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## Physics and Chemistry of Liquids

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### Ionic strength effect on the liquid-liquid extraction of zinc(II) and cadmium(II) from sulphate medium by 1-phenyl-3-methyl-4-benzoylpyrazol-5-one in chloroform

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# IONIC STRENGTH EFFECT ON THE LIQUID–LIQUID EXTRACTION OF ZINC(II) AND CADMIUM(II) FROM SULPHATE MEDIUM BY 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOL- 5-ONE IN CHLOROFORM

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The liquid–liquid extraction of zinc(II) and cadmium(II) from sulphate medium by 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP) in chloroform is studied. The ionic strength effect of the aqueous phase shows that the extraction of the metal increases with decreasing concentration of sulphate. At initially of about  $10^{-4}$  M with three different sulphate concentrations 0.033, 0.16 and 0.33 M in the aqueous phase, Zn(II) and Cd(II) are extracted as the complexes  $Zn(PMBP)_2$  and  $Cd(PMBP)_2$ . Sulphate complexes of Zn(II) and Cd(II) are formed in the aqueous phase. The metal–sulphate interaction has been made in evidence by using the Debye–Huckel extended limiting law of ionic activity coefficient.

*Keywords:* Liquid–liquid extraction; Ionic strength; Zinc(II); Cadmium(II); Activity coefficient

## 1. INTRODUCTION

Liquid–liquid extraction of metals in sulphate medium has not been studied widely because of its complexity [1]. However this medium remains very important from a practical point of view, and the metallic extractions undertaken from sulphuric acid solution are preferred in industrial applications.

At initially about  $10^{-6}$  M in the aqueous phase,  $Zn^{2+}$  is extracted as the complex  $ZnA_2 \cdot 2HA$ . The monosulphate, disulphate and trisulphate complexes of  $Zn^{2+}$  are formed in the aqueous phase in the presence of less than 0.25 M sulphate [2].

In a previous study, it has been shown that the extraction of a metal using a sulphate medium is less better than that in a perchlorate aqueous medium. This arises from

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the fact that the perchlorate being a noncomplexing medium and the sulphate being a moderate complexing commonly used medium [3].

Besides, the extraction of sulphuric acid as well as metallic sulphates is generally very weak because of the hydrophilic character of sulphate anions [4].

In the present work, the study of the liquid–liquid extraction of zinc(II) and cadmium(II) from sulphate medium with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP) in chloroform is carried out. Our interest is to study the effect of the ionic strength of the aqueous sulphate medium on the extraction of  $Zn^{2+}$  and  $Cd^{2+}$  and also to see if the complexes of metals could be formed in the aqueous phase using three different concentrations of sulphate 0.033, 0.16 and 0.33 M.

The Debye–Huckel extended limiting law of ionic activity coefficient has been introduced in order to gain information about the metal–sulphate interaction.

## 2. EXPERIMENTAL

### 2.1 Reagents and Solutions

1-phenyl-3-methyl-4-benzoylpyrazol-5-one was prepared according to Jensen method [5]. Chloroform was pre-equilibrated with aqueous solution which did not contain any metal. The concentrations of  $Na_2SO_4$  of the aqueous medium were 0.033, 0.16 and 0.33 M. The initial compositions of the phases were as follows.

Aqueous phases:  $[Zn^{2+}]_i = 7.65 \times 10^{-4}$  M,  $[Cd^{2+}]_i = 4.45 \times 10^{-4}$  M;

Organic phase :  $[HPMBP]_{i,org} = 0.01, 0.02$  and  $0.04$  M in chloroform.

### 2.2 Extraction and Analytical Procedure

Extractions were performed in thermostated vessels at 25°C. Equal volumes (40 mL) of both phases were contacted under magnetic stirring until the equilibrium was attained (max 30 min) and then separated by gravity. The pH adjusted by NaOH 0.1 M solutions of suitable compositions. For each experimental point, aliquots of the two phases were withdrawn and the metal was stripped from the organic aliquot with 0.1 M  $H_2SO_4$ . Metal concentrations were determined after suitable dilution by flame atomic absorption using a 2380 Perkin Elmer spectrophotometer.

## 3. RESULTS AND DISCUSSION

### 3.1 Liquid–Liquid Extraction of Zinc(II) and Cadmium(II) with HPMBP in Chloroform at Constant Ionic Strength

The overall reaction in the extraction of zinc(II) and cadmium(II) with HPMBP (HL) in chloroform from sulphate aqueous medium of ionic strength ( $I = 1.0 \text{ mol kg}^{-1}$ ), may be expressed as



$M = Zn, Cd$ ; org denotes species in organic phase.

The extraction constant,  $K_{\text{ex}}$ , is defined as Eq. (2) and is rewritten as Eq. (3) by using the distribution ratio,  $D_M$ , of the metals.

$$K_{\text{ex}} = \frac{[\text{ML}_n(\text{HL})_m]_{\text{org}}[\text{H}^+]^n}{[\text{M}^{2+}][\text{HL}]_{\text{org}}^{n+m}} \quad (2)$$

$$\log D_M = \log \frac{[\text{M}]_{\text{org}}}{[\text{M}]} = \log K_{\text{ex}} + (n+m)\log[\text{HL}]_{\text{org}} + n\text{pH} \quad (3)$$

Plots of  $\log D_M$  versus pH for various concentrations of HPMBP, were linear with a slope of 2, as shown in Figs. 1 and 2. Likewise, plots of  $\log D_M$  versus  $\log [\text{HL}]_{\text{org}}$  at constant pH values were also linear with a slope of 2 in all the extraction systems, as shown in Figs. 3 and 4. These results reveal that  $n=2$  and  $m=0$  in Eq. (1), i.e., only a complex,  $\text{ML}_2$ , is extracted into chloroform. The logarithmic values of  $K_{\text{ex}}$  of zinc(II) and cadmium(II) can therefore be calculated for each experimental point ( $\log K_{\text{ex, Zn}} = -6.17$ ;  $\log K_{\text{ex, Cd}} = -9.06$ ).

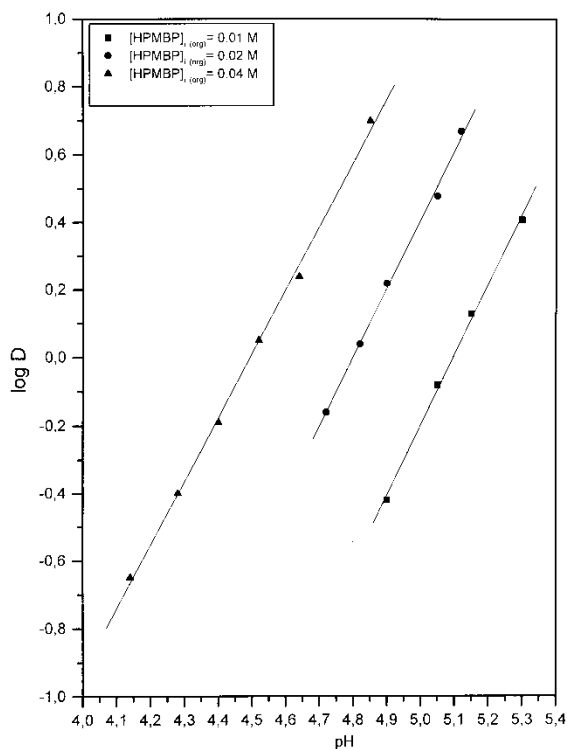


FIGURE 1 pH effect on the  $\text{Zn}^{2+}$  extraction with HPMBP in chloroform; sulphate medium 0.33 M.

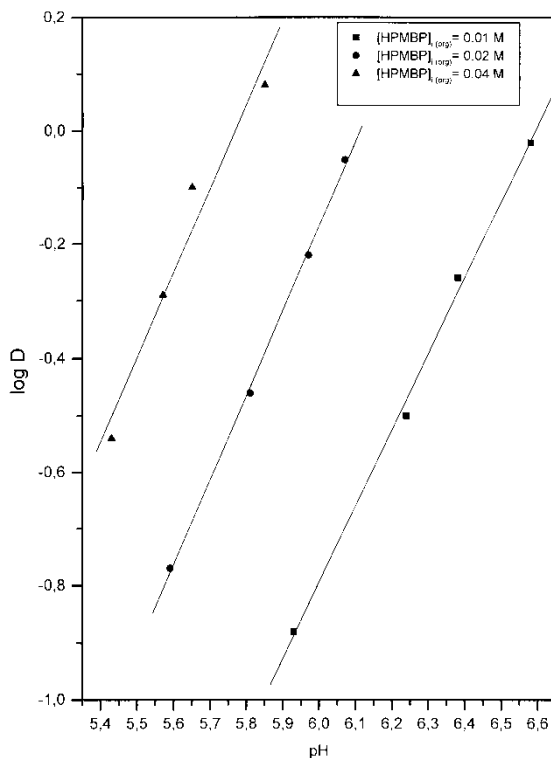


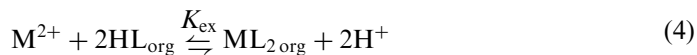
FIGURE 2 pH effect on the  $\text{Cd}^{2+}$  extraction with HPMBP in chloroform; sulphate medium 0.33 M.

### 3.2 Liquid–Liquid Extraction of Zinc(II) and Cadmium(II) with HPMBP in Chloroform for Various Ionic Strengths

Figures 5 and 6 represent plots of  $\log D_M$  versus pH obtained during the extraction of zinc(II) and cadmium(II) at various ionic strengths 0.1, 0.5 and 1.0  $\text{mol kg}^{-1}$  (i.e.  $[\text{Na}_2\text{SO}_4] = 0.033, 0.16$  and  $0.33$  M respectively). As it is shown on these figures, the extraction of the metal increases when the ionic strength decreases.

The activity coefficient may be introduced as a useful parameter to explain the effect of the ionic strength upon the liquid–liquid extraction of zinc(II) and cadmium(II) from sulphate medium into chloroform.

The extraction process may be described by the following equilibrium:



The extraction constant,  $K_{\text{ex}}$ , describing this process may be expressed in terms of the activity coefficients i.e.,

$$K_{\text{ex}} = \frac{[\text{ML}_2]_{\text{org}} [\text{H}^+]^2 \gamma_{\text{ML}_2\text{org}} \gamma_{\text{H}^+}^2}{[\text{M}^{2+}] [\text{HL}]_{\text{org}}^2 \gamma_{\text{M}^{2+}} \gamma_{\text{HL}_{\text{org}}}^2} \quad (5)$$

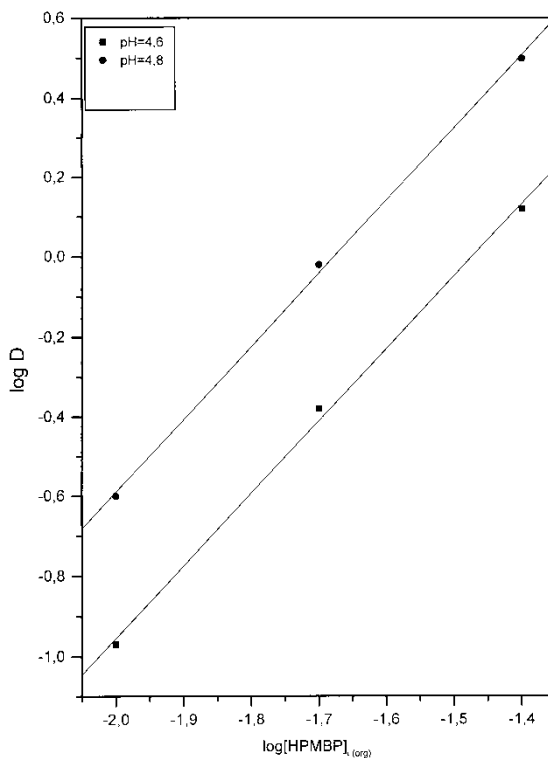


FIGURE 3 Concentration effect of HPMBP in chloroform on the  $Zn^{2+}$  extraction; sulphate medium 0.33 M.

The logarithmic values of  $D_M$  can, therefore, be deduced

$$\log D_M = \log K_{ex} + 2 \log [HL]_{org} + 2pH + \log \frac{\gamma_{HL_{org}}^2}{\gamma_{ML_{2org}}} + \log \frac{\gamma_{M^{2+}}}{\gamma_{H^+}^2} \quad (6)$$

$\log (\gamma_{HL_{org}}^2 / \gamma_{ML_{2org}})$  of the organic phase does not vary because it is independent of the ionic strength of the aqueous phase. Therefore, at constant pH the values of  $\log D_M$  depend upon  $\log (\gamma_{M^{2+}} / \gamma_{H^+}^2)$ .

The ionic activity coefficients can be determined using the extended Debye-Huckel limiting law by taking into account the size of the ions ( $a_i$ ), [6]

$$-\log_{10} \gamma_A = \frac{A_m z_A^2 I_m^{1/2}}{1 + B_m a_i I_m^{1/2}} \quad (7)$$

where, on the molality scale, the constants  $A_m$  and  $B_m$  are defined by

$$A_m = \left( \frac{2\pi N d_0}{1000} \right)^{1/2} \frac{e^3}{2.3026 (kTD)^{3/2}} \quad (8)$$

and

$$B_m = \left( \frac{8\pi N d_0}{1000} \right)^{1/2} \frac{e}{(kTD)^{1/2}} \quad (9)$$

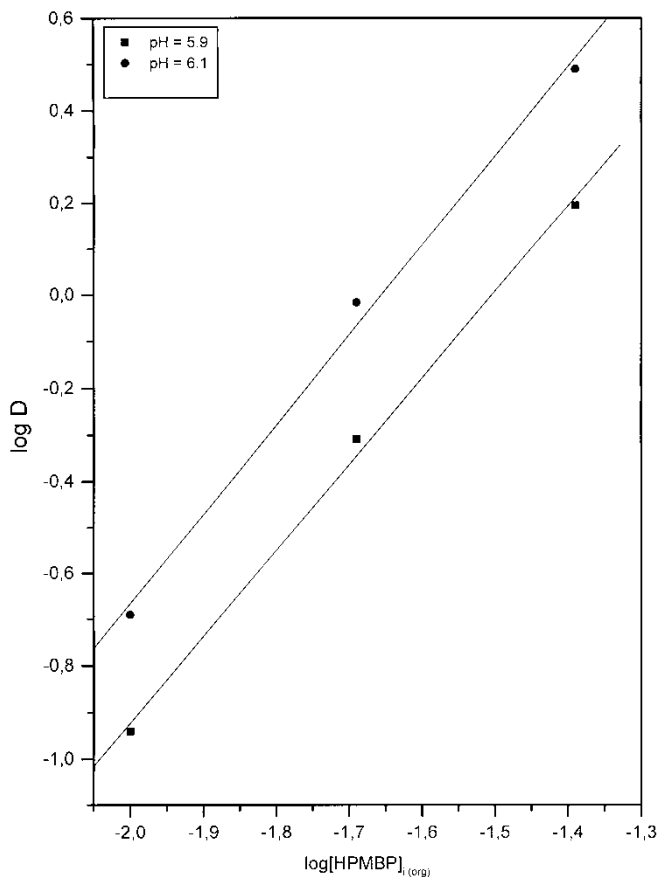


FIGURE 4 Concentration effect of HPMBP in chloroform on the  $\text{Cd}^{2+}$  extraction; sulphate medium 0.33 M.

In the formulae (8) and (9),  $e$ ,  $N$ ,  $d_0$ ,  $k$ ,  $T$ ,  $D$  and  $z_A$  represent respectively the magnitude of the electron charge, the Avogadro constant, the density of the solvent, the Boltzmann constant, the absolute temperature, the dielectric constant of the solvent, and the valency of the cation.

Since in Eq. (7), the ionic size ( $a_i$ ) is not clearly defined [6,7], it has been introduced by us as the radius of hydrated cation. The values of the hydrated radii ( $a_i = r_H$ ) used for the tabulation of the ionic activity coefficient values of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{H}_3\text{O}^+$  are taken from [8]. The calculated values of these ionic activity coefficients are summarised in Table I.

As it is shown on Table I,  $\log(\gamma_{\text{M}^{2+}}/\gamma_{\text{H}^+}^2)$  decreases with increasing values of the ionic strength and, therefore,  $\log D$  decreases according to Eq. (6). This result agrees satisfactorily with the experimental values shown on Figs. 5 and 6.

In addition,  $\Delta \log D$  between two different ionic strengths for zinc(II) and cadmium(II) are deduced graphically from these figures. Their values are reported along with those of  $\Delta \log(\gamma_{\text{Zn}^{2+}}/\gamma_{\text{H}^+}^2)$  and  $\Delta \log(\gamma_{\text{Cd}^{2+}}/\gamma_{\text{H}^+}^2)$  in Table II.

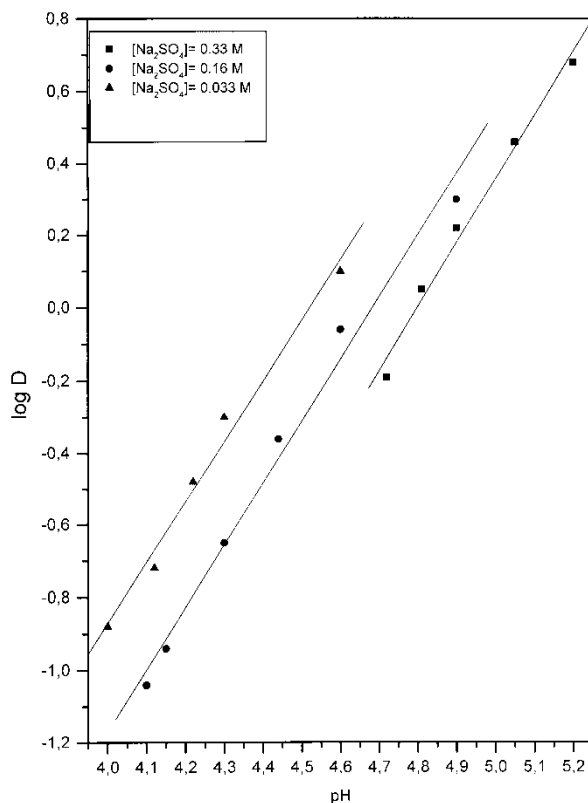


FIGURE 5 Ionic strength effect on the  $\text{Zn}^{2+}$  extraction with HPMBP 0.02 M in chloroform.

It is noticed in Table II that values of  $\Delta \log D_M$  are always different from those of  $\Delta \log (\gamma_{\text{M}^{2+}}/\gamma_{\text{H}^+}^2)$ . This difference may be due to the fact that the  $\text{M}^{2+}-\text{SO}_4^{2-}$  interaction has not been taken into account i.e. ( $a_i=r_{\text{H}}$ ) during the calculation of the ionic activity coefficients using the extended Debye-Huckel limiting law (Eq. (7)).

The curves illustrated by Figs. 5 and 6 could be in good agreement with the formation of the complexes  $\text{ZnSO}_4$  and  $\text{CdSO}_4$  not extractible, which would reduce the concentration of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  and thus decrease their extraction.

In the experimental conditions, this hypothesis becomes valid when the interaction constant of  $\text{M}^{2+}-\text{SO}_4^{2-}$  is taken into account (equilibrium (10)).



The interaction constant value of  $\text{Zn}^{2+}-\text{SO}_4^{2-}$  is equal to 0.42. It has been determined previously by making the difference between the extraction constants of zinc(II) in sulphate and perchlorate aqueous media [9], while the interaction constant of  $\text{Cd}^{2+}-\text{SO}_4^{2-}$  is given by [8] ( $K_{\text{int}} = 2 \times 10^2$ ).



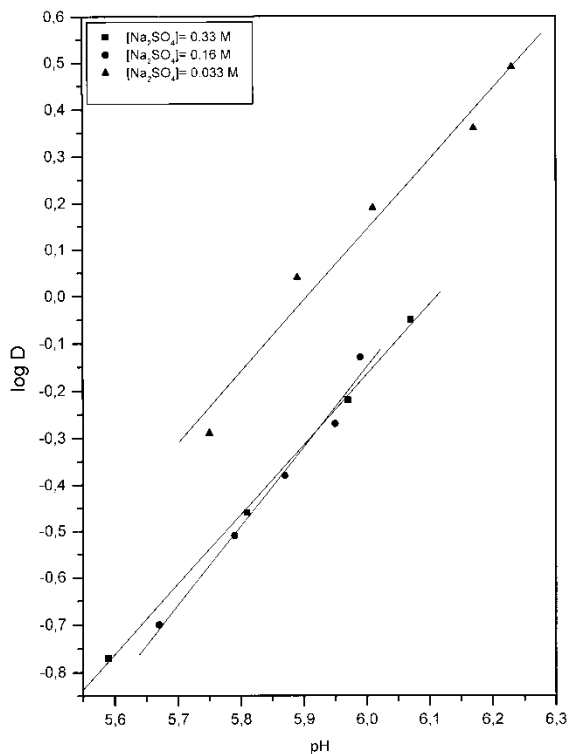


FIGURE 6 Ionic strength effect on the  $\text{Cd}^{2+}$  extraction with HPMBP 0.02 M in chloroform.

TABLE I The calculated values of the ionic activity coefficients of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{H}^+$  at 25°C

Cation	Ionic strength (mol kg <sup>-1</sup> )	Ionic activity coefficient $\gamma_A$	$\log(\gamma_{\text{M}^{2+}}/\gamma_{\text{H}^+}^2)$
$\text{Zn}^{2+}$	0.1	0.4000	-0.2309
$\text{Zn}^{2+}$	0.5	0.2492	-0.3697
$\text{Zn}^{2+}$	1.0	0.2054	-0.4292
$\text{Cd}^{2+}$	0.1	0.3757	-0.2582
$\text{Cd}^{2+}$	0.5	0.2146	-0.4346
$\text{Cd}^{2+}$	1.0	0.1687	-0.5147
$\text{H}^+$	0.1	0.8251	
$\text{H}^+$	0.5	0.7641	
$\text{H}^+$	1.0	0.7429	

TABLE II Comparison between values of  $\Delta \log(\gamma_{\text{M}^{2+}}/\gamma_{\text{H}^+}^2)$  and  $\Delta \log D_M$

Ionic strength variation	$\Delta \log D_{\text{Zn}}$	$\Delta \log(\gamma_{\text{Zn}^{2+}}/\gamma_{\text{H}^+}^2)$	$\Delta \log D_{\text{Cd}}$	$\Delta \log(\gamma_{\text{Cd}^{2+}}/\gamma_{\text{H}^+}^2)$
0.1 → 0.5	0.27	0.1388	0.29	0.1764
0.5 → 1.0	0.21	0.0595	0.01	0.0801
0.1 → 1.0	0.48	0.1983	0.30	0.2565

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