Organophosphorus reagents as extractants: Part 5-Synergic effect of triphenylphosphine oxide on the extraction of iron(III) using 4-phenyl-2,4-butanedione

Tarlok S Lobana* & Pushvinder K Bhatia
Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005
Received 28 July 1993; revised and accepted 1 October 1993

Fe(III) is separated quantitatively from its binary mixtures with Cr(III), Mn(II), Co(II), Ni(II), Zn(II), Hg(II) and Mg(II) and from steel samples using a synergic combination of 4-phenyl-2,4-butanedione (HA) with triphenylphosphine oxide (Ph₃PO). However, copper(II) and silver(I) interfere. The extraction and stability constants of the synergic species Fe(NCS)₂(Ph₃PO) are found to be: 1.2 × 10⁹ and 7.3 × 10⁴ respectively.

The extraction of metals using aryl substituted phosphines¹ and their synergic effect on the extraction of metals using β-diketones²⁻³ or 8-hydroxyquinoline⁴⁻⁵ have been reported from this laboratory recently. In view of relatively few investigations on the use of aryl substituted phosphines⁶⁻⁸ for extraction studies, we have investigated the synergic effect of triphenylphosphine oxide and 4-phenyl-2,4-butanedione on the extraction of Fe(III) and the results are being reported here. The results are compared with those obtained using the synergic combination Hacac-Ph₃PO³.

Experimental

4-Phenyl-2,4-butanedione (HA) and triphenylphosphine (Ph₃P) were purchased from Sisco Chem. Industry, Bombay and used as such. All the metal salts were of laboratory reagent grade and standardised before use⁹. Ph₃PO was prepared by the oxidation of Ph₃P with KMnO₄ in acetone¹⁰. Spectrophotometric measurements were made using a Shimadzu-UV-visible (UV-240) recording spectrophotometer. The rest of the experimental details were the same as described earlier²⁻³.

Results and discussion

The extraction of Fe(III) from thiocyanate medium using 4-phenyl-2,4-butanedione (HA) can be represented by the Eq. 1,

\[ \text{Fe}^{III} + 3\text{SCN}^- + n\text{HA} \rightleftharpoons \text{Fe}_n(\text{NCS})_{m-n} + n\text{HNCS} \]  

The extraction of iron(III) increases with the increase in the HA concentration and reaches 99% at 0.05M HA. In contrast, the maximum extraction (99%) of Fe(III) using 2,4-pentanedione (Hacac) from the same medium was achieved at 0.1M Hacac³. Fig. 1 shows 2 linear regions with slopes 2 and 3 in the HA concentration ranges 0.005-0.01M and 0.035-0.05M indicating the extracted species as Fe(NCS)₂(Ph₃PO) respectively. With Ph₃PO alone, iron(III) is reported to get extracted as Fe(NCS)₃(Ph₃PO) with a maximum of 65% extraction at 0.1M Ph₃PO³.

The synergic extraction of Fe(III) with HA and Ph₃PO may be represented by Eq. 2,

\[ \text{Fe}^{III} + m\text{NCS}^- + n\text{HA} + n\text{Ph}_3\text{PO} \rightleftharpoons \text{Fe}(\text{NCS})_m(\text{Ph}_3\text{PO})_n + n\text{HNCS} \]  

The extraction of Fe(III) with 0.01M HA alone was 69% and with 0.02M Ph₃PO alone, it was 3.2%. The combination of HA (0.01M) and Ph₃PO (0.02M) showed 98% extraction with synergism of 27.0% comparable to the value of 30% observed with 2,4-pentanedione-Ph₃PO pair³. Further, on the basis of log D versus log[HA] considerations, the synergic species was found to be Fe(NCS)₂(Ph₃PO)
similar to Fe(NCS)(acac)\(_2\) (Ph\(_3\)PO)\(^3\). The enhanced extraction is attributed to the replacement of H\(_2\)O from Fe(NCS) (AMH\(_2\)O) by Ph\(_3\)PO.

A striking feature of HA-Ph\(_3\)PO combination is the use of merely 0.01\(M\) HA instead of 0.05\(M\) Hacac used in the previous synergic system, Hacac-Ph\(_3\)PO\(^3\). However, somewhat high molarity (0.02\(M\)) of Ph\(_3\)PO was used in comparison to that used in the case of the Hacac-Ph\(_3\)PO system\(^3\) \([\text{[Ph}_3\text{PO]} = 0.01\text{M}]\). Since the loss of Ph\(_3\)PO is negligible, the use of higher molarity of Ph\(_3\)PO is advantageous. Moreover, a lower time period is needed to arrive at the equilibrium (15 min versus 30 min). Thus, HA-Ph\(_3\)PO is a favoured synergic system. Replacement of one methyl group from CH\(_3\)COCH\(_2\)COCH\(_3\) (Hacac) by phenyl group in PhCOCH\(_2\)COCH\(_3\) (HA) leads to the efficient separation. Using the linear regression analysis\(^1\), we found extraction constants, \(K_{HA}\) and \(K_{HA_L}\), to be \(1.626 \times 10^4\) and \(1.91 \times 10^9\) respectively. Thus, it is clear that \(K_{HA_L}\) is about \(10^5\) times higher than \(K_{HA}\). Further \(K_{HA_L}\) value for HA-Ph\(_3\)PO system was \(10^3\) times higher than that for Hacac-Ph\(_3\)PO system\(^3\) (1.871 \times 10^9). The stability constant (\(\beta\)) for the synergic species was found to be \(7.32 \times 10^4\text{M}^{-1}\) (for Ph\(_3\)PO-Hacac, \(\beta = 1.26 \times 10^3\text{M}^{-1}\))\(^3\).

The synergic pair HA-Ph\(_3\)PO quantitatively separated iron from its binary mixtures with Cr(III), Mn(II), Co(II), Ni(II), Zn(II), Hg(II) and Mg(II); however, Ag(I) and Cu(II) interfered. When Hg(II) solution was added to iron(III) thiocyanate solution, the colour changed from blood red to colourless. However, the extraction of this colourless solution with HA-Ph\(_3\)PO pair separated the Fe(III) from Hg(II), that is, iron(III) went to the organic layer while Hg(II) remained in the aqueous layer. In this way, iron(III) was separated from Hg(II) and both the metal ions were then estimated. This extraction method showed a similar behaviour to that of Hacac-Ph\(_3\)PO in the determination of iron from steel samples\(^2,3\).

Acknowledgement

Financial assistance from the CSIR, New Delhi (Scheme No. 1(1095)/87-EMR(II) and laboratory facilities (to PKB) provided by the Guru Nanak Dev University are gratefully acknowledged.

References