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# Synergistic Solvent Extraction of Zinc(II) and Cadmium(II) from Sulfate Medium by a Mixture of 1 - Phenyl - 3 - Methyl - 4 - Benzoylpyrazol - 5 - One and Methyl - Isobutyl Ketone

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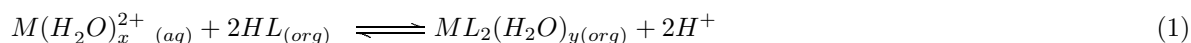
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The solvent extraction of zinc(II) and cadmium(II) from sulfate medium by 1 - phenyl - 3 - methyl - 4 - benzoylpyrazol - 5 - one (HPMBP) was studied in the following parameter functions: pH, concentration of the extractant, nature of diluent, concentration of the mineral anion and synergism. In the absence of the synergic agent methyl - isobutyl ketone (MIBK), the complexes extracted are  $ZnL_2(H_2O)_x$  (*org*) and  $CdL_2(H_2O)_y$  (*org*). In the presence of MIBK, the curves of extraction show the presence of several species of complexes that depend on the concentration of MIBK. For very weak concentrations, the extracted complexes are  $ZnL_2(H_2O)_{x(org)}$  and  $CdL_2(H_2O)_{y(org)}$ . For high concentrations, the extracted complexes are  $ML_2(MIBK)_{(org)}$ ,  $ML_2(MIBK)$ ,  $MIBK_{(org)}$  and  $ML_2(MIBK), 2MIBK_{(org)}$  (M=Zn, Cd). The extraction constants were calculated.

## Introduction

The solvent extraction of metals from sulfate medium has not been studied widely because of its complexity<sup>1</sup>. However, this medium remains very important from a practical point of view, and metallic extractions undertaken from sulfuric acid solution are preferred in industrial applications. The extraction of divalent metals  $M^{2+}$  by the acid extractants (HL) such as the  $\beta$ -diketones has been studied extensively<sup>2-4</sup>. It is generally described by the following equation:



The neutral organo-metallic complex formed often remains hydrated and, consequently, it is slightly extractable<sup>5</sup>. The water molecules of the coordination of extracted metals species can be replaced by polar solvents such as ketones, esters and alcohols<sup>6-7</sup>, or by a second extractant which has sufficient basicity, such

as tri-n-octyl phosphine oxide (TOPO)<sup>8-9</sup> or tributyl phosphate (TBP)<sup>10</sup>. This has a synergistic effect on the extraction since the complex formed becomes more lipophile.

In the present work, the study of the synergistic extraction of zinc(II) and cadmium(II) from sulfate medium with 1 - phenyl - 3 - methyl - 4 - benzoylpyrazol - 5 - one (HPMBP), in the absence and presence of methyl - isobutyl ketone (MIBK) was carried out. The object of the work was the determination of the stoichiometries of the extracted complexes and their extraction constants. Previously, Zn(II) extraction from perchlorate medium with 1 - phenyl - 3 - methyl - 4 - benzoylpyrazol - 5 - one and its mixtures with tri-n-octyl phosphine oxide in chloroform has been reported<sup>2</sup>.

(where aq and org denote the species in the aqueous and the organic phase).

## Experimental

### Reagents

HPMBP was prepared according to the method of Jensen<sup>11</sup>. MIBK was provided by Prolabo. Organic solutions were pre-equilibrated with aqueous solutions which did not contain any metal. The ionic strength of the aqueous medium was assumed to be unity ( $[Na_2SO_4] = 0.33M$ ). The initial concentrations of zinc and cadmium were  $7.65 \times 10^{-4}M$  and  $4.45 \times 10^{-4}M$  respectively (50 ppm).

### Extraction and Analytical Procedures

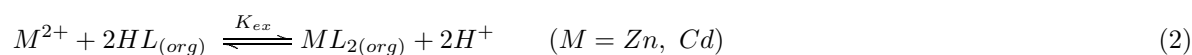
Extractions were performed in thermostated vessels at 25.0°C. In all experiments, 40 ml of aqueous phase containing metal (50 ppm) was shaken with 40 ml of organic solvent. The solutions 0.5 ml were pipetted every 30 minutes in each phase. One can vary the pH by the addition of a small amount NaOH after each withdrawal. The metallic cation of the organic phase was de-extracted by a solution of 0.1 N of acid, that in the aqueous phase was diluted directly. Metal concentrations were determined by flame atomic absorption, using a Perkin-Elmer 2380 spectrophotometer.

## Results and Discussion

### Extraction of Zn and Cd with HPMBP

#### Effect of pH

The overall reaction in the extraction of zinc(II) and cadmium(II) with HPMBP (HL) may be expressed as



The extraction constant,  $K_{ex}$ , is defined in Eq. 3 and is rewritten as Eq. 4 by using the distribution ratio,  $D_M$ , of the metals.

$$K_{ex} = \frac{[ML_2]_{(org)}[H^+]^2}{[M^{2+}][HL]_{(org)}^2} \quad (3)$$

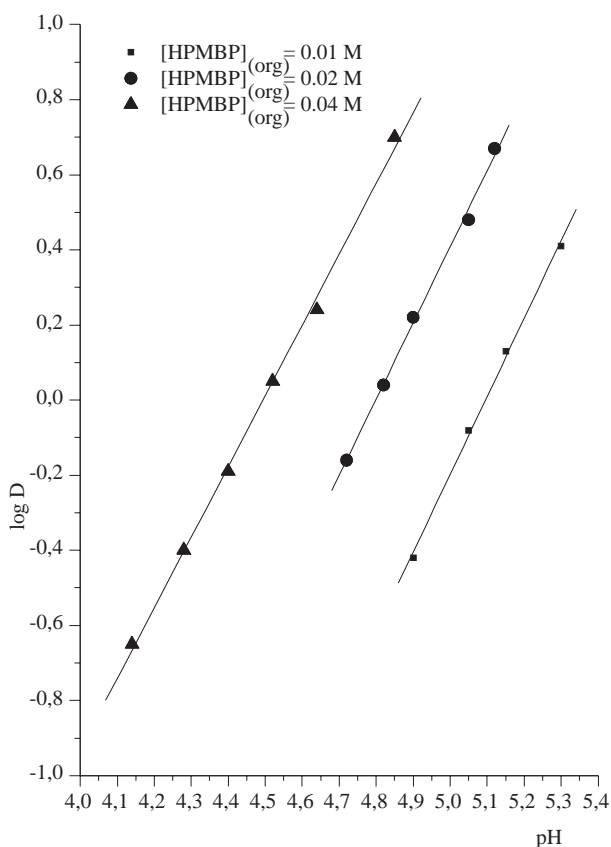
$$\log D_M = \log K_{ex} + 2 \log [HL]_{(org)} + 2pH \quad (4)$$

$$[\text{HL}]_{(\text{org})} = [\text{HL}]_{i(\text{org})} - 2[\text{M}]_{(\text{org})} \quad (5)$$

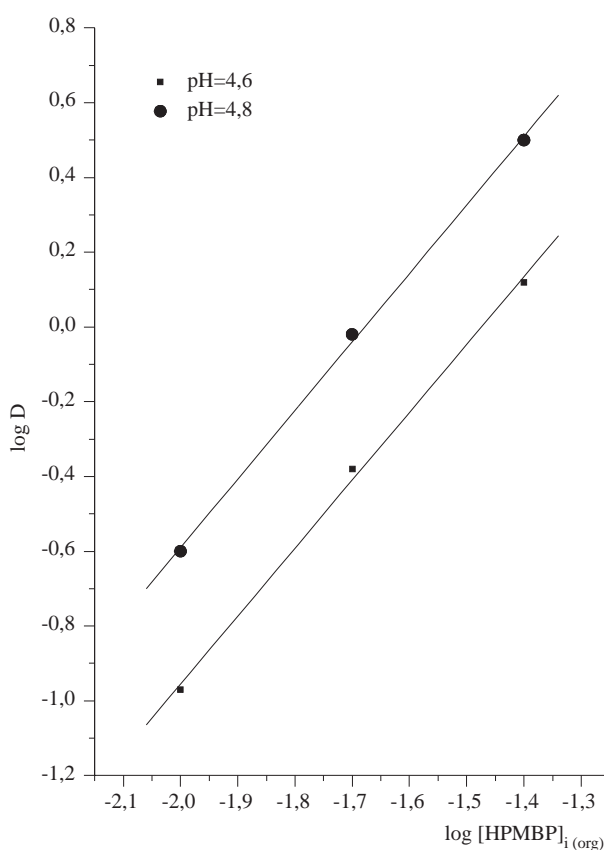
A study of the variation of  $\log D$  as a function of pH to constant  $[\text{HL}]_{(\text{org})}$  was performed in chloroform, toluene and methyl-isobutyl ketone. Figure 1 represents the curves of extraction  $\log D = f(\text{pH})$  at 25°C of zinc from sulfuric acid medium (ionic strength =1) for various concentrations of HPMBP. The curves obtained show that the extraction of zinc and cadmium increases with the concentration of HPMBP. The slopes are equal to 2 in all cases and the order of extraction is MIBK > Toluene ~ Chloroform.

### Effect of concentration of HPMBP

In Figure 2, the variation of  $\log D = f(\log[\text{HL}]_{i(\text{org})})$  to pH = 4.6 and pH = 4.8 of zinc by HPMBP in chloroform is presented. They are straight lines of slope  $\sim 2$ ; this explains the number of molecules of HL coordinated to the metal in the complex. The extraction process is described by equilibrium 2.



**Figure 1.**  $\text{Zn}^{2+}$  Extraction with HPMBP. Diluent: Chloroform. Sulfate Medium 0.33



**Figure 2.**  $\text{Zn}^{2+}$  Extraction with HPMBP. Diluent: Chloroform. Sulfate Medium 0.33 M.

### Effect of diluent

Extraction of zinc and cadmium by HPMBP is realized in by using the diluents chloroform, toluene and methyl-isobutyl ketone, which are described in Figure 3.

We summarize the experimental constant values of extraction  $K_{ex}$  in Table 1.

Moreover, when toluene was used as the diluent, the  $\log K_{ex}$  values of zinc and cadmium obtained were found to be close to those reported in the literature<sup>12</sup>.

**Table 1.**  $\log K_{ex}$  Values of Zinc and Cadmium in Different Diluents

Diluent	Toluene	Chloroform	MIBK
Zinc	- 6.16 - 6.20*	- 6.17	-3.76
Cadmium	- 9.01 - 9.50*	- 9.06	-6.11

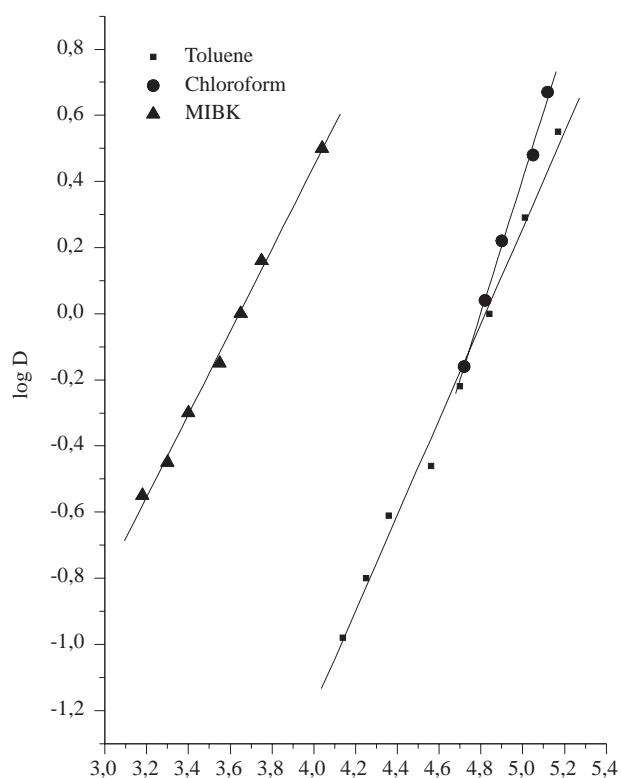
\* ref<sup>12</sup>

For the two metals, the best extraction was according to the following order: MIBK > Toluene ~ Chloroform.

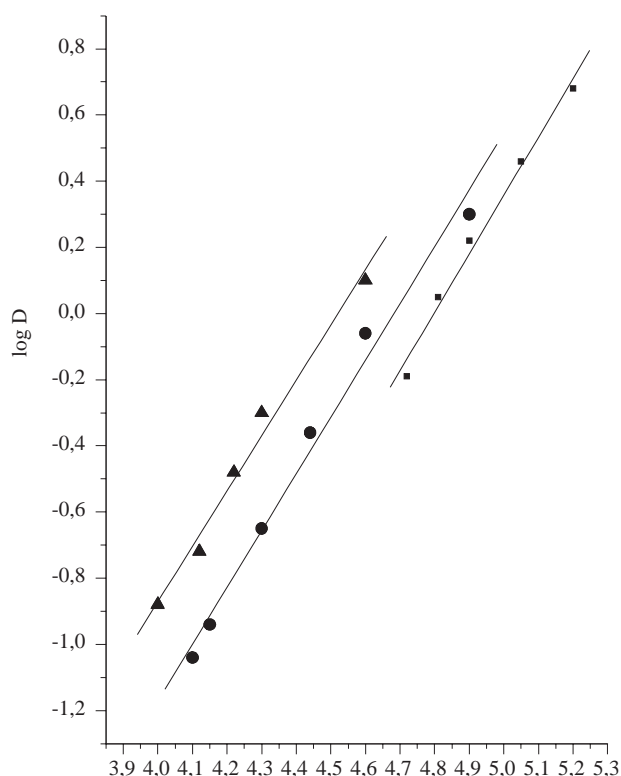
When one takes the methyl-isobutyl ketone as diluent, the extraction is found clearly improved. This explains by the fact that water molecules accompanying the metallic complex in the organic phase are replaced by molecules of MIBK.

### Effect of the ionic strength

Figure 4 represents the curves of variation of  $\log D = f(\text{pH})$  obtained during the extraction of zinc, presents in aqueous sulfate medium of ionic strength 1, 0.5 and 0.1. The analysis of these curves shows that the extraction of the metal increases when the value of ionic strength is between 1 and 0.1.



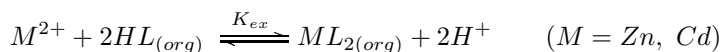
**Figure 3.**  $\text{Zn}^{2+}$  Extraction with  $[\text{HPMBP}]_{i(\text{org})}$  0.02 M. Sulfate Medium 0.33 M.



**Figure 4.**  $\text{Zn}^{2+}$  Extraction with HPMBP 0.02 M. Diluent: Chloroform. Sulfate Medium:  $\blacktriangle$  0.033;  $\bullet$  0.16 and  $\blacksquare$  0.33 M.

**a-Calculatoin of activity coefficients**

The extraction process is described by equilibrium 2:



with

$$K_{ex} = \frac{[ML_2]_{(org)}[H^+]^2\gamma_{ML_2(org)}\gamma_{H^+}^2}{[M^{2+}][HL]_{(org)}^2\gamma_{H^+}\gamma_{HL(org)}} \quad (6)$$

$$\log D_M = \log K_{ex} + 2 \log[HL]_{(org)} + 2pH + \log \frac{\gamma_{HL(org)}^2}{\gamma_{ML_2(org)}} - \log \frac{\gamma_{M^{2+}}}{\gamma_{H^+}^2} \quad (7)$$

The calculation of activity coefficients was made using the approximation of Debye and Hückel<sup>13</sup>.

$$-\log \gamma_A = \frac{0.5085Z_A^2\mu^{1/2}}{1 + 0.3281a_A\mu^{1/2}} \quad (8)$$

$\mu$  = ionic strength

$Z_A$  = the valency of A

$a_A$  = radius of the hydrated ion

We summarize values of activity coefficients  $\gamma_{M^{2+}}$  and  $\gamma_{H^+}$  in Table 2.

**Table 2.** Values of Activity Coefficients  $\gamma_{H^+}$  and  $\gamma_{M^{2+}}$ .

	$\mu$	$\gamma_{H^+}$	$\gamma_{M^{2+}}$	$\log \frac{\gamma_{M^{2+}}}{\gamma_{H^+}^2}$
Zinc	1	0.7437	0.2065	- 0.428
	0.5	0.7649	0.2504	- 0.368
	0.1	0.8258	0.4014	- 0.230
Cadmium	1	0.7437	0.1697	- 0.513
	0.1	0.8258	0.3771	- 0.257

It is noticed from this table that if  $\mu$  passes from 1 to 0.1,  $\log \frac{\gamma_{M^{2+}}}{\gamma_{H^+}^2}$  increases, and consequently  $\log D$  increases. The diminution of the ionic strength increases the extraction of the metal.

**b-Calculatoin of the constant of interaction**

The constant of interaction of  $Zn^{2+} - SO_4^{2-}$  equals 0.044<sup>12</sup> and  $Cd^{2+} - SO_4^{2-}$  equals 2 10<sup>2</sup><sup>13</sup>, as in the following equation:



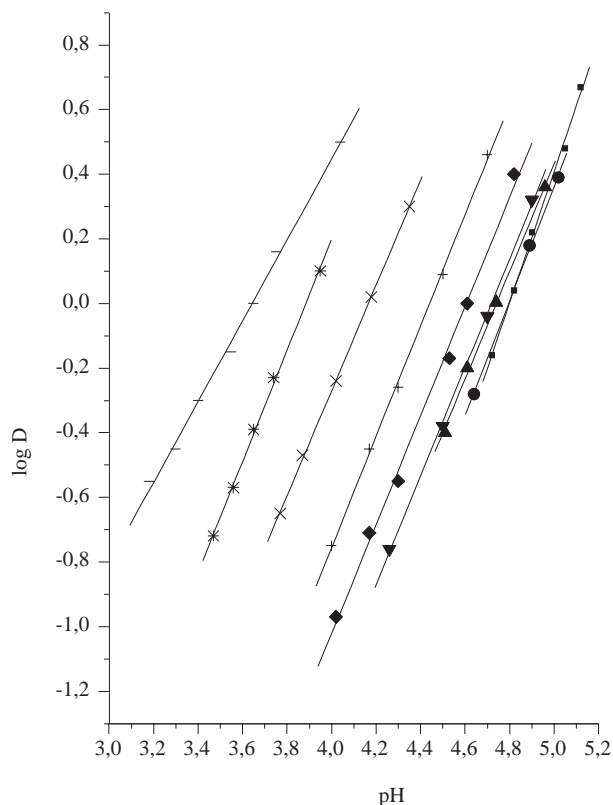
has for constant  $K_{int}$  such that,

$$K_{int} = \frac{[MSO_4]}{[M^{2+}][SO_4^{2-}]} \quad (10)$$

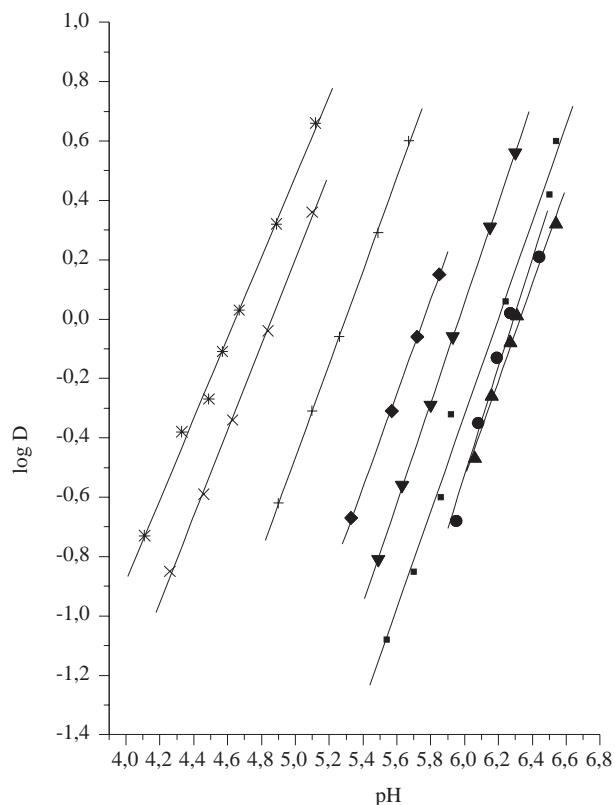
If  $\mu$  passes from 1 to 0.1, the concentration of sulfate ions decreases, and consequently the concentration of free metal ion increases. Therefore, the diminution of the ionic strength increases the extraction of the metal.

### Extraction of the Zn and Cd with HPMBP + MIBK

Figures 5 and 6 represent variations of log D with the pH obtained during the extractions by mixing benzoylpyrazolone and methyl-isobutyl ketone in the chloroform. The curves obtained are straight lines of slope  $\simeq 2$ .



**Figure 5.** Zn<sup>2+</sup> Extraction with [HPMBP]<sub>i (org)</sub> 0.02 M + [MIBK]<sub>i (org)</sub> ■ 0.0; ● 0.003; ▲ 0.01; ▼ 0.04; ◆ 1.0; + 2.0; × 4.0; × 6.0; × 8.0 M. Diluent: Chloroform. Sulfate Medium 0.33 M.



**Figure 6.** Zn<sup>2+</sup> Extraction with [HPMBP]<sub>i (org)</sub> 0.02 M + [MIBK]<sub>i (org)</sub> ■ 0.0; ● 0.01; ▲ 0.04; ▼ 1.0; ◆ 2.0; + 4.0; × 6.0; × 8.0 M. Diluent: Chloroform. Sulfate Medium 0.33 M.

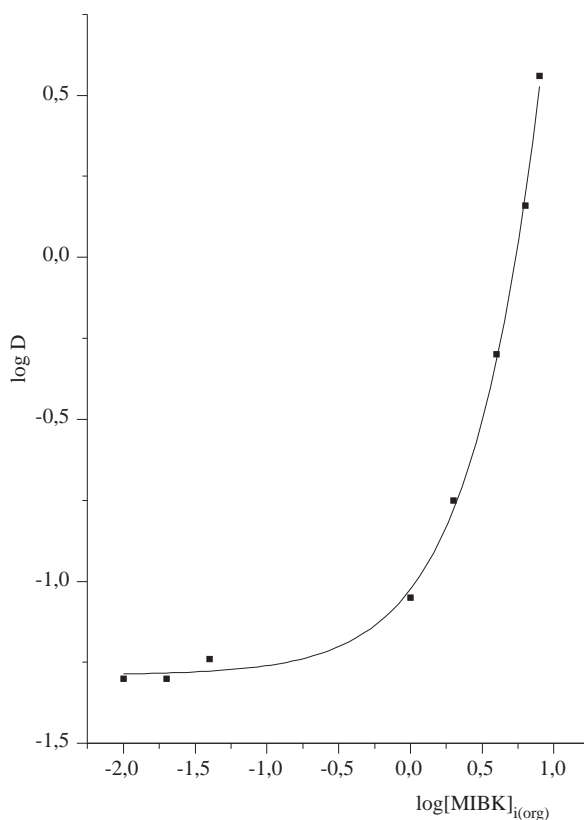
One can observe an important synergism when the concentration of MIBK in chloroform is more than 1 M. In very weak concentrations in MIBK, one observes a zero effect for the zinc and an antagonistic effect for the cadmium.

A study of the variation of log D as a function of [MIBK]<sub>i (org)</sub> to pH constant was performed (Figure 7). In the curve obtained for zinc, the profile is composed of many straight lines connected to each other, where the maximum slope is equal to 3. The slopes of these curves determine the number of molecules of MIBK coordinated to the metal in the complex.

One can observe that the latter curve's slope varies from 0 to 3. There is, therefore, a complex extraction of type  $ML_2$  (org),  $ML_2(MIBK)$  (org),  $ML_2(MIBK)_2$ (org) and  $ML_2(MIBK)_3$ (org).

For very weak concentrations on MIBK, a zero effect of synergism for the zinc can be explain by the interaction of HL and MIBK, and the solubility of MIBK in the aqueous phase of order 0.17 M. The antagonistic effect for the cadmium, other than interaction and the solubility of MIBK, is due to the difference between the interaction constants of Zn<sup>2+</sup> - SO<sub>4</sub><sup>2-</sup> and Cd<sup>2+</sup> - SO<sub>4</sub><sup>2-</sup>,  $K_{int(Zn^{2+}-SO_4^{2-})} = 0.044$

and  $K_{int(Cd^{2+}-SO_4^{2-})} = 2.10^2$ .



**Figure 7.** Zn<sup>2+</sup> Extraction with HPMBP + MIBK. Diluent: Chloroform. Sulfate Medium 0.33 M. pH = 4.0.

The extraction equilibrium synergic may be written as



$K_{e,s}$  was calculated for an experimental point from the equations

$$\log K_{e,s} = \log D - 2pH - 2 \log[HL]_{(org)} - x \log[MIBK]_{(org)} \quad (12)$$

$$[MIBK]_{(org)} = [MIBK]_{i(org)} - x[M]_{(org)} \quad (13)$$

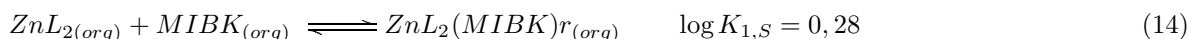
The constants of extraction equilibria of zinc and cadmium are given in Table 3.

**Table 3.** Extraction Processes of Metals with HPMBP + MIBK

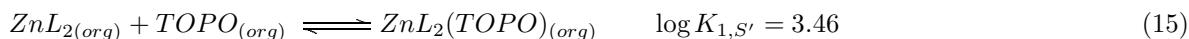
Equilibria	Cadmium	Zinc
$M^{2+} + 2 HL_{(org)} \rightleftharpoons ML_2_{(org)} + 2 H^+$	- 9.06	- 6.17
$M^{2+} + 2 HL_{(org)} + MIBK_{(org)} \rightleftharpoons ML_2(MIBK)_{(org)} + 2 H^+$	- 8.56	- 5.89
$M^{2+} + 2 HL_{(org)} + 2 MIBK_{(org)} \rightleftharpoons ML_2(MIBK)_2_{(org)} + 2 H^+$	- 8.40	- 6.22
$M^{2+} + 2 HL_{(org)} + 3 MIBK_{(org)} \rightleftharpoons ML_2(MIBK)_3_{(org)} + 2 H^+$	- 8.60	- 6.94



The effect of synergism observed in the equilibrium

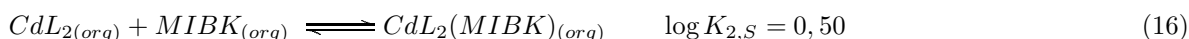


was very weak compared to that observed at TOPO in weak concentrations<sup>2</sup>.

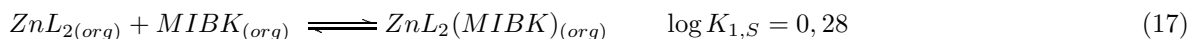


This difference is probably due to the greater possibility of TOPO complexing.

The effect of synergism observed in the equilibrium.

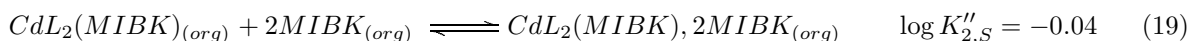


was greater than that observed with zinc.

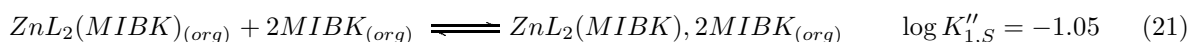


For high concentrations of MIBK, extracted complexes would be  $ML_2(MIBK)$ ,  $MIBK_{(org)}$  and  $ML_2(MIBK)$ ,  $2(MIBK)_{(org)}$ , in which the metal is not in its usual coordination. We think that the second and third molecule of MIBK would be in the second sphere of coordination.

Values of equilibrium constants



were higher than those observed with zinc.



One observes that the effect of cadmium solvation on the extraction is greater than that of zinc. This can be explained by the lower hydration of  $ZnL_{2(org)}$  than  $CdL_{2(org)}$  extracted in the organic phase. That is linked to the greater size of hydrated  $Cd^{2+}$  over the size of hydrated  $Zn^{2+}$ , and that gives the latter less facility to fix one or more molecules of MIBK. Therefore, the solute-solvent interaction is better in the complex of cadmium than in that of zinc.

## Conclusions

The extraction of zinc and cadmium by 1 - phenyl - 3 - methyl - 4 - benzoylpyrazol - 5 - one (HPMBP) in sulfate medium was studied in the following parameter functions:

- Concentration of HPMBP: the extraction increased with the concentration of HPMBP.
- Solvent: the extraction is best according to the following order: MIBK > toluene ~ chloroform.
- Ionic strength of the aqueous medium: the extraction decreased with the concentration of sodium sulfate.

- Synergism: one observes an important synergism when the concentration of MIBK in chloroform is more than 1 M. With very weak concentrations in MIBK, one observes a zero effect with zinc and an antagonistic effect with cadmium.

In the absence of MIBK, extracted complexes are  $ZnL_2(H_2O)_x$  (org) and  $CdL_2(H_2O)_y$  (org).

In the presence of MIBK, the curves of extraction show the presence of several species that depend on the concentration of MIBK. For very weak concentrations, the extracted complexes are  $ZnL_2(H_2O)_x$  (org) and  $CdL_2(H_2O)_y$  (org). For high concentrations, the extracted complexes are  $ML_2(MIBK)$  (org),  $ML_2(MIBK)_2$  (org),  $ML_2(MIBK)_3$  (org) and  $ML_2(MIBK)_4$  (org) ( M = Zn, Cd ).

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