

Synergism in the extraction of cadmium

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ABSTRACT

Synergism in the extraction of cadmium by mixtures of BFA and TOPO or TBP has been investigated. Extraction of cadmium was found negligible in the presence of BFA, TOPO or TBP alone while the addition of alkylphosphorus ester to the β -diketone resulted in considerable enhancement of the extraction. The nature of the adduct was found to be of the type $[\text{Cd}(\text{BFA})_2(\text{TOPO})_2]$ and the equilibrium constant for the reaction was also evaluated. Similar results were observed in the case of TBP, while DPSO did not enhance the extraction, indicating the donor strengths of the synergists to be in the order $\text{TOPO} > \text{TBP} > \text{DPSO}$. The coordination of alkylphosphate to the metal ion was confirmed by infrared spectra of the complexes in benzene.

1. INTRODUCTION

SYNERGISM in the extraction of many metals has evinced considerable interest in recent years.¹⁻⁶ It was earlier considered that synergism was confined only to actinides although later work showed this phenomenon to be rather general. Preliminary experiments indicated that cadmium was not extracted by benzoyltrifluoroacetone (BFA) or HTTA probably due to the coordination of water molecules in the chelate rendering it hydrophilic. Substitution of these by donors like alkylphosphates is likely to improve the extraction. The extraction of cadmium by HBFA/HTTA and trioctylphosphineoxide (TOPO) or tributylphosphate (TBP) has been studied with this in view and the results are presented in this paper.

2. EXPERIMENTAL

Cadmium used in the form of Cd^{115m} (Isotope Division, BARC) was assayed by β -counting using a liquid GM detector (M/s. Electronics Corporation of India Ltd., Hyderabad). TOPO (K and K Labs.) was purified by

the method of Mason *et al.*⁷ TBP (BDH, LR) was purified by washing with sodium carbonate to remove the acidic impurities, then with water and was dried. Benzene (BDH, AnalaR) was used as the diluent. BFA (K and K Labs.), HTTA (Koch-Light Labs.) and DPSO (K and K Labs.) were used without further purification.

Extraction experiments were carried out by equilibrating 10 ml of the aqueous phase containing the metal, sodium perchlorate to keep the ionic strength at 1.0 and acetic acid-sodium acetate buffer (0.02 M) to maintain the pH with an equal volume of the organic phase containing BFA and TOPO or TBP for about eight hours in a mechanical shaker at $30 \pm 1^\circ\text{C}$. After separation of the two phases, cadmium in the organic phase was stripped with an acid solution when the metal was completely transferred to the aqueous phase and was assayed with the liquid GM detector. Cadmium in the aqueous phase was assayed directly. The pH of the aqueous phase was measured using a Beckman Expandomatic SS-2 pH meter.

Infrared measurements were made using a Perkin-Elmer infrared spectrophotometer using CaF_2 cells of 0.1 mm thickness. Benzene was used as the reference.

3. RESULTS AND DISCUSSION

CADMIUM-BFA-TOPO SYSTEM

Preliminary studies indicated the extraction of cadmium to be negligible by TOPO or BFA alone but was however found to be considerable in the presence of the mixture. Hence experiments were carried out at different pH (varied by the addition of sodium hydroxide) and concentrations of BFA and TOPO. The plot of $\log D$ vs. pH at two concentrations of BFA and TOPO yielded straight lines of slope two indicating that two hydrogen ions were liberated in the complexation reaction. As it was difficult to maintain the pH constant by the variation of alkali, sodium acetate-acetic acid buffer (total molarity = 0.02 M) was used in later experiments. Studies were also made at 0.025 M each of BFA and TOPO at a constant acetate ion concentration of 0.02 M. The slope of two suggests that acetate ions do not affect the stoichiometry of the complexes extracted.

Experiments were also carried out at varying concentrations of BFA or TOPO, keeping the concentration of the other extractant constant, at a pH of 4.17 ± 0.02 maintained by the use of acetate buffer. Experiments were also carried out at varying acetate ion concentrations keeping the

pH constant. The results indicated the absence of cadmium adducts with acetate. The results are given in table 1. The slope of two for both the plots of $\log D$ vs. $\log [\text{BFA}]_0$ or $\log [\text{TOPO}]_0$ indicated the extraction of an adduct containing two BFA and TOPO molecules each per complex. The extraction reaction can therefore be written as

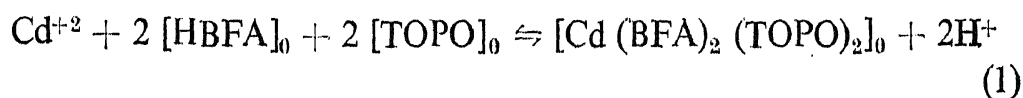


Table 1. Extraction of cadmium with mixtures of BFA and TOPO.

BFA = 0.025 M; HOAc + NaOAc = 0.02 M

pH	[TOPO] $\times 10^2$ M	$\log D$	$-\log K$
4.20	2.50	0.82	1.16
4.30	2.50	1.13	1.06
4.42	2.50	1.24	1.18
4.58	2.50	1.78	0.97
4.82	2.50	2.20	1.00
4.15	0.75	-0.20	1.05
4.11	0.10	-1.91	0.93
4.14	0.20	-1.32	0.99
4.13	0.30	-1.02	1.03
4.16	0.50	-0.57	1.08
4.15	0.20	-1.28	0.95
4.16	0.30	-0.93	0.99
4.16	0.50	-0.55	1.05
4.16	0.75	-0.20	1.06
4.21	1.00	0.05	1.14
4.20	1.50	0.46	1.09
4.24	2.00	0.66	1.22
4.24	2.50	0.91	1.16
4.15	1.00	0.05	1.09
4.18	1.50	0.46	1.04
4.18	2.00	0.62	1.13
4.20	2.50	0.79	1.19

and the equilibrium constant, K , for the extraction reaction given by

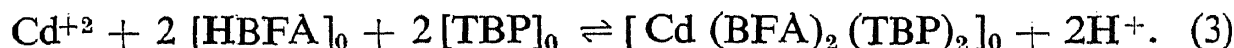
$$K = \frac{[\text{Cd}(\text{BFA})_2(\text{TOPO})_2]_0 [\text{H}]^2}{[\text{Cd}] [\text{HBFA}]_0^2 [\text{TOPO}]_0^2} \quad (2)$$

was calculated as $10^{-1.05}$ (table 1).

CADMIUM-BFA-TBP SYSTEM

TBP represents another related class of compounds similar to TOPO and the extraction of cadmium by a mixture of BFA and TBP was carried out to investigate the effect of the strength of the $\text{P}=\text{O}$ group on synergism.

The results of the extraction experiments studied as a function of pH and concentrations of BFA and TBP (vol. per cent) are presented in table 2. The straight lines of slope two for the plots of $\log D$ vs $\log [\text{BFA}]_0$ or $\log [\text{TBP}]_0$ indicate that the extracted complex contains two molecules each of BFA and TBP. Hence the extraction reaction can be written as



The enhancement of extraction in the case of Cd-BFA-TBP system is much less compared to that observed for the Cd-BFA-TOPO system which is indicative of a lesser donor strength of the $\text{P}=\text{O}$ bond in TBP.

Table 2. Extraction of cadmium with mixtures of BFA and TBP.

Acetic acid + Sodium acetate = 0.02 M

pH	[BFA] $\times 10^2$ M	TBP %	$\log D$	pH	[BFA] $\times 10^2$ M	TBP %	$\log D$
4.28	2.5	2.5	-1.48	4.68	2.5	2.5	-0.70
4.32	2.5	2.5	-1.41	4.78	2.5	2.5	-0.58
4.42	2.5	2.5	-1.37	4.97	2.5	2.5	-0.23
4.45	2.5	2.5	-1.24	5.04	2.5	2.5	-0.03
4.51	2.5	2.5	-1.10	5.13	2.5	2.5	0.19
4.58	2.5	2.5	-0.92	5.31	2.5	2.5	0.52
4.62	2.5	2.5	-0.84	5.67	2.5	2.5	1.21
5.17	2.5	0.1	-2.02	5.20	2.5	2.0	0.12
5.20	2.5	0.2	-1.61	5.12	2.5	5.0	0.76
5.14	2.5	0.3	-1.39	5.14	2.5	7.5	1.06
5.18	2.5	0.4	-1.14	4.83	2.5	10.0	0.64
5.15	2.5	0.5	-1.00	4.89	2.5	15.0	0.97
5.17	2.5	0.8	-0.71	4.92	2.5	20.0	1.21
5.12	0.1	2.5	-2.27	5.12	0.5	2.5	-1.18
5.10	0.2	2.5	-1.93	5.12	1.0	2.5	-0.57
5.10	0.4	2.5	-1.37	5.14	2.0	2.5	0.06

CADMIUM-HBFA-DIPHENYLSULFOXIDE SYSTEM

Diphenylsulfoxide (DPSO) was also tried as a donor ligand to compare the donor strength of $S = O$ group with the $P = O$ group of alkylphosphates from a study of the extraction of cadmium by a mixture of HBFA and DPSO. DPSO does not enhance the extraction under various conditions indicating the weaker donor strength of DPSO. The donor strength of the different ligands can therefore be written as $TOPO > TBP > DPSO$. Extraction of cadmium by HTTA in the presence of DPSO indicated a similar behaviour.

INFRARED SPECTRA OF ADDUCTS

Infrared studies were made on cadmium adducts of HTTA-TOPO, BFA-TOPO as well as HTTA-TBP obtained by equilibrating the mixtures in the ratio of 1:1 under the experimental conditions. The separated organic phase was again equilibrated with the aqueous phase to saturate the organic phase with the metal ion. Benzene was removed by distillation *in vacuo* and the residue (a liquid in the case of Cd-HTTA-TOPO) was freed from water by vacuum. The residue was then dissolved in benzene. The benzene extract was directly used in the case of Cd-HTTA-TBP system.

Infrared spectra in the region of $2000-1000\text{ cm}^{-1}$ were recorded and the characteristic absorption bands are given in table 3. The broad peaks due to the ketone and the enol form of HTTA or HBFA change to sharp absorption peaks of $C = O-M$ and $C-O-M$ suggesting the coordination of these to the metal ion. Similarly, the $P = O$ absorption peak of TOPO at 1170 cm^{-1} changes to 1135 cm^{-1} indicating the coordination of $P = O$ group to the metal. The $P = O-M$ bond for TOPO has been observed in this region by Ferraro *et al.*⁸ The spectra of these adducts with HBFA and HTTA are similar and compare well with those of other adducts indicating a similar type of interaction of the groups. In the case of TBP system, the $P = O$ band changes from the doublet at 1282 and 1265 cm^{-1} to a sharp peak at 1200 cm^{-1} characteristic of the $P-O-M$ group indicating the coordination of the $P = O$ group. Metal β -diketone spectra show absorption due to $C-O-M$ and $C=O-M$ groups. The enolic peak due to $C-O-M$ at 1300 cm^{-1} becomes very sharp in the case of spectra of cadmium complexes with BFA and HTTA while it is small and broad in the case of spectra of, say, HTTA alone. The peak at 1600 cm^{-1} for $C=O-M$ also becomes well defined. Infrared studies confirm the coordination of the alkylphosphorus esters to the metal- β -diketone chelates in agreement with earlier results by solvent extraction.

Table 3. Characteristic absorption bands.

System	Frequency (cm ⁻¹) for			
	P=O—M	C=O—M	C—O—M	C=C
HTTA	..	1600 broad	1280 broad } enolic }	1535
TBP	1282 } 1265 }			
TOPO	1170			
Cd-TTA-TBP	1200	1605	1280	1535
Cd-TTA-TOPO	1135	1610- } 1620 }	1295	1535
Cd-BFA-TOPO	1130	1630 } 1580 } doublet	1285	1530

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