Bull. Chem. Soc. Jpn., 61, 4497—4499 (1988)

Studies in the Extraction of Metals with 3-Phenyl-4-acetyl-5-isoxazolone

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(Received February 22, 1988)

Synopsis. Extraction of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) from aqueous solution with 3-phenyl-4-acetyl-5-isoxazolone (HPAI) in 4-methyl-2-pentanone (MIBK) has been studied and the extraction constants have been calculated for all the systems except cadmium(II). Separation factors have been calculated for the separation of metals.

In the extraction of metals, β-diketones such as thenoyltrifluoroacetone (HTTA)[1] are extensively used. Acylpyrazolones have been proved promising reagents for the extraction of metals from acidic media.[2–8] In our previous paper,[9] we have reported the extraction of iron(II), manganese(II), cobalt(II), nickel(II), zinc(II), cadmium(II), and lead(II) with 3-phenyl-4-benzoyl-5-isoxazolone (HPBI), a new chelating ligand in which the β-diketone moiety is fused to a heterocyclic ring. In continuation of this work, 3-phenyl-4-acetyl-5-isoxazolone (HPAI) has been used to evaluate the potential of this reagent for the extraction of metals. Solid complexes of these metals with HPAI have also been isolated and studied.[10] In common with other β-diketones (like acylpyrazolones) HPAI exists in keto and enol forms (Fig. 1). It has been confirmed by the presence of an enolic peak at δ 12 relative to TMS in the ^{1}H NMR spectrum of ligand HPAI. The present paper deals with the extraction of iron(II), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) into MIBK and the effectiveness of the ligand HPAI in the separation of metals. 4-Methyl-2-pentanone was used as solvent as it is commonly employed in atomic absorption studies and the ligand was soluble to a greater extent in this solvent than other solvents like toluene or chloroform.

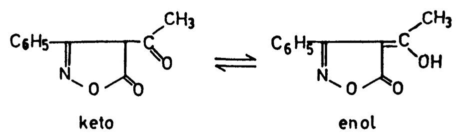

Fig. 1. The enolic and keto forms of the 3-phenyl-4-acetyl-5-isoxazolone.

Experimental

Reagents. Ethyl benzoylacetate (Fluka), acetic anhydride (Merck), sodium acetate (Merck), and hydroxylamine hydrochloride (Sarabhai) were used for the preparation of ligand. MIBK (BDH) was used as solvent for the extraction. The pH of the aqueous phase was maintained by using mixtures of potassium chloride and hydrochloric acid for pH 1—3, sodium acetate-acetic acid for pH 4—6, acetic acid-ammonia for pH 6—8 and ammonium chloride-ammonia for pH 8—10. A constant ionic strengths of 0.1 mol dm^{-3} was maintained by using potassium nitrate solution. Stock solutions were prepared by using AR grade chemicals.

Preparation of the Ligand. The ligand 3-phenyl-4-acetyl-5-isoxazolone (HPAI) was prepared by using 3-phenyl-5-isoxazolone and acetic anhydride in the presence of sodium acetate as described by Korte and Storiko.[11] Mp 140±2 °C, Calcd for $C_{11}H_9O_3N$: C, 65.02; H, 4.43; N, 6.89%. Found: C, 64.86; H, 4.48; N, 6.95%. The UV spectrum of the ligand in 95% ethanol showed two absorption maxima at 285 and 232 nm.

Extraction Procedure. Ten ml of the aqueous solution containing an aliquot of metal solution, five ml of the buffer solution and one ml of 1 mol dm^{-3} KNO_3 solution was equilibrated with ten ml of organic phase containing the required amount of the ligand in a stoppered bottle. The mixture was shaken on a mechanical shaker for one hour at 25±1 °C. After equilibration, the aqueous phase was separated from the organic layer and its pH was measured by using an expanded scale pH meter (ECIL India). The concentration of metal ion was monitored using atomic absorption spectrophotometer. A Pye-Unicam SP-191 unit with air-acetylene burner and the required hollow cathode lamps was utilized in this study. Distribution coefficient K_d (defined as the total concentration of metal in organic phase divided over the total concentration of metal in aqueous phase) was calculated.

Results and Discussion

The extraction curves of each element as a function of pH of the aqueous solution are shown in Fig. 2. Quantitative extraction of iron(II) was observed in the pH range 1.5 to 8.0. Above pH 8.0, the extraction registered a sharp drop and at pH 9.5 iron(II) showed only 90% extraction. Nickel(II) and cobalt(II) were extracted quantitatively from pH 3.0 to 9.0. Between

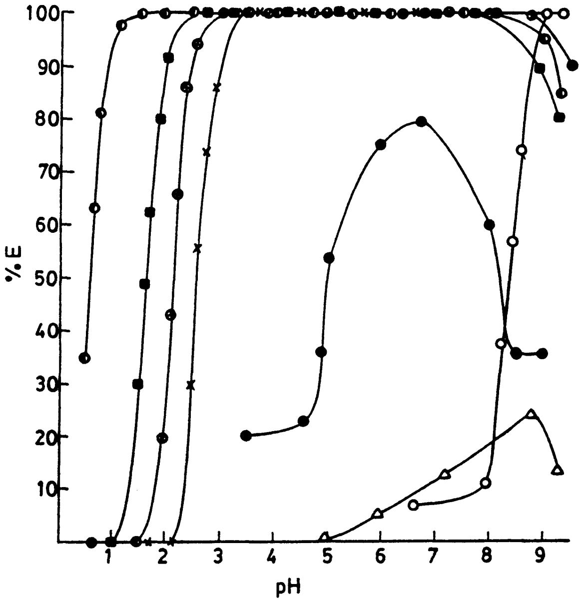

Fig. 2. Plot of %*E* vs. pH. ○=Mn(II); ◐=Fe(II); ■=Cu(II); ⊗=Ni(II); ×=Co(II); ●=Zn(II); △=Cd(II); HPAI 0.01 mol dm^{-3} in MIBK.

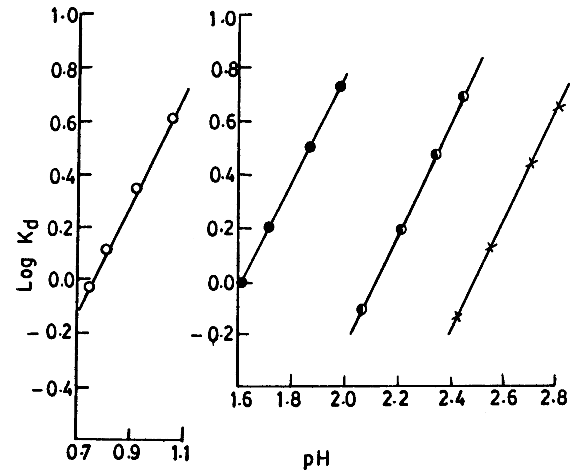

Fig. 3. Plots of $\log K_d$ vs. pH. ○=Fe(II); ●=Cu(II); ◐=Ni(II); X=Co(II); HPAI 0.01 mol dm^{-3} in MIBK.

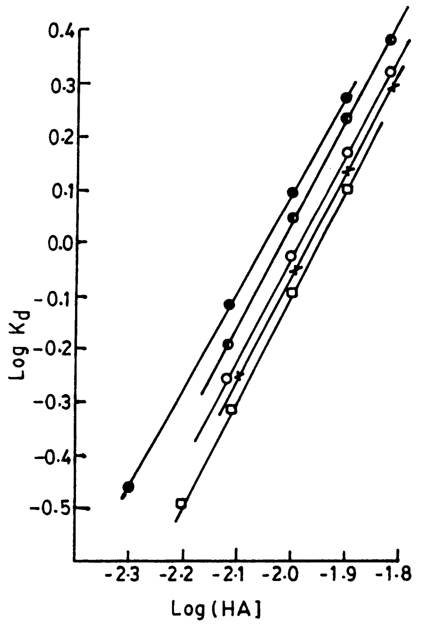

Fig. 4. Plot of $\log K_d$ vs. log[HA]. ○=Mn(II) (pH 8.4); ●=Zn(II) (pH 5.0); X=Cu(II) (pH 1.55); ◐=Fe(II) (pH 0.75); □=Ni(II) (pH 2.05).

pH 9.0 and 9.5 the % extraction dropped to 90%. The extraction of copper(II) was quantitative in the pH range 2.5 to 8.0, then the extraction decreased at higher pH values and at pH 9.0 only 80% of copper(II) was extracted. Maximum extraction of zinc(II) (80%) was observed over the pH range 6.0 to 7.0, then the extraction decreased at higher pH up to 9.0, where only 35% zinc(II) was extracted. Figure 2 shows a sharp rise in the extraction of manganese(II) from pH 8.0 and the quantitative extraction of manganese(II) into the organic phase was observed at pH 9.0. Below pH 6.0 no appreciable quantity of manganese(II) was extracted. Maximum extraction shown by cadmium(II) was only 25% at a pH of 8.8.

Table 1. Extraction Data of Some Metals Using 0.01 mol dm^{-3} HPAI in MIBK

Metal	$pH_{1/2}$(50% extraction)	$\log K_{ex}$	$pH_{1/2}$, 0.15 mol dm^{-3} HTTA in benzene[a)]
Mn(II)	8.4	−12.63	6.05
Fe(II)	0.6	+ 2.57	—
Co(II)	2.6	− 1.10	4.1
Ni(II)	2.1	− 0.51	5.0
Cu(II)	1.6	+ 0.75	1.34
Zn(II)	5.0	− 5.89	5.10
Cd(II)	Only 25% extraction	—	8.0

a) Refs. 12—15.

Table 2. Separation Factors for the Separation of Metals Using 0.01 mol dm^{-3} HPAI in MIBK

Metals to be separated	Separation factor	Metals to be separated	Separation factor
Fe(II)-Mn(II)	1.5×10^{15}	Mn(II)-Cu(II)	2.3×10^{13}
Fe(II)-Co(II)	4.6×10^{3}	Mn(II)-Zn(II)	5.4×10^{6}
Fe(II)-Ni(II)	1.2×10^{3}	Co(II)-Ni(II)	4
Fe(II)-Cu(II)	66	Co(II)-Cu(II)	70
Fe(II)-Zn(II)	2.8×10^{8}	Co(II)-Zn(II)	6.1×10^{4}
Mn(II)-Co(II)	3.3×10^{11}	Ni(II)-Cu(II)	18
Mn(II)-Ni(II)	1.3×10^{12}	Cu(II)-Zn(II)	4.3×10^{6}

In order to understand the extraction behavior in more detail, log of distribution coefficient K_d was plotted against pH and log of ligand concentration at fixed ligand concentration and pH respectively (Figs. 3 and 4). The plots were linear with a slope of ca. 2 indicating the release of two H$^+$ ions and involvement of two molecules of ligand (HPAI) during the extraction process. It can be inferred from these results that the main equilibrium involved in the extraction process is

$$M^{2+} + 2HPAI_{(org)} \rightleftharpoons M(PAI)_{2(org)} + 2H^+ \qquad (1)$$

where, PAI=anion of 3-phenyl-4-acetyl-5-isoxazolone.

The extraction constant values ($\log K_{ex}$) in Eq. 1 were calculated for manganese(II), iron(II), nickel(II), cobalt(II), copper(II), and zinc(II) systems and are given in Table 1. The $pH_{1/2}$ values (pH at which 50% of the metal ion is extracted) for the extracted metals are compared with those of the corresponding systems using thenoyltrifluoroacetone (HTTA) (Table 1). It is evident from the table that the extraction of copper(II), iron(II), cobalt(II), nickel(II), and zinc(II) occurs in the acidic medium as in HTTA. Manganese(II) is extracted from slightly acidic medium with HTTA, whereas with HPAI it is extracted from rather alkaline medium. In case of cadmium(II), quantitative extraction is accomplished from the alkaline medium with HTTA,[12)] in contrast to its partial extraction (25%) with HPAI at higher pH values.

The possibility of utilizing this reagent HPAI for the separation of metals has been investigated by calculating the separation factor S which is the ratio of the distribution coefficients of the elements to be separated.[16)] A separation in which not more than 1% of one element is coextracted will be obtained if $S \geqslant 10^4$ and the product of distribution coefficients is unity. The separation factors calculated are given in Table 2. It can be concluded from the table that the reagent

HPAI would be useful for the separation of manganese(II), and zinc(II) from the other metals reported here. In conclusion, like HTTA and acylpyrazolones, these acylisoxazolones represent a new group of versatile chelating agents with great potential in solvent extraction.

The authors wish to thank CSIR (India) for financial support.

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