

Liquid–Liquid Extraction of Cadmium and Cobalt with Mixtures of 1-Phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole (HPMSP) and *n*-Dodecylamine (DDA) in Toluene

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Summary. The synergistic extraction of cobalt and cadmium (M^{2+}) from sulfate and perchlorate media with mixtures of 1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole (HPMSP, $PMSP^-$ after deprotonation) and *n*-dodecylamine (DDA, $DDAH^+$ after protonation) has been studied in toluene. In sulfate medium, an easy phase separation is observed. The synergistically extracted species is $DDAH \cdot M(PMSP)_3$, which results from the addition of the predominating $DDAH \cdot PMSP$ ion pair on $M(PMSP)_2$ with $\log K_{syn} = 4.05$ (Co) and 4.7 (Cd). In perchlorate medium, in the presence of an excess of $DDAH \cdot ClO_4$, which is the predominating DDA species, a stable emulsion appears in the aqueous phase in contact with a clear organic phase. Due to the interfacial character of the extraction process and to aggregation phenomena, a stronger synergistic effect is achieved with Co than with Cd, leading to an increase of the Co/Cd separation coefficient. The synergistic extraction performed from perchlorate medium is slower than that from sulfate medium.

Keywords. *n*-Dodecylamine; *n*-Dodecylammonium perchlorate; Emulsion; 1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole; Solvent extraction; Synergistic effect.

Flüssig-flüssig-Extraktion von Cadmium und Cobalt mit Mischungen von 1-Phenyl-3-methyl-4-stearoyl-5-hydroxypyrazol (HPMSP) und *n*-Dodecylamin (DDA) in Toluol

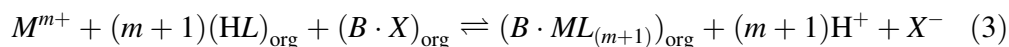
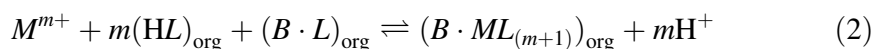
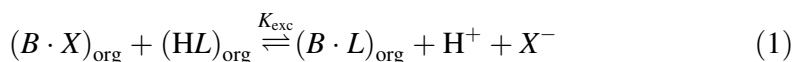
Zusammenfassung. Die synergistische Extraktion von Cobalt und Cadmium (M^{2+}) aus sulfat- und perchlorathaltigen Medien mit Mischungen aus 1-Phenyl-3-methyl-4-stearoyl-5-hydroxypyrazol (HPMSP; nach Deprotonierung: $PMSP^-$) und *n*-Dodecylamin (DDA; nach Protonierung: $DDAH^+$) wurde in Toluol untersucht. In sulfathaltigen Medien beobachtet man eine rasche Phasentrennung. Die synergistisch extrahierte Spezies ist $DDAH \cdot M(PMSP)_3$, die durch Addition des vorherrschenden Ionenpaars $DDAH \cdot PMSP$ an $M(PMSP)_2$ entsteht ($\log K_{syn} = 4.05$ (Co) bzw. 4.7 (Cd)). Perchlorathaltige Medien zeigen in Gegenwart eines Überschusses von $DDAH \cdot ClO_4$, der hauptsächlichen Komponente der DDA-Spezies, eine stabile Emulsion in der wäßrigen Phase neben einer klaren organischen Phase. Aufgrund des Grenzschichtcharakters des Extraktionsvorgangs und von

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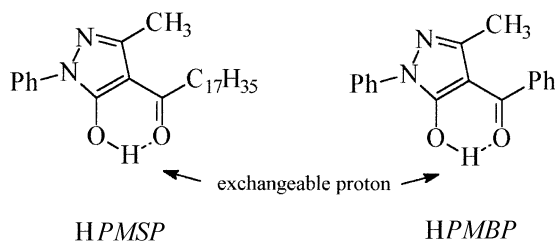
Aggregationsphänomenen ist der synergistische Effekt für Co größer als für Cd, woraus sich ein höherer Trennfaktor für das Paar Co/Cd ergibt. Die synergistische Extraktion aus perchlorathaltigen Medien verläuft langsamer als jene aus sulfathaltigen.

Introduction

During the last twenty years it has been shown that metal cations can be synergistically extracted with mixtures of the acidic chelating extractants β -diketones, 4-acyl-5-hydroxypyrazoles, or 4-acyl-5-hydroxyisoxazoles (HL) and lipophilic ammonium salts ($B \cdot X = B^+X^-$ with B^+ = ammonium and X^- = inorganic anion) [1–3 and Refs. cited therein]. In many cases, a two-phase anionic exchange between $B \cdot X$ and HL occurs (1) leading to the $B \cdot L (=B^+L^-)$ ammonium salt. If X^- itself is not a complexing agent of M^{m+} , $B \cdot L$ appears to be the actual synergist. Then, the synergistic species is $B \cdot ML_{(m+1)} (=B^+ML_{(m+1)}^-)$ which is extracted according to one of the equilibria (2) (high pH range) or (3) (low pH range). The formation of the synergist $B \cdot L$ depends on X^- ; it is favoured following the order perchlorate < nitrate < chloride < sulfate.



A special behaviour has been observed in the extraction of the divalent cations Zn, Co, and Cd with mixtures of *n*-dodecylammonium salts (DDAH·X) and 1-phenyl-3-methyl-4-benzoyl-5-hydroxypyrazole (HPMBP): an emulsion is formed in the aqueous phase due to the amphiphilic character of *n*-dodecylammonium perchlorate and nitrate salts. This results in an interesting synergistic effect observed from very low ammonium salt concentrations, *i.e.* close to the metal concentration [4, 5]. In order to extend this previous work, the synergistic extraction of divalent Co and Cd from sulfate and perchlorate aqueous media in toluene has been studied with 1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole (HPMSP). HPMSP differs from HPMBP by the presence of a long hydrocarbon chain which is expected to appreciably modify its interfacial properties. It is important to note that a good knowledge of such synergistic extraction systems is needed, since new separation processes are now developing which are based on the kinetics of metal complexation in micellar media involving mixtures of amphiphilic acidic chelating agents and ammonium salts [6].



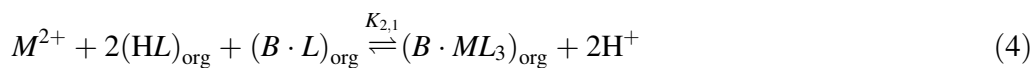
Scheme 1

Results and Discussion

Extraction of Co and Cd from 0.33 M sulfate medium

In the *HPMSP-DDA-toluene-0.33 M sulfate* liquid-liquid system, the extraction of H_2SO_4 with *DDA* is negligible above pH 3 (indicated by a very low pH variation of the aqueous phase), *i.e.* under the present experimental conditions of Co and Cd extractions. Nevertheless, the acidic *HPMSP* reacts with the basic *DDA* in toluene to form *DDAH · PMSP*. As the formation constant of *TOPO · HPMSP* is close to that of *TOPO · HPMBP* ($\log K = 0.80$ and 0.85 , *TOPO* = tri-*n*-octylphosphine oxide [9]), the formation constant of *DDAH · PMSP* is expected to be close to that of *DDAH · PMBP* ($\log K = 2.5$ [4]). It follows that, under the experimental conditions employed, *DDAH · PMSP* is the predominating *DDA* species, since *HPMSP* is always in excess to *DDA*.

Experimental distribution curves $\log D$ vs. pH in the absence and in the presence of *DDAH · PMSP* are shown in Fig. 1. All curves are straight lines with a slope close to 2 according to the exchange of 2 protons per extracted metal. In all cases, both organic and aqueous phases became clear after an easy phase separation by gravity. An important enhancement of the extraction is observed in the presence of *DDAH · PMSP*. It increases regularly with increasing $[\text{DDAH} \cdot \text{PMSP}]_{\text{org}}$: curves $\log D$ vs. $\log[\text{DDAH} \cdot \text{PMSP}]_{\text{org}}$ (constant pH and $[\text{HPMSP}]_{\text{org}}$) are straight lines of slopes close to 1, whereas graphs of $\log D$ vs. $\log[\text{HPMSP}]_{\text{org}}$ (constant pH and $[\text{DDAH} \cdot \text{PMSP}]_{\text{org}}$) are straight lines of slope 2 (Fig. 2). These results agree with the extraction equilibrium (4) where $M = \text{Co}$ or Cd , $\text{HL} = \text{HPMSP}$ and $B = \text{DDAH}$.



$$\log D = \log \left(\frac{[\text{B} \cdot \text{ML}_3]_{\text{org}}}{[M^{2+}]} \right) = \log K_{2,1} + 2\log [\text{HL}]_{\text{org}} + \log [\text{B} \cdot \text{L}]_{\text{org}} + 2\text{pH}$$

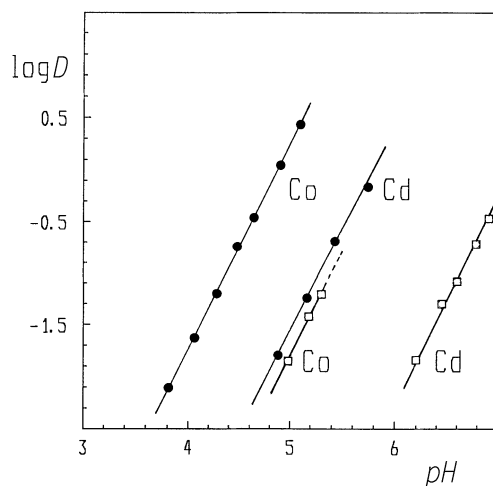


Fig. 1. Extraction of Co and Cd from sulfate medium with mixtures of *HPMSP* (0.02 M) and *DDAH · PMSP* (squares = 0 M, circles = 0.01 M) in toluene at different pH values

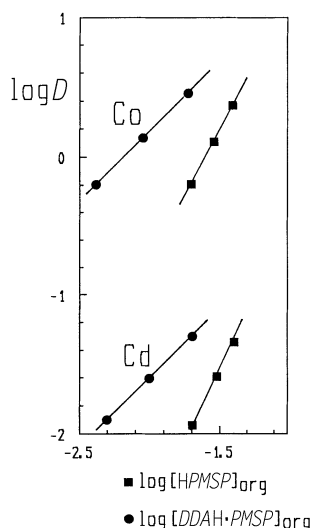
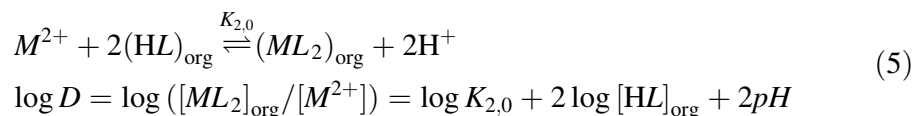
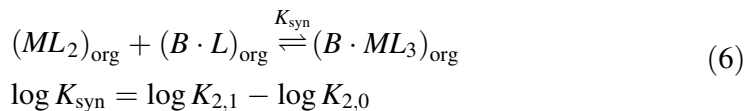


Fig. 2. Extraction of Co and Cd from sulfate medium at pH 4.8 with mixtures of HPMSP and DDAH·PMSP in toluene; circles: $[DDAH \cdot PMSP]_{org}$ variation, $[HPMSP]_{org,i} = 0.03 M$; squares: $[HPMSP]_{org}$ variation, $[DDAH \cdot PMSP]_{org,i} = 0.01 M$; i denotes initial concentrations

In the absence of $DDAH \cdot PMSP_{org}$, the $\log D$ vs. $[HPMSP]_{org}$ curves agree with the extraction equilibrium (5):



The synergism is described by equilibrium (6):



The equilibrium constants are given in Table 1 together with those determined previously with $HL = HPMBP$ or $HPMSP$ and $B \cdot L = TOAH \cdot L$ or $TOMA \cdot L$ ($TOAH^+$ = tri-*n*-octylammonium, $TOMA^+$ = methyl-tri-*n*-octyl-ammonium) [8, 10,

Table 1. Extraction from sulfate medium: equilibrium constants

	Cadmium		Cobalt	
	HPMSP	HPMBP	HPMSP	HPMBP
$\log K_{2,0}$	-10.85	-9.45 ^a	-8.40	-7.60 ^a
$\log K_{2,1}$ (DDAH)	-6.15	-4.25 ^a	-4.35	-2.45 ^a
$\log K_{syn}$ (DDAH)	4.70	5.20 ^a	4.05	5.15 ^a
$\log K_{syn}$ (TOAH) ^b	4.75	5.50	5.35	6.30
$\log K_{syn}$ (TOMA) ^b	-	8.20	8.55	9.15

^a From Ref. [4, 5]; ^b from Ref. [8, 10, 11]

11]. $\log K_{2,0}$, $\log K_{2,1}$, and $\log K_{\text{syn}}$ heavily decrease from *HPMBP* to *HPMSP* due to the weaker complexation of Co^{2+} and Cd^{2+} with PMSP^- than with PMBP^- (formation of ML_2 and ML_3^-).

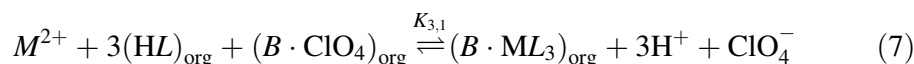
DDAH·PMSP and *TOAH·PMSP* on the one hand and *DDAH·PMBP* and *TOAH·PMBP* on the other hand are close synergistic agents for the extraction of Cd with *HPMSP* and *HPMBP*. A different trend is observed concerning the synergistic extraction of Co: in this case, *DDAH·PMSP* and *DDAH·PMBP* appear to be worse synergists than the related *TOAH·PMSP* and *TOAH·PMBP*, which results from a loss of stability of the extracted $B \cdot \text{CoL}_3$ ion pairs from $B = \text{TOAH}$ to $B = \text{DDAH}$. The stability of both *TOAH·CdL₃* and *DDAH·CdL₃* is probably due to the large size of the CdL_3^- ion compared to CoL_3^- . Although the structures of these very anions are not known, such a difference is expected from the larger ionic radius of Cd^{2+} and weaker complexation of Cd^{2+} with L^- , *i.e.* longer Cd–O bond distances, in comparison with Co^{2+} . This is supported by the “hard soft” classification of *Pearson* [12] that emphasizes the softer character of Cd^{2+} with respect to Co^{2+} , leading to weaker complexes with hard oxygen donor ligands. This is illustrated by the M–O distances in acetylacetonate complexes of Cd(II) (2.23–2.33 Å, [13]) and Co(II) (2.03–2.09 Å, [14]).

The synergistic effect achieved with the quaternary ammonium compounds *TOMA·PMBP* and *TOMA·PMSP* is about three orders of magnitude greater than the effect observed with the related primary and tertiary ones (*DDAH·L*, *TOAH·L*). It is likely that the dissociation of $(B \cdot L)_{\text{org}}$ is easier with the former ones, since in the latter ones the ion pairs $(B \cdot L)_{\text{org}}$ are stabilized by hydrogen bonding between cation and anion. This is supported by the greater ability of *TOMA·L* than *TOAH·L* or *DDAH·L* to exchange its anion L^- with an inorganic anion X^- (equilibrium (1), backward *e.g.*, for $X = \text{ClO}_4$, $\text{HL} = \text{HPMBP}$, and $B = \text{TOMA}$, *TOAH*, and *DDAH*, respectively; $\log K_{\text{exc}} = -7.00$, -3.95 , and -3.80 [4, 10]).

Obviously, the slope analysis of metal distribution curves which gives the stoichiometry of the synergistic extracted species “ ML_2, BL ” is not sufficient to prove its formulation as $B \cdot \text{ML}_3$. Nevertheless, this formulation is very likely since such species have been previously extracted in the presence of the *TOMA·ClO₄* quaternary ammonium salt [8, 10]. Moreover, the crystal structures of *tris*(acetylacetonato) cadmate(II) and cobaltate(II) have been reported in the literature [14] showing that the formation of *tris*(4-acyl-5-hydroxypyrazolonato) metal(II) complexes is highly probable.

Extraction of Co and Cd from 1 M perchlorate medium

With *DDAH·ClO₄* being the predominating dodecylammonium species in the *HPMSP-DDA-toluene-1 M* (Na, H)*ClO₄* liquid–liquid system in the *pH* range of Co and Cd extractions (see Experimental), the synergistic extraction equilibrium (7), where $\text{HL} = \text{HPMSP}$ and $B = \text{DDAH}$, would be expected if no special phenomenon occurs.



Equilibrium (7) can be considered as the sum of equilibria (5), (6), and (1) with $\log K_{2,1} = -7.40$ (Co) and -9.40 (Cd) (equilibrium (5), previously determined in $1 M$ (Na, H)ClO₄ medium [11]), $\log K_{\text{syn}} = 4.05$ (Co) and 4.70 (Cd) (equilibrium (6), determined above in sulfate medium studies), and $\log K_{\text{exc}} = -3.80$ (see Experimental). Accordingly, $\log K_{3,1} = -7.15$ (Co) and -8.50 (Cd). The separation coefficient can therefore be calculated as $\log \alpha(\text{ClO}_4, \text{calc.}) = \log K_{3,1}(\text{Co}) - \log K_{3,1}(\text{Cd}) = 1.35$.

In sulfate medium, the separation coefficient was $\log \alpha(\text{SO}_4) = \log K_{2,1}(\text{Co}) - \log K_{2,1}(\text{Cd}) = 1.80$ (Table 1). Thus, a loss of selectivity from the synergistic extractions performed in sulfate medium to those performed in perchlorate medium would be expected.

Moreover, from equilibrium (7) the following relation with $\text{HL} = \text{HPMSP}$ and $B = \text{DDAH}$ would be valid:

$$\log D = \log K_{3,1} + 3\log [\text{HL}]_{\text{org}} + \log [B \cdot \text{ClO}_4]_{\text{org}} + 3pH + \log [\text{ClO}_4^-]$$

Keeping constant all the other parameters and varying $[\text{DDAH} \cdot \text{ClO}_4]_{\text{org}}$, the curve $\log D$ vs. $\log [\text{DDAH} \cdot \text{ClO}_4]_{\text{org}}$ would be a straight line of slope 1, which is not observed.

In fact, an improvement of selectivity has been observed due to the amphiphilic properties of $\text{DDAH} \cdot \text{ClO}_4$: a white emulsion appears in the aqueous phase which was not present in sulfate medium where the ammonium compounds were only $\text{DDAH} \cdot \text{PMSP}$ or $\text{DDAH} \cdot M(\text{PMSP})_3$. When $[\text{DDAH} \cdot \text{ClO}_4]_{\text{org}} > [M]_{\text{org}}$ ($M = \text{Co}, \text{Cd}$), the aqueous emulsion appears (Fig. 3), and the metal extraction into the clear organic phase is independent on $[\text{DDAH} \cdot \text{ClO}_4]_{\text{org}}$ (Fig. 5) and on $[\text{ClO}_4^-]$ (varying from 0.1 to 1 M). Under these conditions, a unique curve $\log D$ vs. pH is achieved at a constant $[\text{HPMSP}]_{\text{org}}$ which is a straight line of a slope close to 3 (Fig. 4), whereas at constant pH , $\log D$ vs. $[\text{HPMSP}]_{\text{org}}$ curves are straight lines of slope 3 (Fig. 5). The experimental results agree with the following statistical extraction equilibrium (8)

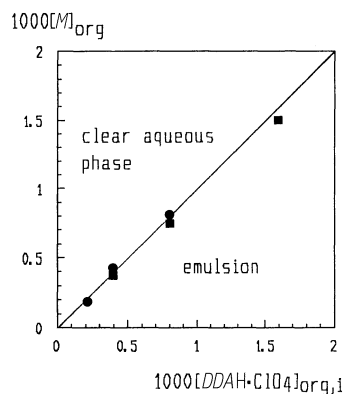
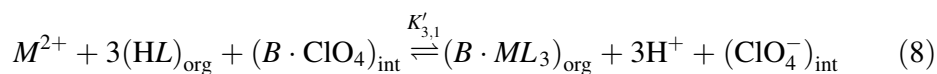


Fig. 3. Extraction of Co (squares) and Cd (circles) from perchlorate medium with mixtures of HPMSP (0.02 M) and $\text{DDAH} \cdot \text{ClO}_4$ in toluene; aqueous emulsion broken edge vs. $[\text{DDAH} \cdot \text{ClO}_4]_{\text{org},i}$

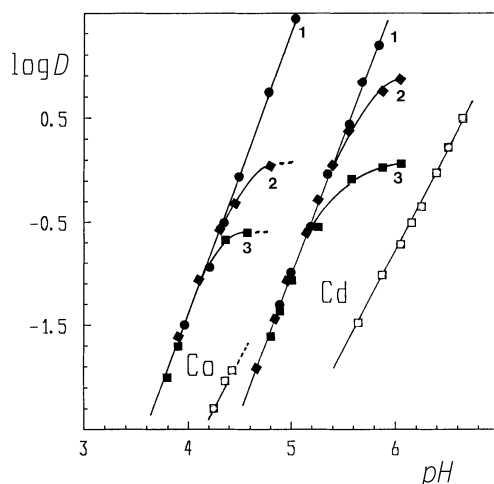


Fig. 4. Extraction of Co and Cd from perchlorate medium with mixtures of HPMSP (0.02 M) and DDAH·ClO₄ in toluene at different pH values; [DDAH·ClO₄]_{org,i} = open squares, 0 M; full symbols: 0.01 M (1), 0.0008 M (2), 0.0004 M (3)

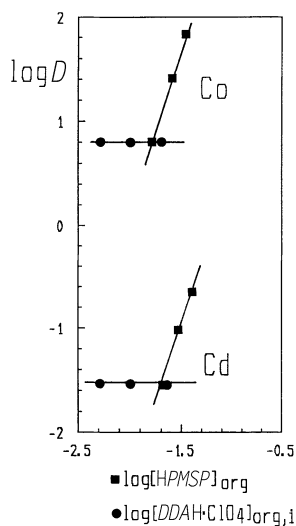


Fig. 5. Extraction of Co and Cd from perchlorate medium at pH 4.8 with mixtures of HPMSP and DDAH·ClO₄ in toluene; circles: [DDAH·ClO₄]_{org} variation, [HPMSP]_{org,i} = 0.02 M; squares: [HPMSP]_{org} variation, [DDAH·ClO₄]_{org,i} = 0.01 M

where HL = HPMSP and B = DDAH. (B·ClO₄)_{int} and (ClO₄⁻)_{int} are assumed to be interfacial species at invariable concentration, (B·ClO₄)_{int} species likely being aggregates. According to the equilibrium (8),

$$\begin{aligned} \log D &= \log K'_{3,1} + 3 \log [\text{HL}]_{\text{org}} + \log [\text{B} \cdot \text{ClO}_4]_{\text{int}} + 3pH - \log [\text{ClO}_4^-]_{\text{int}} \\ &= \log K_{\text{int}} + 3 \log [\text{HL}]_{\text{org}} + 3pH \end{aligned}$$

with $\log K_{\text{int}} = \log K'_{3,1} + \log [\text{B} \cdot \text{ClO}_4]_{\text{int}} - \log [\text{ClO}_4^-]_{\text{int}}$.

Table 2. Extraction from perchlorate medium: equilibrium constants

	Cadmium		Cobalt	
	<i>HPMSP</i>	<i>HPMBP</i> [5]	<i>HPMSP</i>	<i>HPMBP</i> [4]
$\log K_{2,0}$	-9.40	-8.20	-7.40	-7.20
$\log K_{\text{syn}}^a$	4.70	5.20	4.05	5.15
$\log K_{\text{exc}}$	-3.8	-3.8	-3.8	-3.8
$\log K_{3,1}$	-8.50	-6.80	-7.15	-5.85
$\log K_{\text{int}}$	-10.85	-8.30	-8.20	-6.10

^a Values from sulfate medium

The experimental values of $\log K_{\text{int}}$ are -8.20 (Co) and -10.85 (Cd), which gives the experimental separation coefficient $\log \alpha(\text{ClO}_4, \text{exp.}) = \log K_{\text{int}}(\text{Co}) - \log K_{\text{int}}(\text{Cd}) = 2.65$, which is higher than that found in sulfate medium (1.80) as already emphasized above and than that expected in the absence of emulsion (1.35).

The same trend has previously been observed with the *HPMBP* – *DDAH* · ClO_4 synergistic system (Table 2) [4, 5]. $\log \alpha$ increases from 1.80 in sulfate medium to 2.20 in perchlorate medium ($\log \alpha(\text{ClO}_4) = 0.95$, calculated in the absence of interfacial or aggregation phenomena). The high experimental separation coefficient obtained in perchlorate medium could be explained by the higher ability of cobalt than cadmium to be extracted as species containing aggregated ammonium salts. With $\text{HL} = \text{HPMBP}$ it has previously been shown that Co was extracted as $\text{DDAH} \cdot \text{ClO}_4 \cdot \text{DDAH} \cdot \text{Co}(\text{PMBP})_3$ at very low $\text{DDAH} \cdot \text{ClO}_4$ concentrations, whereas Cd was extracted as $\text{DDAH} \cdot \text{Cd}(\text{PMBP})_3$ [4, 5]. Under the same experimental conditions, the extraction of only $\text{DDAH} \cdot \text{Co}(\text{PMSP})_3$ and $\text{DDAH} \cdot \text{Cd}(\text{PMSP})_3$ has been observed. Nevertheless, it is likely that the formation of ammonium aggregates also occurs at higher $\text{DDAH} \cdot \text{ClO}_4$ concentrations, which could explain that at a given *pH*, the synergistic effect upon Co extraction is stronger than upon Cd; note that this difference of synergistic effect is actually improved with *HPMBP*.

A noticeable point is the slow extraction of Co and Cd from perchlorate medium with mixtures of *HPMSP* and *DDAH* · ClO_4 in toluene which needs 30–60 minutes to reach the equilibrium. Less than 15 minutes are sufficient in the case of *HPMBP*. Moreover, the addition of *n*-octanol (6% v/v) to the organic phase leads to the clarification of the turbid aqueous phase and to an acceleration of the Co and Cd phase transfer. The equilibrium is then reached after less than 15 minutes. The extraction process remains unchanged (same extraction curves in the presence as in the absence of *n*-octanol). It is likely that the aqueous emulsion turns into a micro-emulsion which could explain the extraction acceleration and confirm the interfacial character of the extraction mechanism. The lower extraction rates observed with *HPMSP* than with *HPMBP* presumably results from the long hydrocarbon chain of *HPMSP* which can easily interact with the dodecyl chain of *DDAH* · ClO_4 in the interfacial region.

Conclusions

As previously observed with *HPMBP* [4, 5], Co and Cd are synergistically extracted with *HPMSP* in toluene in the presence of *n*-dodecylamine, *DDA*, that predominates as *DDAH*·*PMSP* and *DDAH*·*ClO*₄ organic species in contact with aqueous sulfate and perchlorate media respectively.

In the extraction performed from sulfate medium, the extracted species is *DDAH*·*M*(*PMSP*)₃, and the synergistic effect is higher with Cd than with Co, which is explained by a lower stability of the *DDAH*·*Co*(*PMSP*)₃ ion pair compared to *DDAH*·*Cd*(*PMSP*)₃.

In the extraction performed from perchlorate medium, a white emulsion appears in the aqueous phase due to the amphiphilic character of *DDAH*·*ClO*₄. The metal phase transfer is slower than in sulfate medium. It is accelerated in the presence of *n*-octanol which likely extends the liquid–liquid interfacial surface, thus supporting the important role of the interfacial region in the extraction mechanism. The selectivity of the Co/Cd extraction increases from sulfate to perchlorate medium which indicates that the synergistic extraction of cobalt is improved, presumably because of the higher ability of *DDAH*·*Co*(*PMBP*)₃ and *DDAH*·*Co*(*PMSP*)₃ species than the related Cd species to form aggregates with *DDAH*·*ClO*₄ in the organic phase. The interfacial character of the synergistic extractions performed from perchlorate medium with mixtures of *HPMSP* or *HPMBP* and *DDAH*·*ClO*₄ in toluene improves the synergistic effect even at very low [*DDAH*·*ClO*₄]_{org}, close to the extracted metal concentrations.

Experimental

Reagents and solutions

HPMSP was synthesized according to *Jensen* [7]. *n*-Dodecylamine (Merck “Zur Synthese”) was used without further purification. Diluents and inorganic reagents were of analytical quality. The organic phases were preequilibrated with aqueous solutions, free of extractable metals, and of the same composition as those used in the metal extraction experiments. The ionic strength of the aqueous phase was kept constant ($I \approx 1$) using sulfate (0.33 *M*) or perchlorate (1 *M*) sodium salts. The initial aqueous cobalt and cadmium concentrations were 1.7 and 0.9×10^{-3} *M* respectively.

Liquid–liquid extraction and analytical procedures

The distribution experiments were performed in a thermostatted vessel ($25.0 \pm 0.2^\circ\text{C}$) using a batch technique. Equal volumes of both phases were shaken for a time sufficient to reach the equilibria (20 minutes in sulfate medium and 30 to 60 minutes in perchlorate medium) and separated by gravity. Aliquots of both phases were withdrawn and analyzed after suitable dilution (stripping into 0.1 *M* *HNO*₃ for the organic phases) by flame atomic absorption using a 2380 Perkin-Elmer spectrophotometer. When the aqueous solutions remained turbid (stable emulsion formation in perchlorate medium), the aqueous concentration was determined by mass-balance calculations.

Symbols, extraction constant determination, errors

The distribution coefficient is $D = [M]_{\text{org}}/[M]$, where $[M]_{\text{org}}$ and $[M]$ are the analytical concentrations of *M* (*M* = Co, Cd) in the organic and aqueous phases measured when the equilibrium is attained.

“i” denotes initial concentrations before contacting the phases, “org” denotes species in the organic phase. The ion pairs (C^+A^-) are noted ($C \cdot A$). $DDAH^+$ is the protonated form of DDA (n -dodecylamine). TOA denotes tri- n -octylamine. X^- always denotes an inorganic anion. $PMSP^-$ is the deprotonated form of $HPMSP$ (1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole). $PMSP^-$ is easily formed in the aqueous phase by two-phase titration of $HPMSP$, e.g. with $NaOH$, or by anionic exchange in the organic phase, e.g. between $HPMSP$ and the quaternary lipophilic ammonium salt $TOMA \cdot Cl$ (methyl-tri- n -octylammonium chloride) leading to the ion pair $TOMA \cdot PMSP$ [8] according to equilibrium (1).

The stoichiometry of every extracted species has been determined by varying successively the concentration of the different chemical species (CS) involved in the extraction system, i.e. $[H^+]$, $[HPMSP]_{org}$, and $[DDAH \cdot PMSP]_{org}$ (sulfate medium) or $[DDAH \cdot ClO_4]_{org}$ (perchlorate medium). The stoichiometry is given by the slopes of the distribution curves $\log D$ vs. $\log [CS]$ and by considering the electroneutrality of the extracted species.

Equilibrium extraction constants have been determined for each experimental point taking into account the quantities of extractant involved in the extracted species. Thus, the following relations have been considered:

$[HPMSP]_{org} = [HPMSP]_{org,i} - 2[M]_{org}$ for the extraction of $M(PMSP)_2$ by $HPMSP$ alone;
 $[DDAH \cdot PMSP]_{org} = [DDAH \cdot PMSP]_{org,i} - [M]_{org}$ and $[HPMSP]_{org} = [HPMSP]_{org,i} - 2[M]_{org}$ for the extraction of $DDAH \cdot M(PMSP)_3$ from sulfate medium by ($HPMSP + DDAH \cdot PMSP$); and
 $[HPMSP]_{org} = [HPMSP]_{org,i} - 3[M]_{org}$ for the extraction of $DDAH \cdot M(PMSP)_3$ from perchlorate medium by ($HPMSP + DDAH \cdot ClO_4$)

The errors upon the logarithmic values of the extraction constants determined in the present work vary from ± 0.05 to ± 0.10 .

Anionic exchange between $HPMSP$ and $DDAH \cdot ClO_4$

A 0.01 M DDA toluene solution was shaken for at least thirty minutes with an equal volume of 1.0 M $NaClO_4$ aqueous solution at $pH = 2.00$ in order to protonate DDA . At equilibrium, the pH was measured ($pH_0 = 3.84$). The pH variation indicates that $[DDAH \cdot ClO_4]_{org} \gg [DDA]_{org}$. The same experiment was repeated in the presence of $HPMSP$ at various concentrations ($c = 0.01, 0.02$, and $0.03 M$); at equilibrium, $pH = pH_C$.

Assuming that the difference between pH_C and pH_0 is due to the formation of $DDAH \cdot PMSP$ from $DDAH \cdot ClO_4$, $[DDAH \cdot PMSP]_{org} = 10^{-pH_C} - 10^{-pH_0}$. Since it appears that $[DDAH \cdot PMSP]_{org} \ll [DDA]_{org,i}$ and $[HPMSP]_{org,i}$, $[DDAH \cdot ClO_4]_{org} \approx [DDA]_{org,i}$, $[HPMSP]_{org} \approx [HPMSP]_{org,i}$; thus, K_{exc} (equilibrium (1)) can be estimated: $K_{exc} = [DDAH \cdot PMSP]_{org} \cdot 10^{-pH_C} \cdot [HPMSP]_{org}^{-1} \cdot [DDAH \cdot ClO_4]_{org}^{-1}$.

In these calculations, aggregation phenomena were arbitrarily neglected. The obtained $\log K_{exc} = -3.8$ value is the same as that previously determined with $HPMBP/DDAH \cdot ClO_4$ mixtures [4].

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