

Organophosphorus reagents as extractants—Part 4: Synergic effect of bi(diphenylphosphinyl)ethane on the extraction of iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) using 8-hydroxyquinoline

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A series of 3d-metals (Fe, Co, Ni, Cu and Zn) have been quantitatively separated from binary mixtures using suitable synergic combinations of bis(diphenylphosphinyl)ethane, with 8-hydroxyquinoline. There is synergic effect of 10-18% in the extraction of metals versus the use of 8-hydroxyquinoline alone. The formation of the extracted species is established using the slope analysis method. The extraction constants for the synergic species as well as stability constants are determined from the metal distribution data using linear regression analysis.

In literature, it has been observed that the aryl substituted tertiary phosphine oxides act as better extractants or synergists as compared to the alkyl substituted analogues^{1,2}. With this principle in view, triphenyl phosphine oxide was used as a synergist in the extraction of Co and Zn using 8-hydroxyquinoline³ and of iron using acetylacetone⁴. Further, it was noted that phosphine oxides have been rarely used as synergists in the extraction of metals using 8-hydroxyquinoline^{1,3}.

In this paper, the synergic influence of bis(diphenylphosphinyl)ethane (hereafter dpeO₂) on the extraction of Fe, Co, Ni, Cu and Zn using 8-hydroxyquinoline (hereafter HL) is described.

Experimental

Ferrous ammonium sulphate, cobalt chloride hexahydrate, nickel nitrate hexahydrate, copper acetate dihydrate and zinc sulphate heptahydrate used were of reagent grade and used as such⁵. 8-Hydroxyquinoline was purchased from Sisco-Chem Industry, Bombay. Bis(diphenylphosphino)ethane (Ph₂PCH₂-CH₂PPh₂) and its oxide Ph₂P(O)CH₂CH₂P(O)Ph₂ were prepared by the literature methods^{6,7}. All the metal salts used for checking their interference were of laboratory grade and were standardised before

use⁵. Spectrophotometric measurements were made with Shimadzu UV-visible (UV-240) recording spectrophotometer.

A stock solution of Fe(III) was prepared by treating Mohr salt (0.070 g) with conc. HNO₃ (5 ml) two or three times, followed by evaporation of the excess acid and addition of KSCN (3.884 g, 0.4M) and made the volume to 100 ml using distilled water (molarity $1.78 \times 10^{-3} M$; 1 ml contained 0.1 mg Fe). The pH of the solution was 2.77-2.80.

Similarly stock solutions (0.01M) of CoCl₂·6H₂O (0.238 g in 100 ml) Ni(NO₃)₂·6H₂O (0.291 g in 100 ml), Cu(CH₃COO)₂·2H₂O (0.200 g in 100 ml) and ZnSO₄·7H₂O (0.287 g in 100 ml) were prepared in the distilled water. The stock solutions of HQ (0.2M), dpeO₂ (0.2M) and dpbO₂ (0.2M) were prepared in CHCl₃. A stock solution of *o*-phenanthroline (0.05M) was also prepared in CHCl₃. The solutions of low molarities of HQ and dpeO₂ or dpbO₂ were prepared by dilution.

For studying the effect of the different metal ions, solutions of different molarities of metal ions (0.1M) were also prepared. Each solution was standardised using 0.01M EDTA with xylene orange as the indicator⁵.

For spectrophotometric determination of Fe(III), a calibration curve in the range of 0.10-0.22 mg Fe per ml was prepared from the Mohr salt solution (0.070 g) and KSCN (0.01M) (λ_{\max} 460 nm)⁴. For spectrophotometric determination of Co(II), Ni(II) and Cu(II), the calibration curves were prepared by using sodium N,N-diethyldithiocarbamate method⁸ [range 0.1 mg - 1.9 mg Co²⁺/ml, λ_{\max} 650 nm; range 0.01-0.1 mg Ni²⁺/ml; λ_{\max} 390 nm; and range 0.02-0.2 mg Cu²⁺/ml, λ_{\max} 435 nm]. Similarly for Zn(II), a calibration curve in the range of 0.1-1.0 mg per ml was prepared by dithizone method (λ_{\max} 510 nm)⁹.

Procedure for extraction

With HL—To a solution of Fe(III) (2 ml, 0.1 mg/ml), distilled water (3 ml) was added, the resulting mixture was equilibrated with HL (5 ml, 0.0005 to 0.005M) in CHCl₃, stirred for 30 min on a magnetic stirrer and two layers were separated by using a separatory funnel. For the organic layer, stripping with conc. HNO₃ (1 ml) and distilled water (5 ml) transferred Fe(III) to the aqueous layer. Both the solutions were evaporated to dryness to remove excess acid and then a few ml of distilled water was added

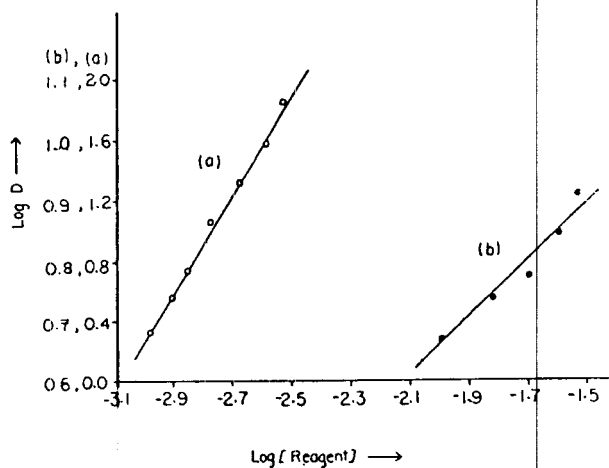


Fig. 1—Plot of log D versus (a) log [HQ] at constant [dpeO₂] and (b) log [dpeO₂] at constant [HQ] for Fe(III)

and Fe(III) from both the layers was estimated using 0.01 M KSCN (5 ml)⁴.

For Co, Ni and Cu, the quantities used were: 1 ml of M(II) solution (0.01 M), 4 ml of distilled water and 5 ml of HL (0.01-0.10 M for Co(II), 0.005-0.08 M for Ni(II), and 0.0005-0.007 M for Cu(II)); while for Zn(II), quantities used were 1 ml of Zn²⁺ solution (0.01 M), 7 ml of distilled water, 5 ml of HL (0.005-0.15 M) and 3 ml of *o*-phenanthroline (0.05 M) which avoided precipitation of HL as its hydrate in CHCl₃ layer. The pH of these solutions was 6.00. The contents were stirred for 15 min, the two layers were separated, and stripping of the organic layers with conc. HCl (1 ml) and distilled water (4 ml) transferred these metal ions to the aqueous layers. After stripping, these metal ion solutions were transferred into measuring flasks and made upto 25 ml by distilled water and metal ions such Co²⁺, Ni²⁺, Cu²⁺, Fe³⁺ and Zn²⁺ were estimated using spectral methods.

With dpeO₂—By using dpeO₂ alone, Co(II) and Ni(II) showed no extraction while for Fe(III), Cu(II) and Zn(II), the procedure was the same as described above except that no addition of *o*-phenanthroline was required for the extraction of Zn(II).

Synergic combinations of HL with dpeO₂: The following synergic combinations were used: (i) Fe(III) (2 ml), HL (5 ml, 0.003 M), dpeO₂ (5 ml, 0.01 M) and 8 ml of distilled water; (ii) Co²⁺ (1 ml, 0.01 M), HL (5 ml, 0.09 M), dpeO₂ (5 ml, 0.05 M) and 9 ml distilled water; (iii) Ni²⁺ (1 ml, 0.01 M), HL (5 ml, 0.05 M), dpeO₂ (5 ml, 0.05 M) and 9 ml distilled water; (iv) Cu²⁺ (1 ml, 0.01 M) HL (5 ml, 0.005 M), dpeO₂ (5 ml, 0.005 M) and 9 ml distilled water; (v) Zn²⁺ (1 ml, 0.01 M), HL (5 ml, 0.082 M) dpeO₂ (5 ml, 0.01 M); *o*-phenanthroline (3 ml,

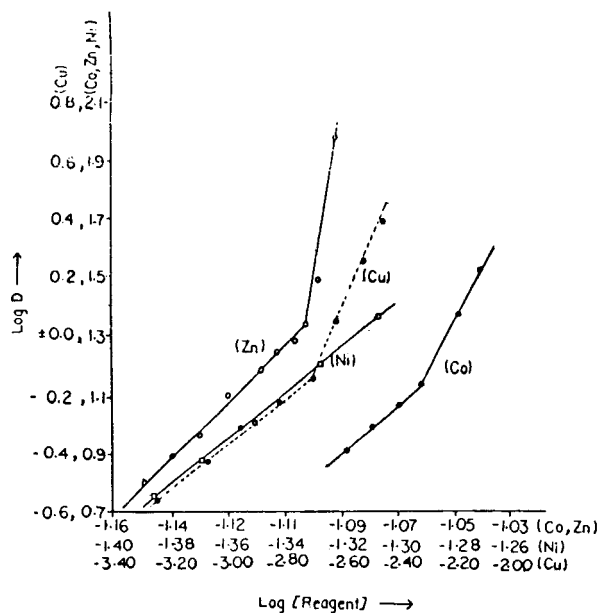


Fig. 2—Plot of log D versus log [HQ] at constant [dpeO₂] for (a) Co(II), (b) Cu(II), (c) Zn(II) and (d) Ni(II)

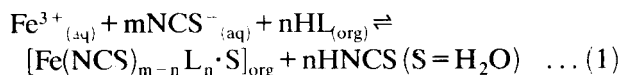
0.05 M) and 12 ml distilled H₂O. Rest of the procedure was the same as described above.

Using these synergic combinations, these metal ions were separated from the binary mixtures made with different metal salts. CrCl₃, MnSO₄·6H₂O, Fe(NO₃)₃·9H₂O, CoCl₂·6H₂O, Co(NO₃)₂·6H₂O, NiCl₂·6H₂O, Ni(NO₃)₂·6H₂O, Ni(CH₃COO)₂·4H₂O, ZnSO₄·6H₂O, ZnCl₂·2H₂O, Cu(CH₃COO)₂·2H₂O, CuSO₄·5H₂O, MgCl₂·6H₂O, Mg(NO₃)₂·6H₂O, HgCl₂, AgNO₃, Pb(NO₃)₂ and CdCl₂.

Here a metal salt solution (1 ml) of a given molarity (0.1 M) was added to the above mentioned systems for extraction. The remaining procedure was similar. The metal ions added were estimated by EDTA method⁵ using xylenol orange as the indicator while Hg(II) and Ag(I) were estimated by KSCN method⁵.

Results and discussion

The extraction of iron(III) using HL alone may be represented by the equation:



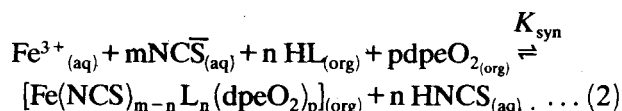
The extraction of iron increases with the increase in concentration of HL and from a linear plot of log D versus log[HL] in the HL concentration range 0.0005-0.003 M, a slope of 2 suggests Fe(NCS)L₂(H₂O) as the extracted species.

The extraction of iron using HL alone (0.003 M) was 82.0% and with 0.01 M dpeO₂ alone, there was

Table 1—Extraction constants and overall stability constants

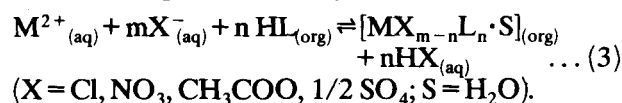
Species extracted	K_{syn}	σ	β
Fe(NCS)L ₂ (dpeO ₂)	1.04 × 10 ⁸	6.27	0.14 × 10 ³
CoL ₂ (dpeO ₂)	4.91 × 10 ⁵	7.50	0.29 × 10 ³
Ni(NO ₃)L(dpeO ₂)	1.22 × 10 ⁵	10.50	1.69 × 10 ³
CuL ₂ (dpeO ₂)	2.41 × 10 ⁸	10.14	0.45 × 10 ³
ZnL ₂ (dpeO ₂) ₂	3.86 × 10 ⁶	20.60	3.77 × 10 ³

no measurable extraction of iron. However, a combination of HL with dpeO₂ (0.003M HL + 0.01M dpeO₂) enhanced extraction to ~ 98% registering a synergism of 16%. This synergic extraction can be represented by the equation:



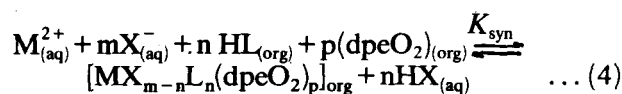
From the log D versus log[HL] plot at constant [dpeO₂] (Fig. 1a) and that of log D versus log [dpeO₂] at constant [HL] (Fig. 1b), slopes of 2 and 1 respectively were obtained. These data reveal the formation of [Fe(NCS)L₂(dpeO₂)] as the extracted species.

The extraction of the divalent metals (Co, Ni, Cu and Zn) using HL alone may be represented as:



The extraction of the metals reaches 98.5% at HL concentrations of 0.1 M, 0.08M, 0.007M and 0.15M for Co, Ni, Cu and Zn respectively. From log D versus log [HL] plots formation of ML₂·H₂O (M = Co, Cu, Zn) and [Ni(L)(NO₃)·H₂O] was established.

As in the case of iron, the synergic extraction of the divalent metals may be represented as:



Using suitable synergic combinations of HL with dpeO₂ [Co, 0.09M HL + 0.05M dpeO₂; Ni, 0.05M HL + 0.05M dpeO₂; Cu, 0.005M HL + 0.005M dpeO₂; and Zn, 0.082M HL + 0.01M dpeO₂], there was enhancement in extraction of the metals as follows: Co, 11%; Ni, 13%; Cu, 18% and Zn, 18%.

The slopes of the plots of log D versus log [HL] at constant concentration of dpeO₂ are two for Co, Cu and Zn [Fig. 2(a-c)] and one for Ni [Fig. 2(d)]. Similarly for the plot of log D versus log[dpeO₂] at constant [HL], the slopes are 1 and 2 for Cu and Zn respectively. The variations in the concentration of

Table 2—Separation of metals from binary mixtures

Metal separated	Binary mixtures	Interference by
Fe	Fe - Cr, Fe - Mn, Fe - Co, Fe - Zn, Fe - Hg, Fe - Mg	Cu, Ag
Co	Co - Cr, Co - Hg, Co - Ag, Co - Mg, Co - Al	Cu, Pb, Cd, Fe, Mn
Ni	Ni - Cr, Ni - Hg, Ni - Ag, Ni - Mg, Ni - Al	-do-
Cu	Cu - Cr, Cu - Mn, Cu - Co, Cu - Ni, Cu, Zn, Cu - Cd, Cu - Hg, Cu - Ag, Cu - Mg, Cu - Pb	Fe
Zn	Zn - Cr, Zn - Hg, Zn - Ag, Zn - Mg, Zn - Al	Cu, Pb, Cd, Fe, Mn

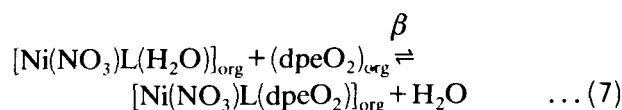
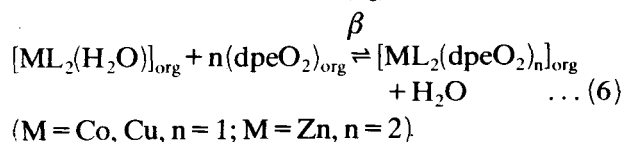
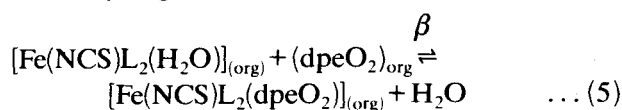
HL or dpeO₂ are in the vicinity of the synergic concentrations mentioned above. For Co and Ni, the variations in [dpeO₂] do not have any effect and same % extraction has been obtained as the one shown by synergic concentration taken. The synergic species identified are therefore formulated as: CoL₂(dpeO₂), CuL₂(dpeO₂) and ZnL₂(dpeO₂)₂ and Ni(L)(NO₃)(dpeO₂) [HL = 8-hydroxyquinoline].

It may be concluded that the addition of dpeO₂, an hydrophobic reagent showed synergism of 10-18% for all the metals as compared to the use of the reagent HL alone. The replacement of dpeO₂ by Ph₂P(O)(CH₂)₄P(O)Ph₂ made no difference and thus any increase in chain length from 2 to 4 gave same synergic effect.

The synergic extraction constants (K_{syn} , Table 1) were calculated from the distribution coefficient data (D values) for the metals using linear regression analysis¹⁰. A general expression for the distribution coefficient can be written as follows:

$$D_{syn} = K_{syn} [HL]^m [dpeO_2]^n \text{ (from Eqs 2 and 4) where } m = 2 \text{ for Fe, Co, Cu and Zn and } 1 \text{ for Ni; and } n = 1 \text{ for Fe, Co, Ni and Cu and } 2 \text{ for Zn;}$$

The overall stability constants (β values, Table 1) for the synergic reactions 5 to 7.



are determined from expression (8).

$$\beta = K_{\text{syn}} / K_{\text{HL}} \dots (8)$$

(K_{HL} , M : 7.39×10^5 , Fe; 1.69×10^3 , Co; 0.73×10^2 , Ni; 5.32×10^5 , Cu; 1.02×10^3 , Zn)

Table 2 gives details of separation of metals from binary mixtures. Most significant separations take place in the case of Cu or Fe. Further, Cu and Fe mutually interfere. In the case of Cu, a significant observation is that when a higher concentration of dpeO₂ (e.g. 0.01M instead of 0.005M as given above) was used, Hg(II) and Ag(I) also get transferred to the organic layer in a manner similar to that displayed by Ph₃PO³. In such a situation, stripping of the organic layer with 1 ml of concentrated HCl released Cu(II) to the aqueous layer while Hg(II) and Ag(I) remained in the organic layer. Further stripping of the organic layer with 1 ml of conc. HNO₃ transferred Hg(II) or [Ag(I)] to the aqueous layer which were estimated by the given methods.

Acknowledgement

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