracted and was separated from antimony(III) by differential stripping. Antimony(III) was first stripped with $8.5 M H_2SO_4$ followed by tin(IV) with 4.0 $M$ HCl. The other metal ions, bismuth(III), lead(II), thallium(I), copper(II) and nickel(II) were not extracted.

Antimony(III) was also separated from different multicomponent mixtures. Sb(III) and Sn(IV) were first separated from Pb(II) by first extracting with $1.5 \times 10^{-1} M$ PC-88A in toluene from 0.1 $M$ HCl as Pb(II) remained unextracted and then Sb(III) was separated from Sn(IV) by stripping with $8.5 M H_2SO_4$ while tin(IV) with 4.0 $M$ HCl. The mixture [Sb(III), Bi(III), Cu(II)] was separated by first extracting antimony(III) with $1.5 \times 10^{-1} M$ PC-88A in toluene from 0.1 $M$ HCl. The aqueous phase was maintained at 0.1 $M$ NH\textsubscript{4}NO\textsubscript{3}, its pH was adjusted to 1.5 and then equilibrated with $6 \times 10^{-1} M$ PC-88A in toluene. Bismuth(III) extracted in the organic phase was stripped with 2.0 $M$ HNO\textsubscript{3} while copper(II) remained unextracted.

Antimony(III) and tin(IV) were first extracted from the mixtures [Sb(III), Sn(IV), Bi(III), Th(II)] and [Sb(III), Sn(IV), Bi(III), Pb(II)] on equilibrating with $1.5 \times 10^{-1} M$ PC-88A in toluene from 0.1 $M$ HCl. Antimony(III) was then stripped with $8.5 M H_2SO_4$ while tin(IV) with 4.0 $M$ HCl. The aqueous phase was maintained at 0.1 $M$ NH\textsubscript{4}NO\textsubscript{3} and its pH was adjusted to 1.5 and then equilibrated with $6 \times 10^{-1} M$ PC-88A in toluene. Bismuth(III) extracted in the organic phase was stripped with 2.0 $M$ HNO\textsubscript{3} while thallium(I) and lead(II) remained unextracted. Thus, antimony(III) was successfully separated from the multicomponent mixtures.

Applications

100 mg of tin base alloy (BCS 178/2) was treated with concentrated nitric acid and its sample solution was prepared. A known amount of the solution was used for the extraction of antimony(III) by proposed method. Simi-
larly 1 ml of sodium stibogluconate injection containing 100 mg of Sb(V) was evaporated to dryness and the residue was decomposed, then leached and diluted to 500 ml with 0.5 M sulphuric acid. An aliquot of the solution was treated with ascorbic acid to reduce Sb(V) to Sb(III) and used for the extraction by proposed method. The results obtained for the above samples were found to be in good agreement with the theoretical values (Table 2).

Acknowledgement

The authors thank Daihachi Chemical Industries Ltd., Japan for supplying PC-88A.

References