Synergistic extraction of some divalent metal cations with 3-phenyl-4-benzoylisoxazol-5-one and P=O donor ligands in chloroform

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Abstract. The synergistic extraction of some divalent cations (Cd, Cu, Mn and Zn) in chloroform, with 3-phenyl-4-benzoylisoxazol-5-one (HPBI) in the presence of various synergistic agents: trioctylphosphine oxide (TOPO), octyl(phenyl)(N,N-diisobutylcarbamoylmethyl)phosphine oxide (CMPO) and bis(diphenylphosphinyl)methane (BDPPM) has been studied. It is compared with the extraction in toluene. Due to various factors (e.g. extractant-diluent or extractant-synergist interactions), the stoichiometry of the extracted species, the selectivity and the magnitude of the synergism depend on the diluent and on the synergist. In chloroform, the extraction with HPBI and TOPO follows the order Cu > Zn > Mn > Cd (Mn > Zn in toluene). In chloroform, the synergistic extraction of cadmium follows the order BDPPM > CMPO > TOPO (TOPO > CMPO in toluene). The formation constants of Cd(PBI)$^+$ and Cd(PBI)$_2$ in aqueous medium have been evaluated.

Key words. 3-Phenyl-4-benzoylisoxazol-5-one – cadmium – diluent effect – liquid-liquid extraction – synergism.

Introduction

4-Acylisoxazol-5-ones are highly acidic β-ketoenols ($0.5 < pK_a < 1.5$). They were considered for the first time in 1987 as metal extractants by Jyothi and Rao [1] who studied the extraction of divalent cations with 3-phenyl-4-benzoylisoxazol-5-one (HPBI). They found that the extraction is effective at lower pH values with HPBI than with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP, $pK_a = 4$) or with 2-thenoyltrifluoroacetone (HTTA, $pK_a = 6.5$). This is a very interesting property in view of the separation of metal cations from acidic nuclear wastes. Thus, most of the following papers dealt with the extraction of rare earths and actinides [2-8], supporting the possibility of extraction from very acidic media. This possibility may be improved by using synergistic effects. Nevertheless, only a few papers concerning the synergistic extraction of metal cations with HPBI in the presence of solvating extractants (e.g. trioctylphosphine oxide, TOPO) [5, 8-12] are available. The present work deals with the synergistic extraction of some divalent cations (Cd, Cu, Mn, Zn) with HPBI in the presence of TOPO or of the bidentate ligands, octyl(phenyl)(N,N-diisobutylcarbamoylmethyl)phosphine oxide (CMPO) or bis(diphenylphosphinyl)methane (BDPPM) in chloroform. A previous study of the extraction of the same cations by acylpyrazolones or acylisoxazolones in the presence of TOPO in toluene emphasized the role of the interactions between the extractants upon the extraction efficiency and selectivity. Since chloroform was shown to limit this inter-

action [11,12] and also to hinder the formation of third phases which often occur in HPBI-toluene extraction systems in absence of synergistic agents [12], it has been chosen for the present study. Some of the extractions described in this paper have also been studied in toluene to allow a better knowledge of the diluent effect. Since our aim is a better understanding of the synergistic extractions with mixtures of chelatants and solvatants, a comparison is made with similar extractions using HPMBP.

Experimental

HPBI and HPMBP reagents were prepared as previously described [11,13 and incl. ref.], BDPPM according to [14]. TOPO (Aldrich) and CMPO (M&T) were crystallized from hexane. Other chemicals were of analytical grade. Distribution measurements were performed with a batch technique, in vessels at 25.0±0.2 °C. Equal volumes (40 mL) of the two phases were contacted under magnetic stirring until the equilibrium was attained (< 30 min). The pH was adjusted by NaOH (1 mol·L^{-1}) solutions of suitable composition (1 mol·L^{-1} NaNO$_3$) to keep constant the ionic strength {1 mol·L^{-1} (Na,H)NO$_3$}. For each experimental point, aliquots of the two phases were withdrawn and the metal was stripped from the organic aliquot with 1 mol·L^{-1} HNO$_3$. Metal concentrations were determined after suitable dilution (if necessary) by flame atomic absorption using a 2380 Perkin Elmer AA spectrophotometer. Initial concentrations

were typically: M^{2+} 2×10^{-4} mol·L^{-1}, HL_{org} and $S_{org} \leq 0.04$ mol·L^{-1} in wet chloroform (or toluene).

Abbreviations

$D = [M]_{org} / [M]$, M = Cd, Cu, Mn, Zn

S = BDPPM or CMPO or TOPO

HL = HPMBP or HPBI

BDPPM = bis(diphenylphosphinyl)methane: $(C_6H_5)_2P(O)$-CH_2-$P(O)(C_6H_5)_2$

CMPO = octyl(phenyl)(N,N-diisobutylcarbamoylmethyl) phosphine oxide:
n-$C_8H_{17}(C_6H_5)P(O)$-CH_2-$C(O)$-$N(iso$-$C_4H_9)_2$

HPBI = 3-phenyl-4-benzoylisoxazol-5-one

HPMBP = 1-phenyl-3-methyl-4-benzoylpyrazol-5-one

HTTA = thenoyltrifluoroacetone: F_3C-$C(O)$-CH_2-$C(O)$-C_4H_3S

TOPO = trioctylphosphine oxide: $(n$-$C_8H_{17})_3PO$

Results and discussion

The following equilibria have been considered to explain the experimental data:

$$HL \rightleftharpoons HL_{org} \qquad (K_d) \quad (1)$$

$$HL \rightleftharpoons H^+ + L^- \qquad (K_a) \quad (2)$$

$$HL_{org} + S_{org} \rightleftharpoons S.HL_{org} \qquad (K_{int}) \quad (3)$$

$$M^{2+} + 2\ HL_{org} \rightleftharpoons ML_{2,org} + 2\ H^+ \qquad (K_{1,2}) \quad (4)$$

$$M^{2+} + 2\ HL_{org} + sS_{org} \rightleftharpoons ML_2S_{s,org} + 2\ H^+ \ (K_{1,2,s}) \ (5)$$
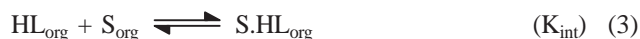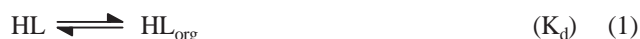
The pK_a values of HPBI, 0.87 (0.2 mol·L^{-1} NaCl) [8], 1.23 (0.1 mol·L^{-1} NaClO$_4$) [5] or 0.68 (thermodynamic value) [15] are largely lower than that of HPMBP: 4.09 (0.1 mol·L^{-1} NaClO$_4$) [16]. HPBI is less lipophilic than HPMBP. The HPBI pK_A ($K_A = [HL]_{org} / [H^+][L^-] = K_a/K_d$ = biphasic dissociation constant) are 3.52 and 4.25 in toluene and chloroform, respectively (1 mol·L^{-1} NaNO$_3$ [13]).

Note that all the extraction constants given in this article are apparent conditional constants which do not take into account the metal complexation with nitrate ions in the aqueous phase. Thus, the given extraction constants must be multiplied by the correcting factor $(1 + \Sigma\beta_i[NO_3^-]^{-i})$ to take into account this complexation. β_i are the formation constants of the $M(NO_3)_i^{(2-i)+}$ complexes [17].

Interactions between the extractants (equilibrium 3)

In toluene, HPBI, like HPMBP, interacts with TOPO by H-bond formation between its exchangeable H atom and the phosphoryl oxygen [18]. The HPBI-TOPO interactions are

HPBI   **HPMBP**
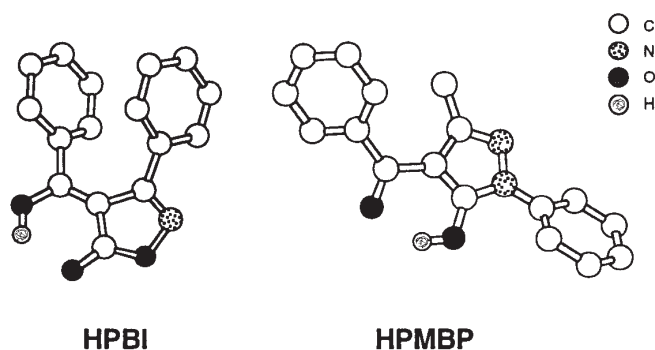
Scheme : The acidic extractants.

quite important (logK_{int} = 1.85) in comparison to the HPMBP-TOPO ones (logK_{int} = 0.85) [11,12]. They must be taken into account to analyse the metal distribution data. The HPBI-CMPO interaction constant has been determined from the Cd-CMPO-HPBI-toluene extraction data according to the method described in [12]: logK_{int} = 1.0. It is weaker than the HPBI-TOPO one: the electron withdrawing of the phenyl groups on the electron donor P=O group limits its ability to accept protons. Interactions are negligible with DBPPM.

In chloroform, no noticeable influence of HPBI-solvatant interaction upon the extraction was observed, due to the competitive interaction of the diluent itself with the solvatants by P=O…HCCl$_3$ H-bond formation [18]. These interactions follow the same order as the S-HPBI ones for the same reasons.

In both diluents, no aggregation of HPBI has been observed [18].

Metal extraction with HL alone (equilibrium 4)

Most of the extraction constants (Tab. I) were already published. They indicate that higher extractions are obtained with isoxazolones than with pyrazolones, i.e. extractions occur at lower pH values. The likely formation of strongly hydrated M(PBI)$_2$ complexes (M = Zn, Cd, Mn) leads to the formation of third phases in toluene systems and limits the extraction in chloroform.

**Table I.** Extraction of ML$_2$: log$K_{1,2}$ (1 mol L^{-1} NaNO$_3$) (log$K_{1,2}$ standard deviation < 0.1).

Diluent	Extracted species	Cu	Zn	Cd
Toluene	M(PMBP)$_2$	0.49 [12]	−5.35 [19]	−8.65 [19]
Toluene	M(PBI)$_2$	1.15 [12]	t.p.	t.p.
Chloroform	M(PMBP)$_2$	0.25*	−5.55 [20]	−8.40 [20]
Chloroform	M(PBI)$_2$	0.96*	−4.00 [13].	−4.80 [13]

t.p.: third phase formation. *: this work.

Original articles

Synergistic extraction with HPBI + S in chloroform
*(equilibria 5 and 6)*

Analysis of the distribution curves $\log D$ *vs.* pH, *vs.* $\log[HL]_{org}$ and *vs.* $\log[S]_{org}$ agree with the extraction of ML_2S_s, with s = 1 or 2. Typical experimental curves are shown in figures 1 to 5.
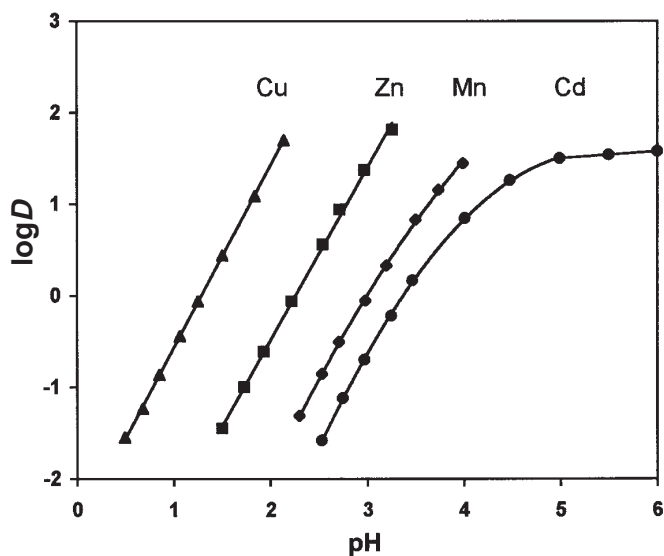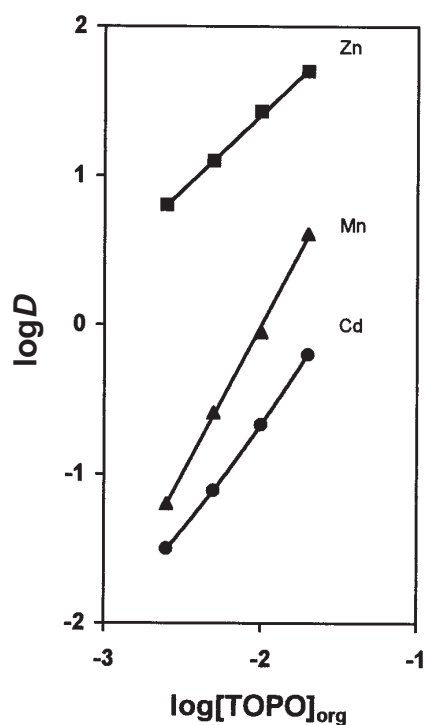

**Figure 1.** Extraction of Cu, Zn, Mn, Cd with HPBI (0.01 mol·L^{-1}) and TOPO (0.01 mol·L^{-1}) in chloroform (NaNO$_3$ 1 mol·L^{-1}).
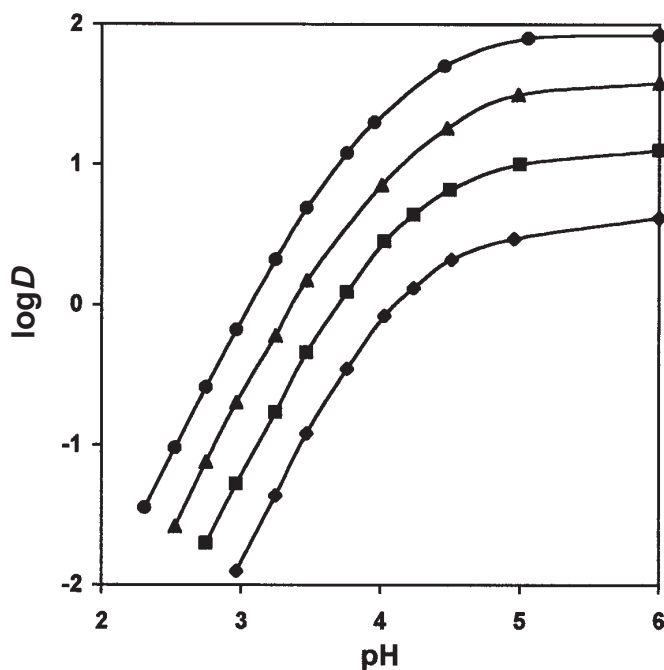
Figure 2. Extraction of cadmium with TOPO (0.01 mol·L^{-1}) and HPBI (from bottom to top: 0.0025, 0.005, 0.01, and 0.02 mol·L^{-1}) in chloroform.
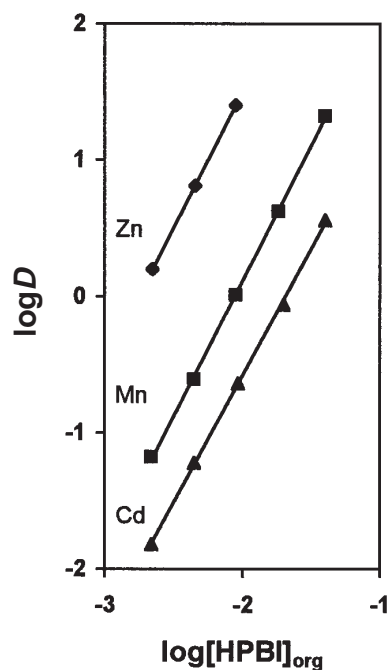
Figure 3. Extraction of Zn, Mn, Cd, at pH 3, with HPBI and TOPO (0.01 mol·L^{-1}) in chloroform.

Figure 4. Extraction of Zn, Mn, Cd, at pH 3, with HPBI (0.01 mol·L^{-1}) and TOPO in chloroform (for Cu, at pH 1.5, $\log D = 1.02 \log[TOPO]_{org} + 2.50$ with $R^2 = 0.9983$).
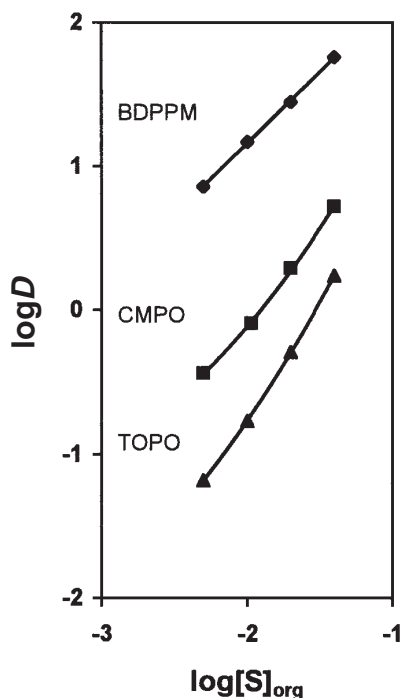
Figure 5. Extraction of cadmium, at pH 3.25, with HPBI (0.005 mol·L^{-1}) and BDPPM, CMPO and TOPO in chloroform (for Zn, at pH 2.25, logD = 0.99 log[BDPPM]$_{org}$ + 2.08 with R^2 = 0.9986).

Table II. Synergistic Extraction Constants : log $K_{1,2,s}$ (1 mol L^{-1} NaNO$_3$) (log$K_{1,2,s}$ standard deviation < 0.1).

Diluent	Extracted species	Cu	Zn	Cd	Mn
Toluene	M(PMBP)$_2$(TOPO)$_2$	n.o.	n.o.	–0.14	0.74
Toluene	M(PMBP)$_2$(TOPO)	3.07*	–0.30*	n.o.	n.o.
Toluene	M(PBI)$_2$(TOPO)$_2$	n.o.	5.24*	5.12*	5.70*
Toluene	M(PBI)$_2$(TOPO)	5.10*	2.90	n.o.	n.o.
Chloroform	M(PBI)$_2$(TOPO)$_2$	n.o.	n.o.	1.05	2.13
Chloroform	M(PBI)$_2$(TOPO)	3.46	1.53	–1.00	n.o.
Toluene	M(PBI)$_2$(CMPO)$_2$	—	4.30	4.08	—
Chloroform	M(PBI)$_2$(CMPO)$_2$	—	—	1.35	—
Chloroform	M(PBI)$_2$(CMPO)	—	—	–0.10	—
Chloroform	M(PBI)$_2$(BDPPM)	—	2.20	1.26	—

n.o.: complex not observed. —: system not investigated. *: ref. [12] and incl. ref.

Below pH = 3.5, all the logD *vs.* pH distribution curves (*e.g.* Fig. 1 and 2), at constant [HPBI]$_{org}$ and [S]$_{org}$ concentrations, are straight lines of slope close to 2 in agreement with the exchange of 2 protons per extracted divalent metal atom. Accordingly, the curves logD *vs.* log[HPBI]$_{org}$ at constant pH and [S]$_{org}$ (*e.g.* Fig. 3) are also straight lines of slope close to 2 indicating that 2 HPBI molecules are involved in the extraction of 1 metal atom. The curves logD *vs.* log[S]$_{org}$ at constant pH and [HPBI]$_{org}$ are more complex (e.g. Fig. 4 and 5) and depend on S and M. For S = BDPPM, the curves are straight lines of slope 1 (M = Cd, Zn) in agreement with the extraction of M(PBI)$_2$BDPPM species. For S = TOPO, the curves are straight lines of slope 1 (M = Cu, Zn) or 2 (M = Mn) indicating the extraction of Cu(PBI)$_2$(TOPO)$_1$, Zn(PBI)$_2$(TOPO)$_1$ and Mn(PBI)$_2$(TOPO)$_2$ whereas the slope of the cadmium extraction curves increases from 1 to 2 when increasing [TOPO]$_{org}$ because of the extraction of both species Cd(PBI)$_2$(TOPO)$_1$ and Cd(PBI)$_2$(TOPO)$_2$. In the same way, the extraction of Cd(PBI)$_2$(CMPO)$_1$ and Cd(PBI)$_2$(CMPO)$_2$ has been observed. A quantitative analysis of the experimental data, that takes into account the decrease of the concentrations of the extractants due to their interactions and to the metal complex formation, leads to the extraction constants logK$_{1,2,s}$ given in table II.

Over pH = 3.5, the acidic dissociation of HPBI becomes more and more important and must be considered to understand the experimental distribution curves logD *vs.* pH (extraction of Mn and Cd, Fig. 1 and 2). Since pK$_A$ = 4.25 (chloroform system), more than 90 % of HPBI are dissociated in the aqueous phase at pH = 5.25. Thus, over pH = 5, cadmium is possibly extracted in chloroform with HPBI + TOPO following the equilibrium (6) which is independent on pH. Indeed the cadmium extraction remains constant when increasing the pH over 5. Note that the formation of cadmium hydroxo complexes remains negligible in the experimental pH range [17].

$$Cd^{2+} + 2\ PBI^- + sS_{org} \rightleftharpoons Cd(PBI)_2S_{s,org}\ (K'_{1,2,s})\ (6)$$

The extraction constants $K'_{1,2,s}$ (s = 1 and 2) are obtained by combining equilibria (5), (1) and (2), with:

$$\begin{aligned}\log(K'_{1,2,s}) &= \log(K_{1,2,s}) - 2\ \log(K_a) + 2\ \log(K_d) \\ &= \log(K_{1,2,s}) + 2\ pK_A = \log(K_{1,2,s}) + 8.5\end{aligned}$$

which gives $\log(K'_{1,2,1})$ = 7.5 and $\log(K'_{1,2,2})$ = 9.55.

Using these values, and considering the pH range higher than 5.5 in which HPBI is entirely dissociated, theoretical values of the distribution coefficient can be calculated :

$$\begin{aligned}D_{calc.} &= [Cd]_{org}\ /\ [Cd^{2+}] \\ &= ([Cd(PBI)_2S_1]_{org} + [Cd(PBI)_2S_2]_{org})\ /\ [Cd^{2+}] \\ &= D_{1,2,1} + D_{1,2,2}\end{aligned}$$

with $\log D_{1,2,1} = \log(K'_{1,2,1}) + 2\ \log[PBI^-] + \log[TOPO]_{org}$
$\log D_{1,2,2} = \log(K'_{1,2,2}) + 2\ \log[PBI^-] + 2\ \log[TOPO]_{org}$.

Thus, for [TOPO]$_{org}$ = 0.02 M and [PBI$^-$] = 0.0025 M, logD$_{calc.}$ = 0.63, in agreement with the very close experimental value logD = 0.62 (Fig. 2).
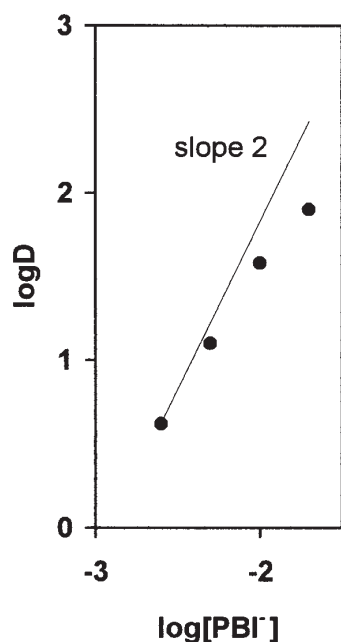
Figure 6. Extraction of cadmium, at pH 6, with HPBI and TOPO (0.01 mol·L^{-1}) in chloroform.

Nevertheless, at constant [TOPO]$_{org}$, logD does not increase linearly with increasing log[PBI$^-$] (Fig. 6), which shows that the equilibrium (6) is not sufficient to explain the experimental data. Thus, for [PBI$^-$] > 0.0025 M, the complexation of cadmium with PBI$^-$ in the aqueous phase has been also considered:

$$Cd^{2+} + i\ PBI^- \rightleftharpoons Cd(PBI)_i^{(2-i)+}\quad (\beta_i)\ (i = 1\ and\ 2)\ (8)$$

It follows that

$$D = [Cd(PBI)_2S_s]_{org}\ /\ [Cd^{2+}]\ (1 + \beta_1[PBI^-] + \beta_2[PBI^-]^2)\ (9)$$

The experimental data obtained at [TOPO]$_{org}$ = 0.01 M and [PBI$^-$] = 0.005, 0.01 and 0.02 M, fit with logβ_1 = 1.7 ± 0.05 and logβ_2 = 3.4 ± 0.1. The results have been confirmed at [TOPO]$_{org}$ = 0.02 M and [PBI$^-$] = 0.005 M. At [TOPO]$_{org}$ = 0.04 M, D is too high to be accurately measured. For lower values of [TOPO]$_{org}$, like in the absence of TOPO, a third phase appears probably due in both cases to the extraction of high concentrations (> 1.10^{-5} M) of the binary complex Cd(PBI)$_2$, likely hydrated. Its partition constant K$_{D,Cd}$ = [Cd(PBI)$_2$]$_{org}$/[Cd(PBI)$_2$] can be calculated by combining the equilibria (1), (2), (4) and (8):

$$logK_{D,Cd} = 2\ logK_d - 2\ logK_a + logK_{1,2} - log\beta_2 = 0.3$$

Its value is largely lower than that of the comparable copper complex Cu(PBI)$_2$ (logK$_{D,Cu}$ = 3, calculated with logβ_2 = 6.5 [12]) which is probably extracted without coordinated H$_2$O. This observation agrees with a strong hydration of Cd(PBI)$_2$, a factor favouring the formation of third phases.

Diluent effect

The synergistic extraction of divalent cations (alkaline earths, Cu and less extensively Zn, Mn, Cd, Co, Ni) with HPBI in the presence of TOPO in toluene has been described in recent papers [11,12]. Complementary experiments using toluene as diluent have been performed in the present work, *i.e.* the extraction of Cd and Mn with HPMBP and TOPO – extracted species M(PMBP)$_2$(TOPO)$_2$ –, the extraction of Zn and Cd with HPBI and CMPO – extracted species M(PBI)$_2$(CMPO)$_2$ –, and the extraction of Zn with HPBI and TOPO *at low concentrations* – extracted species Zn(PBI)$_2$(TOPO)$_1$ –. The main results are summarized in table II.

In the presence of S = TOPO or CMPO, Zn and Cd are extracted in toluene with HPBI as Zn(PBI)$_2$S$_2$ and Cd(PBI)$_2$S$_2$ species, likely hexacoordinated with two monodentate S groups. Thus, CMPO is bonded through its more basic phosphoryl group. The lower basicity of the P=O group of CMPO than that of TOPO leads to lower stabilities of its extracted complexes and therefore to lower extractions (ΔlogK$_{1,2,2} \cong$ 1). For both solvatants S, the extraction constants of Cd(PBI)$_2$S$_2$ noticeably decrease from toluene to chloroform: logK$_{1,2,2}$ decreases from 5.12 to 1.05 (Δ_{2TOPO} = –4.07) for Cd(PBI)$_2$(TOPO)$_2$, and from 4.08 to 1.35 (Δ_{2CMPO} = –2.73) for Cd(PBI)$_2$(CMPO)$_2$. Since the extraction of ML$_2$ species in toluene and chloroform are expected to be close (see Tab. I), the quite different synergistic extractions of ML$_2$S$_2$ species are likely due to the solvation of S with chloroform that leads to an important loss of the S activities. Since these interactions follow the order TOPO > CMPO > BDPPM, the decrease of logK$_{1,2,2}$ between toluene and chloroform is more important for TOPO than for CMPO. Thus, CMPO becomes a better synergist than TOPO in chloroform.

To allow some comparisons between the ligation of various S upon Cd(PBI)$_2$, let us define the constants $K^*_{1,2,n}$ corrected from the S-CHCl$_3$ interaction. For Cd(PBI)$_2$S$_2$:

$$logK^*_{1,2,2} = logK_{1,2,2}\ (toluene) = logK_{1,2,2}(CHCl_3) + \Delta_{2S}$$

Considering now the extraction of Cd(PBI)$_2$S species of lower stoichiometry (S/Cd = 1), the order of magnitude of the effect of the solvation of S upon the synergistic extraction constant would be divided by 2, since the concentration of free S is present at the second power in $K_{1,2,2}$ and at the first power in $K_{1,2,1}$. This leads to the estimation of extraction constants, corrected from the S-CHCl$_3$ interaction:

$$logK^*_{1,2,1} = logK_{1,2,1}(CHCl_3) + \Delta_{2S}/2$$

thus $logK^*_{1,2,1}$ = –1.0 + 4.07/2 = 1.04 for Cd(PBI)$_2$(TOPO)

$logK^*_{1,2,1}$ = –0.1 + 2.73/2 = 1.26 for Cd(PBI)$_2$(CMPO).

Considering $\log K^*_{1,2,1}$ values, CMPO appears as a stronger ligand than TOPO in $Cd(PBI)_2S$; therefore, it is probably bound by both its P=O and C=O donor groups, the stability of its complex being reinforced by chelate effect. For the least basic BDPPM, the interaction with $CHCl_3$ is negligible and $\log K^*_{1,2,1} \cong \log K_{1,2,1}(CHCl_3) = 1.26$. Thus, in the same way, BDPPM would be also bidentate in $Cd(PBI)_2(BDPPM)$. Though the extraction of $Zn(PBI)_2(BDPPM)$ in chloroform ($\log K_{1,2,1} = 2.2$) is higher than that of $Zn(PBI)_2(TOPO)$ ($\log K_{1,2,1} = 1.53$), it is difficult to conclude to the bidentate character of BDPPM on Zn. Indeed, after correction to counterbalance the TOPO-$CHCl_3$ interaction, the extraction is expected to be close to that in toluene, *i.e.* $\log K^*_{1,2,1} = 2.9$, which is clearly higher than 2.2 ($\log K^*_{1,2,1} \cong \log K_{1,2,1}$ for BDPPM). These conclusions are similar to those of Umetani *et al.* [14] who concluded that BDPPM is bidentate in $Cd(PMBP)_2(BDPPM)$ and monodentate in $Zn(PMBP)_2(BDPPM)$. This can be related to the shorter ionic radius of Zn^{2+} than that of Cd^{2+}.

In toluene, the synergistic extraction with HPBI and TOPO follows the order Cu > Mn > Zn $\cong$ Cd. In chloroform, the order is Cu > Zn > Mn > Cd with an inversion Zn/Mn.

In chloroform, the Zn/Cd separation factor with HPBI alone is given by $\Delta \log K_{1,2} = 0.8$. A maximum separation factor is achieved with TOPO at low concentrations with $\Delta \log K_{1,2,1} = 2.53$. It is weaker in the presence of BDPPM (0.94).

Conclusions

The extraction of some divalent cations (Cd, Cu, Mn, Zn) with HPBI and P=O donor ligands in chloroform has been compared with experiments performed in toluene [11,12 and results herein]. The main following conclusions can be drawn out:

– Interactions between HPBI and the solvatants in toluene lower the expected synergistic extraction of metal cations. This interaction is cancelled in chloroform which interacts itself with the solvatants. Both interactions decreases from TOPO to CMPO to be negligible with BDPPM. These interactions lead to important differences of the synergistic extractions in the different diluents and to noticeable variations of selectivity.

– The synergistic extraction of Cu, Zn, Cd an Mn with HPBI and TOPO (and CMPO for Cd) largely decreases from toluene to chloroform as diluents because of the strong interaction which occurs between these solvatants and chloroform. This decrease depends upon the stoichiometries of the extracted complexes: with TOPO, $K_{1,2,1}$, the extraction constant of species involving one TOPO per metal, decreases of 1.5 to 2 orders of magnitude whereas $K_{1,2,2}$, the extraction constant of species involving two TOPO per metal, decreases of 3 to 4 orders of magnitude. Thus, the synergistic extraction of Mn with HPBI and TOPO is higher than that of Zn in toluene and lower in chloroform.

– For the same reasons, the synergistic extraction of cadmium (and zinc) follows the order BDPPM > CMPO > TOPO in chloroform, and the order TOPO > CMPO in toluene.

From distribution curves, the apparent formation constants of $Cd(PBI)^+$ and $Cd(PBI)_2$ in 1 mol·L^{-1} $NaNO_3$ aqueous medium have been evaluated ($\log \beta_1 = 1.7$ and $\log \beta_2 = 3.4$) which allowed to estimate the partition constant $\log K_{D,Cd} = \log[Cd(PBI)_2]_{org}/[Cd(PBI)_2] = 0.3$ indicating the strong hydration of that extracted species.

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