Effect of several auxiliary ligands on the extraction of cadmium (II) with 2-thenoyltrifluoroacetone

G N RAO* and ROMA LAHIRI

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

Abstract. The effect of tributylphosphate (TBP), trioctylphosphineoxide (TOPO), pyridine (PY) and some derivative bases of pyridine as auxiliary ligands on the extraction of cadmium (II) by 2-thenoyltrifluoroacetone (TTA) from an aqueous-buffered solution into benzene was studied. A synergistic enhancement was observed in all the systems. The equilibrium constant and adduct formation constant have been calculated. The results showed that the synergistic extraction was attributable to the formation of the base adducts Cd $(TTA)_2$ B and Cd$(TTA)_2$B$_2$. The main factor affecting the stability of the adduct was considered to be the base strength of the synergist.

Keywords. Synergistic extraction; thenoyltrifluoroacetone; extraction constant; adduct formation constant; cadmium.

1. Introduction

While extraction of several metals with thenoyltrifluoroacetone (TTA) has been investigated in detail (Marcus and Kertes 1969) no detailed report on cadmium (II) extraction with TTA has been published. In a general survey of the extraction of cadmium with different chelating agents a pH half (pH at which half of the total metal ion is extracted with 0·1 M TTA) value for extracting cadmium (II) with TTA into chloroform has been mentioned (Schweitzer and Randolph 1962). The current concern over increased cadmium level in the environment and the evidence that it has an adverse effect on immunologic phenomenon make this an object of immediate study. In the present paper,therefore, an attempt has been made to study cadmium (II) extraction with thenoyltrifluoroacetone and compare the coordinating abilities of tributylphosphate (TBP), trioctylphosphine oxide (TOPO), pyridine (PY), 3-methylpyridine (3MP), 4-methylpyridine (4MP), pyridineoxide (PO), 2-methylpyridineoxide (2MPO), 4-methylpyridine oxide (4MPO) towards *bis* (2-thenoyltrifluoroacetonato) cadmium (II).

2. Experimental

TTA, PO, 2-MPO, 4-MPO (Fluka), PY, 3-MP, 4-MP (BDH), TBP (IDPL), TOPO (Eastman Organic Chemicals) were used. Acetate buffers were used for pH variation studies. A constant ionic strength of 0·1 M was maintained by using potassium nitrate solution. Stock solutions were prepared by weighing AR grade chemicals. Analytical reagent grade benzene was used without further purification.

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* To whom all correspondence should be addressed.

Ten ml of the aqueous layer containing 2 ml of 100 ppm cadmium acetate solution, 5 ml of buffer solution and 1 ml of 1 M potassium nitrate solution was equilibrated with 10 ml of benzene containing TTA and the auxiliary ligand at required concentrations for 2 hr in a thermostatic shaker at $30 \pm 1°C$. After equilibration the two layers were allowed to settle. Preliminary experiments indicated that equilibrium was attained after shaking for 1 hr but a shaking time of 2 hr was employed as a precautionary measure. The concentration of cadmium 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).

3. Results and discussion

Extraction behaviour of cadmium (II) with TTA can be understood by determining K_d values for different pH values keeping the ligand concentration constant at 0·01 M. Plot of $\log K_d$ vs pH gave a straight line with a slope of $\simeq 2$. A similar study of variation of K_d with ligand concentration at constant pH indicated 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 $\simeq 2$ and the slope of $\log K_d$ vs $\log [HA]$ at constant pH is also $\simeq 2$, the extraction equilibrium may be represented as

$$\text{Cd}_{aq}^{2+} + 2HA_{org} \rightleftharpoons \text{Cd } A_{2org} + 2\text{H}_{aq}^+, \tag{1}$$

where HA represents the ligand (TTA). Equilibrium constant (also called extraction constant) for this equation is given by

$$K_{ex} = [\text{Cd } A_2]_{org} [\text{H}^+]_{aq}^2 / [\text{Cd}^{2+}]_{aq} [HA]_{org}^2. \tag{2}$$

If it is assumed that $\text{Cd}A_2$ concentration is negligible in the aqueous phase, the distribution ratio is given by

$$K_d = [\text{Cd } A_2]_{org} / [\text{Cd}^{2+}]_{aq}. \tag{3}$$

From (2) and (3) we have

$$\log K_{ex} = \log K_d - 2 \log [HA]_{org} - 2 \text{ pH}. \tag{4}$$

The value of K_{ex} is calculated from (4), using the experimental values of K_d, $[HA]$ and pH.

The effect of adding auxiliary ligands on cadmium (II) extraction with TTA has also been similarly investigated by determining K_d value as a function of concentration of auxiliary ligand (B) at constant pH and TTA concentration. From the plot of $\log K_d$ vs $\log [B]_{org}$ the number of molecules of B incorporated in the extracted species has been determined.

Extraction of cadmium (II) in the presence of auxiliary ligand B may be represented as

$$\text{Cd}_{aq}^{2+} + 2 HA_{org} + mB_{org} \rightleftharpoons \text{Cd } A_2 B_{m \, org} + 2\text{H}_{aq}^+ \tag{5}$$

with equilibrium constant K'_{ex} given by

$$K'_{ex} = [\text{Cd } A_2 B_m]_{org} [\text{H}^+]_{aq}^2 / [\text{Cd}^{2+}]_{aq} [HA]_{org}^2 [B]_{org}^m \tag{6}$$

and

$$\log K'_{ex} = \log K_d - 2 \log [HA]_{org} - 2 \text{pH} - m \log [B]_{org} \tag{7}$$

K_s, *i.e.* the adduct formation constant for the equilibrium Cd $A_{2\text{org}} + mB_{\text{org}} =$ Cd $A_2 B_{m\,\text{org}}$ is given by

$$\log K_s = \log K'_{\text{ex}} - \log K_{\text{ex}} \qquad (8)$$

One of the possible side reactions by adding pyridine base is the protonation of the base in the aqueous phase. When $[\text{Cd}]_{\text{total}} \ll [B]_{\text{total}}$, the following equation is obtained by mass balance,

$$[B]_{\text{total}} \simeq [B]_{\text{org}} + [B] + [\text{BH}^+], \qquad (9)$$

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

$$[B]_{\text{total}} \simeq [B]_{\text{org}} (1 + P_B^{-1} + P_B^{-1} K_{\text{BH}^{-1}} [\text{H}^+]) = [B]_{\text{org}} \, \alpha B(\text{H}), \qquad (10)$$

where $\alpha B(\text{H})$ is a variable defined only by the concentration of hydrogen ion and the kind of base; $[B]_{\text{org}}$ for pyridine and pyridine N-oxides has been calculated by using (10).

Adduct stability constants (K_s) and the values of K'_{ex} are listed in table 2.

The values of P_B and PK_{BH} for the pyridines and pyridine N-oxides have been listed in table 1 (Al-Niami *et al* 1973).

Figure 1 shows the plots of $\log K_d$ against $\log [B]_{\text{org}}$ for PY, 3-MP and 4-MP at pH 6·2, TBP (pH = 5·8) and TOPO (pH = 5·3) at constant ligand concentration (0·01 M of TTA). Two moles of PY, 3-MP, 4-MP, TBP or TOPO are present in the extracted adduct as indicated by a slope value of $\simeq 2$.

Table 1. Partition coefficients (P_B) and dissociation constant (pk_{BH}) values of the heterocyclic bases and heterocyclic N-oxides*

	PY	3MP	4MP	PO	2MPO	4MPO
P_B	3·52	11·86	14·52	0·0026	0·0143	0·0034
pk_{BH}	5·44	5·88	6·24	0·602	1·034	1·086

* Al-Niami *et al* (1973).

Table 2. Extraction constants and formation constants of the adducts formed between the complex Cd $(\text{TTA})_2$ and various auxiliary ligands.

Auxiliary ligand	$\log K'_{\text{ex}}{}^*$	$\log K_s{}^*$
PY	−3·26	7·74
3-MP	−2·92	8·08
4-MP	−2·70	8·30
Pyridine-N-oxide	−6·92	4·08
2-methylpyridine N-oxide	−6·27	4·73
4-methylpyridine N-oxide	−5·58	5·42
TBP	−5·12	5·88
TOPO	−1·48	9·52
Nil	−11·0	—

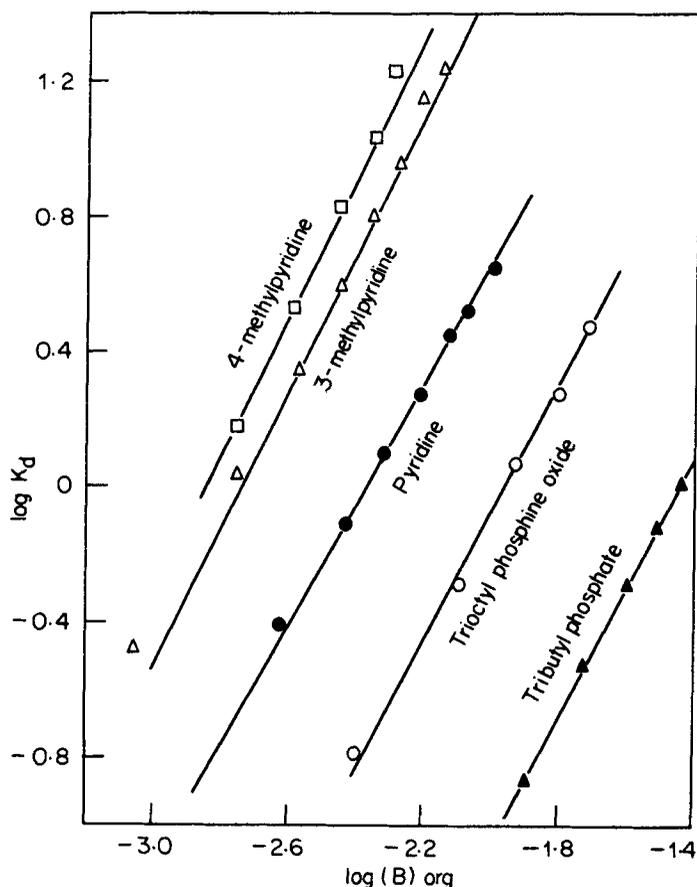* Estimated uncertainty in the numerical values is ±0·1 unit.

Figure 1. Plot of log K_d vs log $[B]_{org}$. The vertical axis has been shifted to the positive side by 0·2 and 0·6 log units in the case of pyridine and TOPO respectively. The axis has been shifted to the negative side by 0·2 log units in the case of tributyl phosphate.

Figure 2 shows the plots of log K_d vs log $[B]_{org}$ at constant pH (7·4, 7·3 and 6·9 respectively for PO, 2-MPO and 4-MPO) at constant ligand concentration (0·005 M TTA for PO and 2-MPO and 0·01 M TTA for 4-MPO).

One mole of PO, 2-MPO or 4-MPO is present in the extracted adduct as indicated by the slope value of $\simeq 1$.

A comparison of the values of K'_{ex} with that of K_{ex} indicates synergism in all these systems. The main factors affecting the synergistic extraction of a metal chelate are stability and organophilic property of the resulting adduct.

In pyridine bases a competing reaction between the formation of the adduct in question and that of BH^+ also affects the extent of synergism. The present results clearly indicate that the variation of the adduct formation constant is in accordance with the order of basicities of the auxiliary ligands. The formation constant of the adduct formed by $Cd(TTA)_2$ with an N-base is greater than that formed with the corresponding N-oxide. Synergistic extraction studies of $Cu(TTA)_2$ with N-bases and N-oxides have shown similar trends (Al-Niami and Rasoul 1974). On the other hand,
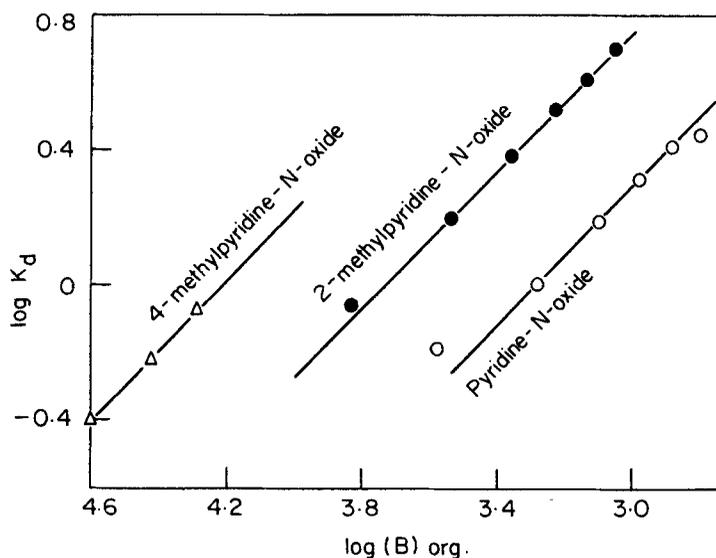
Figure. 2. Plot of log K_d *vs* log$[B]_{org}$.

formation constants of the adduct formed between Co(PMBP)$_2$ and N-oxides were greater than those formed with the N-base (Al-Niami *et al* 1973). These results can be interpreted by assuming metal to ligand back-bonding, which can be achieved by back donation of electrons from the filled metal *d*-orbitals to the empty π^* antibonding orbitals of the N–O bonds in the ligand. The energy level of this π^* orbital increases when a methyl group is introduced in the 4th position of the ring thereby decreasing the energy match between the filled orbitals of the metals and the π^* orbital and hence decreasing the contribution of back bonding.

There are not many reports where the effect of phosphorous esters is compared with those of heterocyclic bases or heterocyclic base N-oxides under identical conditions. This work indicates that TOPO exhibits the maximum synergistic effect among the ligands studied. Adduct formation constant value for TOPO is greater than that with TBP with the Lewis acid Cd(TTA)$_2$ as expected. It is interesting to note that TBP is more effective than all the N-oxides but less effective than all the N-bases studied. Formation constants of the adducts decreased in the order.

Trioctylphosphineoxide > 4-methylpyridine > 3-methylpyridine > pyridine > tri-butylphosphate > 4-methylpyridine oxide > 2-methylpyridine oxide > pyridine oxide.

Solvent extraction techniques are normally used for preconcentration before atomic absorption spectrophotometric determination of metals. The present results would be of interest in the preconcentration of traces of cadmium in pollution studies.

Acknowledgement

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