Effect of Several Auxiliary Ligands on the Extraction of Manganese(II) With 4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone

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The effect of 2-methyl pyridine N-oxide, 4-methyl pyridine N-oxide, pyridine N-oxide, 8-aminoquinoline, dibenzyl sulfoxide on the extraction of manganese(II) by 4-benzoyl-3-methyl-1-phe-nyl-5-pyrazolone (BMPP) in benzene from an aqueous buffered solution was studied. Synergistic enhancement was observed in all systems. Equilibrium extraction constants and adduct formation constants were calculated. The results showed that synergistic extraction is due to the formation of adducts such as $Mn(BMPP)_2B$ where B represents the auxiliary ligand.

INTRODUCTION

While the extraction of some metals with BMPP has been reported (Thakur and Rao, Zolotov), no detailed report on the extraction of manganese(II) with BMPP using auxiliary ligands has appeared so far. In a general survey of the extraction of manganese(II) with different chelating agents a pH half (pH at which half of the total metal ion is extracted with 0.01 M BMPP) value for extracting manganese(II) with BMPP in benzene has been mentioned. In the present paper results of the study of the extraction of manganese(II) with 4-benzoyl-3 methyl-1 phenyl-5-pyrazolone (BMPP) using different auxiliary ligands, such as 2-methyl pyridine N-oxide, pyridine N-oxide, 4-methyl pyridine N-oxide, dibenzyl sulfoxide and 8-aminoquinoline are reported.

EXPERIMENTAL

Pyridine N-oxide (Fluka), 2-methyl pyridine N-oxide (Fluka), 4-methyl pyridine N-oxide (Fluka), 8-aminoquinoline (Eastman Organic Chemicals), Dibenzyl sulfoxide (Fluka) were used. The ligand (BMPP) was prepared according to the method of Jensen[1] by using 1-phenyl-3-methyl-5-pyrazolone, *i. e.* MPP (B.D.H) and benzoyl chloride (Fluka). Acetate buffers were used for pH variation studies. A constant ionic strength of 0.1 M was maintained by using potassium nitrate solution. Ten ml of the aqueous layer containing two ml of fifty ppm manganese sulphate solution, five ml of buffer solution and one ml of one molar potassium nitrate solution was equilibriated with ten ml of benzene containing BMPP and the auxiliary ligand at required concentrations for thirty minutes in a thermostatic shaker at $30 \pm 1 \,^\circ C$. After equilibriation the two layers were allowed to settle. Preliminary experiments indicated that equilibrium was attained after shaking for ten minutes but a shaking time of thirty minutes was employed as a precautionary measure. The concentration of manganese in the aqueous layer was measured by an SP 191 atomic absorption spectrophotometer. The pH of the aqueous layer was measured

by an expanded scale pH meter (ECIL India). Partition coefficient K_d is defined as the total concentration of metal in the organic phase divided over the total concentration of the metal in the aqueous phase.

RESULTS AND DISCUSSION

Extraction behaviour of manganese(II) with 4-benzoyl-3-methyl-1-phenyl--5-pyrazolone (BMPP) was studied by determining K_d values for different pH values keeping the ligand concentration constant at 0.01 M BMPP. The plot of log K_d vs. pH gave a straight line with a slope of ~ 2. A similar study of variation of K_d with ligand concentration at constant pH (6.1) indicates the number of ligand molecules involved in the extracted species. Since the slope of the plot of log K_d vs. pH at constant ligand concentration is ~ 2 and the slope of log K_d vs log [HT] at constant pH is also ~ 2, the extraction equilibrium may be represented as

$$Mn^{2+}_{aq} + 2HT_{org} \rightleftharpoons MnT_{2\ org} + 2H^+_{aq} \tag{1}$$
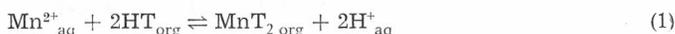
where HT represents the ligand BMPP. Equilibrium constant can be calculated, as usual from the equation

$$K_{ex} = [MnT_2]_{org} [H^+]^2_{aq}/[Mn^{2+}]_{aq} [HT]^2_{org} \tag{2}$$

However, manganese(II) present in the aqueous phase may exist in the form of complexes with acetate, namely $[Mn(Ac)^+]$. Therefore, the total concentration of manganese in the aqueous phase is given by

$$[Mn^{II}]_{aq} = [Mn(Ac)^+]_{aq} + [Mn^{2+}]_{aq} \tag{3}$$

The distribution ratio is given by

$$K_d = [Mn(T_2)]_{org}/([Mn^{2+}]_{aq} + [Mn(Ac)^+]_{aq})$$

$$K_d = \frac{[MnT_2]_{org}}{[Mn^{2+}]_{aq} (1 + \beta_1 [Ac^-])} \tag{4}$$

From the stability constants it is calculated that total Mn(II) in the aqueous phase is made up of seventy percent manganous ion and thirty percent of $[Mn(Ac)^+]$. β_1 the change in the relative concentration of $[Mn(Ac)^+]$ to manganous ion is small when the pH is varied. The value of log $[Mn(Ac)^+]/[Mn^{2+}]$ was calculated as a function of the observed pH by using the stability constant for $[Mn(Ac)^+]$ (Table I.)[12]

TABLE I

Relative Concentrations of Acetate Complexes

pH	4.49	4.53	4.66	4.87	5.21
log $\frac{[Mn(Ac)^+]}{[Mn^{2+}]}$	0.17	0.18	0.17	0.16	0.13

Hence, from equation (4) the relationship between K_d and K_d' is given by

$$K_d = \frac{K_d'}{1 + \beta_1 [Ac^-]} \quad \text{where } K_d' = \frac{[MnT_2]_{org}}{[Mn^{2+}]_{aq}} \tag{5}$$

From equations (2) and (4) we get

$$\log K_{ex} = \log K_d - 2 \log [HT]_{org} - 2pH + \log (1 + \beta_1 [Ac^-]) \tag{6}$$

The value of K_{ex} was calculated from (6) using the experimental values of $K_{d'}$ [HT] and pH. The effect of adding auxiliary ligands on the manganese(II) extraction with BMPP was similarly investigated by determining the K_d value as a function of the concentration of auxiliary ligand (B) at constant pH and BMPP concentrations. From the plot of $\log K_d$ *vs.* $\log [B]_{org}$ the number of molecules of B incorporated in the extracted species was determined. Extraction of manganese(II) in the presence of auxiliary ligand B may be represented as

$$Mn_{aq}^{2+} + 2HT_{org} + mB_{org} \rightleftharpoons MnT_2B_{m\,org} + 2H_{aq}^+ \tag{7}$$

with the equilibrium constant K_{ex} given by

$$K_{ex}' = [MnT_2 B_m]_{org} [H^+]_{aq}^2 / [Mn^{2+}]_{aq}$$

$$[HT]_{org}^2 [B]_{org}^m \tag{8}$$

From equations (5) and (8)

$$\log K_{ex}' = \log K_d - 2 \log [HT]_{org} - 2\,pH - m \log [B]_{org} + \log (1 + \beta_1 [Ac^-])$$

where

$$K_d = [MnT_2B_m]_{org}/[Mn^{2+}]_{aq} (1 + \beta_1 [Ac^-]) \tag{9}$$

The adduct formation constant (K_s) for the equilibrium

$$MnT_{2\,org} + mB_{org} \rightleftharpoons MnT_2B_{m\,org}$$

is given by

$$\log K_s = \log K_{ex}' - \log K_{ex} \tag{10}$$

One of the possible side reactions caused by adding a pyridine base is the protonation of the base in the aqueous phase where $[Mn]_{total} \ll [B]_{total}$, the following equation is obtained by mass balance

$$[B]_{total} \simeq [B]_{org} + [B]_{aq} + [BH^+]_{aq} \tag{11}$$

into which the distribution coefficient p_B

$$p_B = \frac{[B]_{org}}{[B]_{aq}}$$

and dissociation constant K_{BH} for the protonated form of the base are introduced and the resulting situation is given by

$$[B]_{total} = [B]_{org} \left(1 + \frac{1}{P_B} + \frac{[H]^+}{P_B K_{BH}} \right) = [B]_{org}\, \alpha\, B(H) \tag{12}$$

where $\alpha\, B(H)$ is a variable defined only by the concentration of the hydrogen ion and the kind of the base $[B]_{org}$ for pyridine N-oxides has been calculated using equation (12). The values of p_B and pK_{BH} for the pyridine N-oxides are listed[2] in Table II.

TABLE II

*Partition Coefficients (P_B) and Dissociation Constants pK_{BH} Values of the Hetero Cyclic Base N-Oxides**

Auxiliary Ligand	P_B	pK_{BH}
Pyridine N-oxide	0.0026	0.602
2-methyl pyridine N-oxide	0.0143	1.034
4-methyl pyridine N-oxide	0.0034	1.086

* Estimated uncertainty in numerical values is ±0.1 unit.

Adducts formation constants (K_s) and the values of K'_{ex} are listed in Table III.

TABLE III

Extraction Constants and Formation Constants of the Adducts Formed Between the Complex Mn[BMPP]₂ and Various Auxiliary Ligands

Auxiliary ligand	$\log K_{ex}'$	$\log K_s$*
Pyridine N-oxide	—3.89	4.21
2-mehyl pyridine N-oxide	—4.38	3.72
4-methyl pyridine N-oxide	—3.62	4.48
dibenzyl sulfoxide	—5.50	2.60
8-amino quinoline	—5.63	2.41
nil	—8.10	

* Estimated uncertainty in numerical values is ±0.10 unit.

Figure 1 shows the plots of log K_d vs. log $[B]_{org}$ for 2-methyl pyridine N-oxide (pH = 5.60), 4-methyl pyridine N-oxide (pH = 5.70) and pyridine N-oxide (ph = 5.60) at constant ligand concentration (BMPP = 0.01 M). One mole of 2-methyl pyridine N-oxide, 4-methyl pyridine N-oxide or pyridine N-oxide is present in the extracted adduct as indicated by the slope value of ~ 1. Figure 2 shows the plots of log K_d vs. log $[B]_{org}$ for dibenzyl sulfoxide (pH = 5.0) and 8-amino quinoline (pH = 5.50) at constant ligand concentration (BMPP = 0.01 M). One mole of dibenzyl sulfoxide or 8-amino quinoline is present in the extracted adduct as indicated by the slope value of ~ 1. Plots of log K_d vs. log [HT] at constant $[B]_{org}$ in all cases gave a slope of ~ 2 indicating the presence of two moles of BMPP in all the adducts.

The main factors affecting the synergistic extraction of a metal chelate are considered to be the stability and the organophilic property of the resulting adduct. A competing reaction between the formation of the adduct in question and that of BH⁺ also affects the extent of synergism. One of the major factors affecting the stability of a metal complex is the basicity of the ligand, which is essentially the same as the affinity of the ligand towards protion. The formation constants of the adducts decreased in the order 4-methyl pyridine N-oxide > pyridine N-oxide > 2-methyl pyridine N-oxide > dibenzyl sulfoxide > 8-amino quinoline. Akaiwa and Kawamoto[5] showed that stabilities of
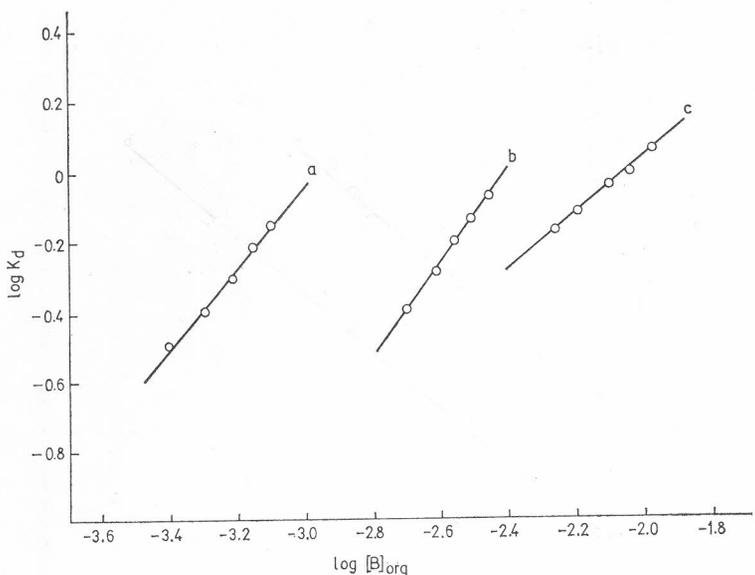
Figure 1. Plot of $\log K_d$ *vs.* $\log [B]_{org}$ for the extraction of Mn(II) with 10 mM BMPP in benzene. $[B]_{org}$ represents (a) 4-methyl pyridine *N*-oxide (pH = 5.70) (b) pyridine *N*-oxide (pH = 5.60) (c) 2-methyl pyridine *N*-oxide (pH = 5.60).

the adducts of Mn(II) thenoyltrifluroacetonate with pyridine bases follow this order. The stability constants of metal complexes having structurally similar ligands often show a roughly linear dependence on the basic strength of the ligands.[6] Major deviations from the expected trend are attributed to the steric effects.[13] Other deviations from normal rules of the stability constants may probably be caused by the presence of π bonds.[14] These results can be interpreted by assuming metal to ligand back bonding, which can be achieved by back donation of electrons from the half filled metal d-orbitals to the empty π^* antibonding orbitals of the N—O bonds in the ligand.[10] The energy level of this π^* orbital increases when a methyl group is introduced in the fourth position of the ring, thereby decreasing the energy match between the half filled orbitals of the metals and the π^* orbital and thus decreasing the contribution of back bonding. Lower values of $\log K_s$ for 2-methyl pyridine *N*-oxide and 8-aminoquinoline may be attributable to the steric effects of these bases. In fact, 2-methyl-pyridine adduct of bis (acetyl acetonato) manganese(II) has been reported to be unstable compared with its pyridine adduct.[16]
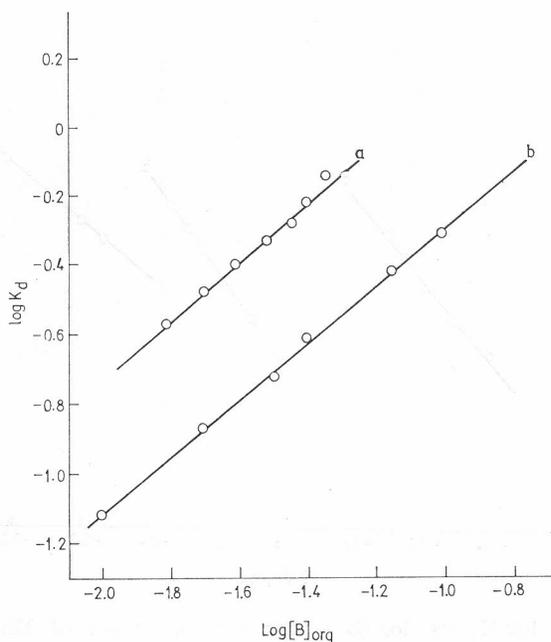
FIG. 2.

Figure 2. Plot of $\log K_d$ vs. $\log [B]_{org}$ for the extraction of Mn(II) with 10 mM BMPP in benzene. $[B]_{org}$ represents (a) dibenzylsulfoxide (pH = 5.0) (b) 8-amino-quinoline (pH = 5.50).

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SAŽETAK

Utjecaj nekoliko pomoćnih liganda na ekstrakciju mangana(II) s 4-benzoil-3-metoksi-1-fenil-4-pirazolonom

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Proučavan je utjecaj 2-metilpiridin-*N*-oksida, 4-metilpiridin-*N*-oksida, piridin-*N*-oksida, 8-aminokinolina i dibenzilsulfoksida na ekstrakciju mangana(II) 4-benzoil-3-metil-1-fenil-5-pirazolonom (BMPP) u benzenu iz vodenih puferiranih otopina.

Izračunane su konstante ekstrakcije i konstante nastajanja adukata. Sinergistički efekt uočen je u svima proučavanim sistemima, a postignut je nastajanjem adukata Mn(BMPP)$_2$B, u kojima je B pomoćni ligand.