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Synergistic Extraction of Copper with Resacetophenone Oxime in the Presence of Hetrocyclic Nitrogen Compounds

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Equilibrium distribution coefficients have been determined for the extraction of copper(II) with resacetophenone oxime as a function of pH and reagent concentration, at ambient temperature. RAPOX forms simple 1 : 2 chelate with copper(II). Pyridine and its methyl derivatives were found to enhance the extraction of copper into cyclohexanone with RAPOX. Monoadducts were observed and the adduct formation constant of 1 : 1, chelate to the adducting ligands, adducts were evaluated.

INTRODUCTION

It was as early as 1930, when Ephraim showed that salicylaldoxime could be used for the detection and estimation of copper in neutral or acetic acid medium[1]. Beside this reagent, he studied several other compounds of aromatic o-hydroxyaldoxime and ketoxime series and showed that Cu^{2+} as well as other metal ions behave in almost similar manner with these reagents as with salicylaldoxime and showed that they have a specificity for copper[2,3]. The pair of groups, OH, =NOH which is common to all these compounds was regarded as a specific reacting pair of groups for copper. Kadarmandalgi reported the chelation and separation of copper from cadmium using resacetophenone oxime[4], abbreviated as RAPOX. RAPOX was extensively studied as an analytical reagent in spectrophotometry for several metal ions[5].

Copper forms an yellowish-brown precipitate with RAPOX in slightly acidic medium[2] which could be extracted in an organic solvent like cyclohexanone. A solvent extraction study was undertaken of copper(II) using RAPOX, spectrophotometrically[6]. Zinc under similar conditions does not form any chelate with RAPOX. Advantage was taken of this fact for the carrier-free separation of $^{64,67}Cu$ from pile irradiated zinc[7,8]. Recently a synergistic extraction of cobalt(II) with RAPOX in the presence of heterocyclic and organophosphorous compounds, in cyclohexanone, was reported[9]. The paper reports the extraction study of copper(II) with RAPOX in cyclohexanone and in the presence of pyridine and its methyl derivatives, radiometrically. The extraction constants and the adduct formation constants have been evaluated and the relative effectiveness of the different bases, as synergists, compared.

EXPERIMENTAL

For the equilibration study, a Kahn type shaking machine fitted with a wooden box, in which stoppered centrifuge tubes (10 ml) could be accommodated, was used at ambient temperature (27° ± 2°C). Radioactivity was counted on a NaI(Tl) detector connected to a scintillation spectrometer, supplied by ECIL (India).

High specific activity $^{64}Cu_{(t_{1/2}=12h)}$ was supplied by Isotope Group, B. A. R. C., Trombay as $CuSO_4$. The activity was sufficiently diluted with distilled water. 0.2 ml aliquots of the stock solution, diluted with buffer solution, were taken for distribution study. The copper solution gave $\sim 6 \times 10^5$ c.p.m. after final dilution. A set of Clarke and Lubs buffer solutions were prepared with pH varying successively by 0.2 units. Requisite amounts of sodium perchlorate were added to the buffers to maintain a constant ionic strength of 0.1 M. RAPOX, i.e. resacetophenone oxime or 2,4-dihydroxyacetophenone oxime, $C_8H_9O_3N$, was synthesized from resorcinol and glacial acetic acid in presence of zinc chloride and was recrystallised from alcohol as described earlier[10]. Pyridine, 2-picoline, 3-picoline, 4-picoline, 2,4-lutidine, 3,5-lutidine and 2,4,6-collidine (Fluka AG) were purified by distillation after drying over potassium hydroxide. Freshly distilled cyclohexanone (E. Merck) was used.

Procedure

The extraction of copper with RAPOX was investigated in two sets. In the first set, 5 ml buffered ^{64}Cu solution, at constant ionic strength ($\mu = 0.1$ M) at various pH (3.0 – 8.0) and 5 ml RAPOX solution of varying concentration ($10^{-3} - 10^{-2}$ M) in cyclohexanone, were equilibrated by shaking for one hour, at ambient temperature (27° ± 2°C). In the second set, 5 ml of the buffered ^{64}Cu solution at constant ionic strength and pH(5.0) and 5 ml of the reagent solutions (RAPOX + varying amounts of heterocyclic nitrogen base) were equilibrated by shaking for one hour. After equilibration, the two phases were separated by centrifugation at high speed and aliquots of both the phases were pipetted and counted separately at constant geometry.

RESULTS AND DISCUSSION

For a simple solvent extraction system containing a divalent metal ion, Cu^{2+} and a chelating acid HR, the overall extraction equilibrium can be written as

$$Cu^2 + 2HR_0 \overset{K_{ex}}{\rightleftharpoons} CuR_{2_0} + 2H^+ \qquad (1)$$

The equilibrium constant, K_{ex} is given as

$$K_{ex} = [CuR_2]_0[H^+]^2/[Cu^{2+}][HR]_0^2 \quad (2)$$

and the distribution coefficient

$$D_0 = [CuR_2]_0/[Cu^{2+}] \quad (3)$$

from equation (2) and (3),

$$D_0 = K_{ex}[HR]^2/[H]_0^2 \quad (4)$$

Thus,

$$\log D_0 = \log K_{ex} + 2 \log [HR]_0 + 2 \text{ pH} \quad (5)$$

As per equation (1), the extraction of a simple chelate is shown by a plot of log D vs. pH, at constant reagent concentration in the organic phase. These plots essentially consist of two linear portions, the log D increasing initially in the low pH region then eventually reaching a constant pH-independent value, determined by K_{DC}, the distribution coefficient of the chelate,

$$K_{DC} = \frac{[CuR_2]_0}{[CuR_2]} \quad (6)$$

An increase in reagent concentration causes the initial linear portion of the curve shifting to a lower pH, i.e. the left. Fig. 1 shows the extraction

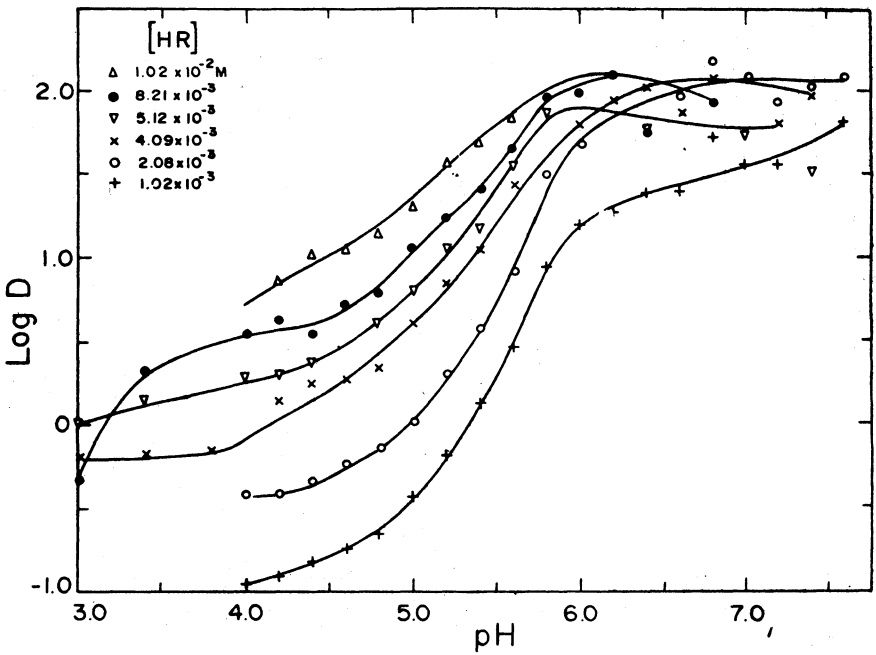

Fig. 1. Plots of log D vs. pH. Extraction of Cu(II) with RAPOX at different concentrations of the reagent at various pH $+1.02\times10^{-3}$; ○ 2.08×10^{-3}; $\times 4.09\times10^{-3}$; □ 5.12×10^{-3}; ● 8.22×10^{-3}; △ 1.02×10^{-2}

curves, the plots of log D vs. pH of copper for various concentrations of the reagent. All the curves in the plateau region at higher pH almost at a constant log D, merge indicating the formation of a simple chelate in the extraction system log D_{max}, where all the plots merge give directly the value of distribution coefficient of the chelate CuR_2, log K_{DC}. The log K_{DC} of Cu-RAPOXimate was found to be 2.1.

The plots of log D vs. log $[HR]_0$ at constant pH are linear and give slope two, thus, confirming the earlier findings obtained by Job's method[6] that the extractable complex is a simple 1:2 chelate since only two reagent molecules per copper ion are involved in the extraction as per equation (5) (Fig. 2). From the intercepts of these plots on y axis, the value of log K_{ex} could be calculated. A plot of log D $[H^+]^2/[HR]_0^2$ against log $[HR]_0$ takes

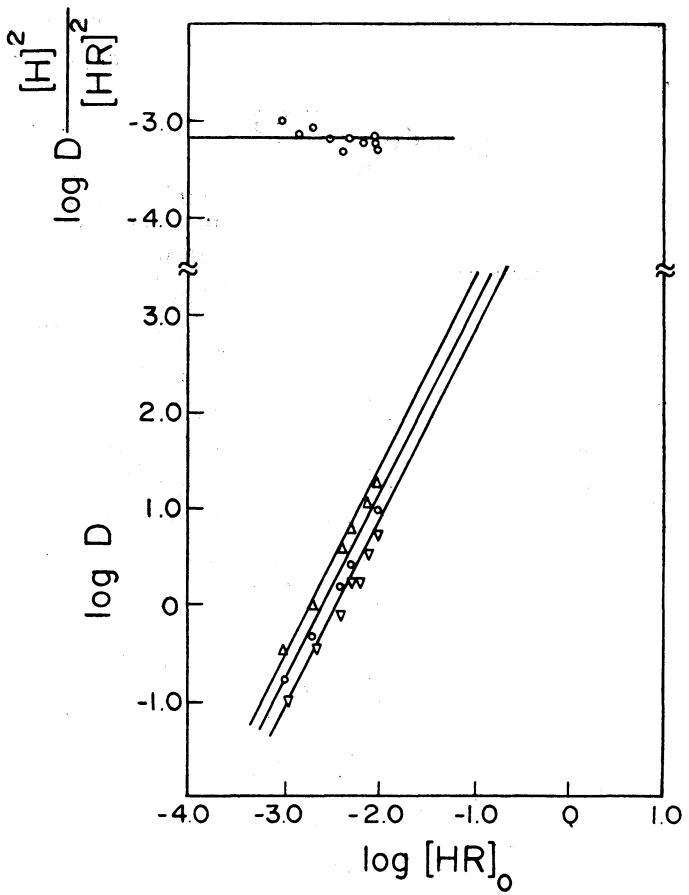

Fig. 2. (a) Plots of log D vs. log $[HR]_0$. Dependence of the extraction of Cu(II) with RAPOX at different pH : ▽ 4.0; ○ 4.5; △ 5.0; slope = 2
(b) Plot of log $D[H]^2/[HR]_0^2$ vs. log $[HR]_0$

into account the variation both in pH and in the reagent concentrations simultaneously. This plot is given in the same fig. 2. The horizontal line giving an intercept on y axis corresponds log K_{ex}. The mean value of log K_{ex} obtained by these plots is -3.2.

The overall formation constant, log K_f, of the copper chelate in the aqueous phase could be evaluated from the plot of log D vs. pR^- where pR^- is the negative logarithm of the RAPOX anion concentration in the aqueous phase which takes into account the variations in the pH and the reagent concentrations simultaneously giving two straight lines. Knowing the value of pK and the distribution coefficient of the reagent K_{DR}, pR^- could be calculated. The pK value of RAPOX was taken as 6.7 as determined earlier[11], and log K_{DR} as 3.0. From the intersection of the two lines obtained in this plot, the value of log K_f was obtained, $pR^- = 1/2$ log K_f (Fig. 3). The value of log K_f was found to be 12.3. K_f, the formation constant could also be obtained from the value of K_{ex} wher $K_{ex} = K_f K_a^2 K_{DC}/K_{DR}^2$, K_{DR} and K_a values being obtained from literature[12,13].

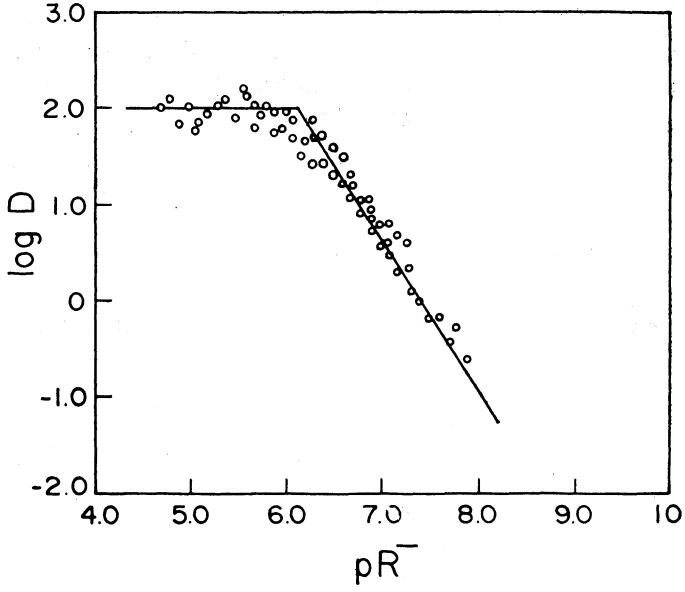

Fig. 3 Plots of log D vs pR^-.

The adduct formation of copper RAPOXimate with heterocyclic nitrogn compounds is given by the equation

$$Cu^{2+} + 2HR_0 + nP_0 \rightleftharpoons Cu_2P_{n0} + 2H^+ \quad (7)$$

with equilibrium constant

$$\beta nK_{ex} = [CuR_2Pn]_0[H^+]^2/[Cu^{2+}][HR]_0^2[P]_0^n \quad (8)$$

where

$$\beta n = [CuR_2P_n]_0/[CuR_2][P]_0^n \quad (9)$$

then

$$\log D[H^+]^2/[HR^2] = \log K_{ex}\{1 + \beta_1[P]_0 + \beta_2[P_0^2] \ldots \beta_n[P]_0^n\} \quad (10)$$

substituting the value of log K_{ex} from equation (4),

$$\log D/D_0 = \log \{1 + \beta_1[P]_0 + \beta_2[P]_0^2 \ldots + \beta_n[P]_0^n \quad (11)$$

where D and D_0 are the distribution coefficients in presence and absence P, respectively. The plot of log D/D_0 vs. $[P]_0$ has two asymtotes

(i) $$P \rightarrow O, \log D[H^+]^2/[HR]^2 = \log K_{ex} \quad (12)$$

and $\log D/D_0 = 0$

(ii) $$\text{for } L \rightarrow \infty, \log D[H^+]^2/[HR]^2 = \log K_{ex}\, \beta_n[P]_0^n \quad (13)$$

and $$\log D/D_0 = \log \beta_n[P]^n = \log \beta_n + n \log [P]_0 \quad (14)$$

At the point of intersection, $\log D/D_0 = 0$

$$\log \beta_n = -n \log [P]_0 \quad (15)$$

The slope of the plot log D/D_0 vs log $[P]_0$ gives the number of pyridine molecules, *n* and β_n is the adduct formation constant in the organic phase of the copper chelate and *n* moles of the adduct forming heterocylic nitrogen base, P. Thus, a plot of log D vs. log $[P]_0$ when plotted at constant $[HR]_0$ and pH, gives two straight lines. The horizontal line represen-

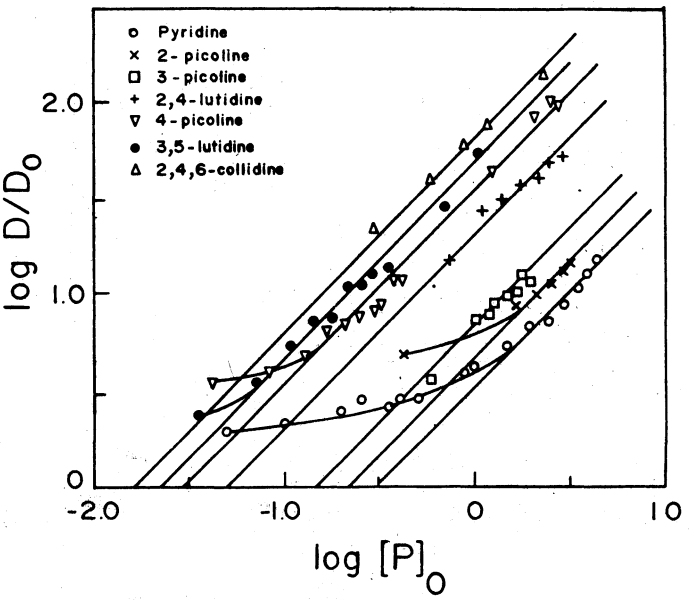

Fig. 4 Plots of log D/D_0 vs. log $[P]_0$. Distribution of pyridine adducts of Cu-RAPOXimate between cyclohexanone and water at pH = 4.0 slope = 1. ○ pyridine; × 2-picoline; □ 3-picoline; + 2,4-lutidine, ▽ 4-picoline; ● 3,5-lutidine; △ 2,4,6-collidine. Final $[HR]_0 = 1.03 \times 10^{-3}$M.

ting log D_0 i.e. in the absence of adduct forming ligand, intercepts the other curve and the point of intersection gives directly the value of adduct formation constant from equation (15).

Plots of log D/D_0 vs. log $[P]_0$ are depicted in fig. 4. The slope of all these plots is one, indicating that only one molecule of pyridine base is attached to the copper chelate, thus forming an extractable monoadduct, giving an empirical formula, CuR_2P. The adduct formation constants of various pyridines with the copper RAPOXimate are given in Table 1.

TABLE 1

ADDUCT FORMATION CONSTANTS FOR VARIOUS PYRIDINE ADDUCTS OF Cu-RAPOXimate IN CYCLOHEXANONE

Base	pK[15,16]	log β
Pyridine	5.17	0.5125
2-Picoline	5.97	0.6625
3-Picoline	5.68	0.83
4-Picoline	6.02	1.525
2,4-Lutidine	6.72	1.2875
3,5-Lutidine	6.14	1.64
2,4,6-Collidine	7.48	1.7875

The stability of the pyridine adducts of copper RAPOXimate decrease in the following order:

2,4,6-collidine> 3,5-lutidine> 4-picoline> 2,4-lutidine> 3-picoline >2-picoline>pyridine.

The adduct formation constants, log β, were found to decrease in the order of decrease in the respective pK values of the bases, with the exception of 2,4-lutidine and 2-picoline. This is not unexpected as both these bases contain steric hindering groups at 2-position. With the result, the adduct formation constant of 2,4-lutidine was found to be lower than that of 3,5-lutidine, although its pK value is higher than 3,5-lutidine and 4-picoline. Similar is the case of with 2-picoline whose pK value is higher than that of 3-picoline. 2,4,6-collidine forms the most strongest adduct among all the nitrogen bases, inspite of having two steric hindering groups present at 2- and 6-positions. The basicity due to the presence of all the methyl group counteract the steric hindering effect produced by the methyl groups at 2- and 6-positions. Both the steric hindering groups present seem not to have affected its adducting ability.

A very interesting linear correlation was observed on plotting log β vs. pK values of the bases. Two separate plots were obtained wherein formation constants of the bases having steric hindering groups lie on one plot whereas those of other bases lie on another plot. Thus, a separate linear correlationship is maintained by two different groups of bases i.e. one with steric hindering group present and other absence of any steric hindering group (see Fig. 5).

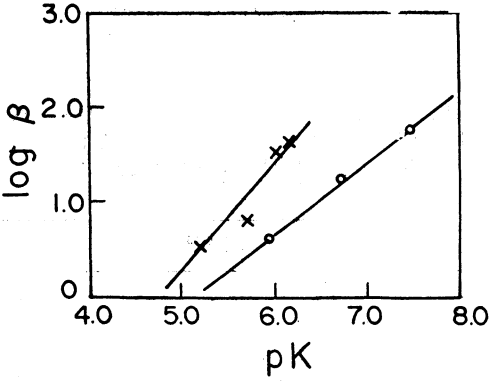

Fig. 5 Correlation between adduct formation constant and the basicities of the pyridine bases.

The formation of monoadduct suggests penta coordinate structure in the pyridine adduct of copper RAPOXimate. The question of water molecule occupying the sixth coordination site of copper ion is ruled out as copper does not form hydrated chelate with RAPOX. This was observed when the chelate was isolated in solid state. Freiser et al.[12] had observed similar monoadduct formation in the extraction of pyridine adducts of zinc oxinate. They assumed that one of the water molecules was pushed out of the coordination sphere by the adducting ligand and other occupied the sixth coordination site. This argument does not hold good in the present extraction of copper adduct simply because water molecules do not participate during the chelate formation. Hence pentacoordination is the most probale structure of the pyridine adducts of copper RAPOXimate. If a planar structure is assumed for the copper RAPOXimate, then the two molecules of RAPOX would form the square base of a pyramid. For bonding and steric reasons the highest symmetry is generally the energetically preferred one; that is, the unidentate ligand is in axial position of a square base pyramid (point group C_{4v})[14]. The extracted species are, thus, the pentacoordinate adducts having a square base pyramidal structure.

Unlike cobalt, weak synergism was observed when extraction of copper (II) with RAPOX was tried in presence of organophosphorous compounds like tri-n-butyl phosphine oxide (TBPO) and tri-n-octyl phosphine oxide

(TOPO) in cyclohexanone. Up to one molar concentration of the organophosphorous compounds in cyclohexanone were tried when the slope of the plot of log D/D_0 vs. log P obtained was <0.5. Further concentration of the organophosphorous compounds could not be tried because of their low solubility in cyclohexanone.

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