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# Study of Complex Formation Between Iodoquinol (IQ) and $\text{Co}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ and $\text{Zn}^{2+}$ Cations in Binary Aqueous / Non-aqueous Solvent Using Spectrophotometry

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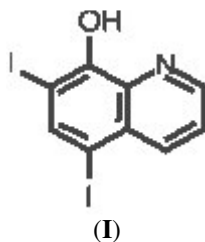
**Abstract:** The complexation reactions between iodoquinol and  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  cations were studied in different DMF/ $\text{H}_2\text{O}$  binary mixtures at the ionic strength of 0.1 (using  $\text{NaNO}_3$ ). The spectrophotometric method was used for the determination of formation constants and the stoichiometries. The stoichiometry of the complexes is established 1:1 by Job's and mole ratio methods. It was found that the stability constants of the complex formed between the ligand (IQ) and the cations in the all cases increase with increasing of the non-aqueous solvent. In the most cases the maximum formation constants between  $\text{Zn}^{2+}$  ion and IQ were obtained respect to the other cations.

**Keywords:** Iodoquinol, spectrophotometry, binary solvent, cation, formation constant

## Introduction

Iodoquinol is an amebicidal drug. It is one of the iodinated derivations of 8-hydroxyquinoline that has been widely used in the treatment of various intestinal and vaginal infections<sup>1</sup>. The chemical structure of IQ is shown in (I).

The complexation ability of some quinolines with different cations such as Sn(IV), Cu(II), Co(II), and Nb(V) have been investigated using different spectrophotometric techniques<sup>2-6</sup>. The colorimetric<sup>7</sup> and HPLC methods for the separation and determination of Nickel(II) complexes with 8-hydroxyquinolines has been reported<sup>8</sup>.



There is an increasing interest in the study of the complexation reactions in binary mixed solvent systems and their interpretation in terms of solute's preferential solvation by one of the mixed solvent components<sup>9-20</sup>. Actually, there is a simple coordination model in mixed solvents which assumes that all the thermodynamic changes in the system results from the successive replacement of the molecules of one solvent by those of a second solvent in the coordination sphere of the solute<sup>21,22</sup>. Various physicochemical methods have been used to obtain the stability constants of complexes. From the various techniques the spectrophotometry has proved to be a useful means for investigation of both the stoichiometry and the stability of complexes.

In this paper the spectrophotometric method for the study of  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  complexes with IQ in various DMF/ $\text{H}_2\text{O}$  mixtures was used to investigate the effect of solvent properties on the stabilities of the resulting complexes.

## Experimental

### *Reagents and solvents*

sodium nitrate, lead(II) nitrate, manganese(II) chloride, cobalt(II) chloride, zinc(II) nitrate, cadmium(II) nitrate acetic acid, sodium acetate and *N,N*-dimethyl formamide were obtained from Merck as analytical reagent grade materials and were used without further purification. Iodoquinol was purchased from Aldrich. All dilute solutions were prepared from double-distilled water, with specific conductance equal to  $(1.3 \pm 0.1) \mu\Omega^{-1}\text{cm}^{-1}$ .

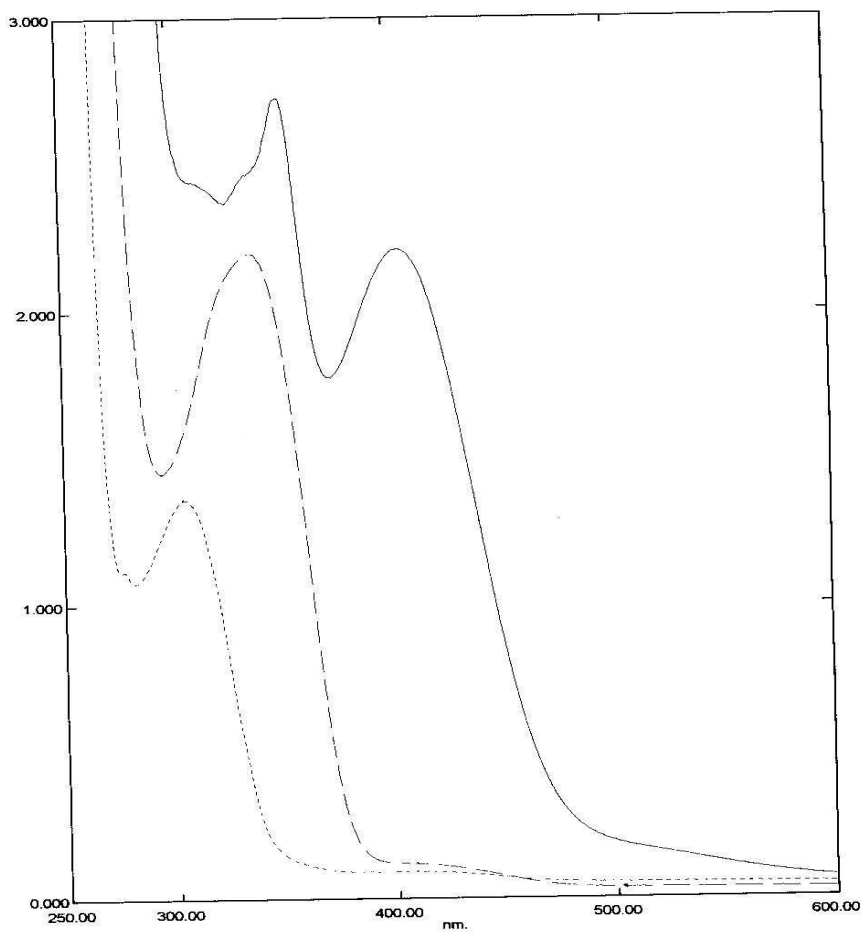
### *Apparatus*

UV-VIS absorption spectra and measurements were performed with a SHIMADZU, UV-VIS-2550 spectrophotometer. All measurements were done at pH 7.3 (using acetic acid /sodium acetate) and room temperature. The ionic strength was fixed at 0.1 using  $\text{NaNO}_3$  solution.

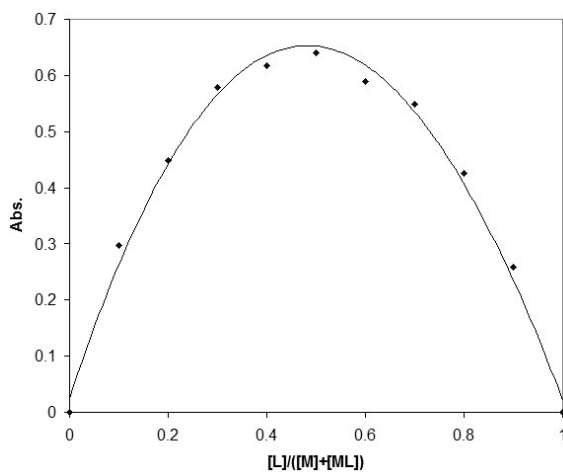
## Results and Discussion

The UV-VIS spectra corresponding to the cations, ligand and complexes were obtained in DMF system. The concentration of cations and ligand were 0.1mM. Figure 1, shows the  $\text{Zn}^{2+}$ -IQ complex spectra in DMF solution. As it is shown in Figure 1, the maximum absorption is at 404.5 nm.

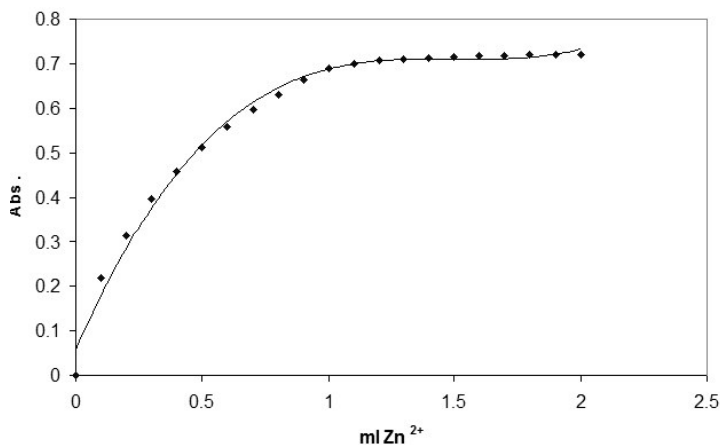
The stoichiometry of the complexes in DMF solvent were obtained by Job and molar ratio methods<sup>23,24</sup>. A sample of resulting plots are shown in Figure 2 (Job method) and Figure 3 (mole ratio method). In the molar ratio method, the cation solutions (5 mM) were added to the ligand solution (10 mL, 0.5 mM) in separate steps. The ligand doesn't dissolve in water, so we dissolved it in DMF. The stoichiometry of the all complexes that is studied in this work were obtained 1:1.



**Figure.1.** The UV-VIS spectra of Zn<sup>2+</sup> (.....) ; IQ (-----) and Zn<sup>2+</sup>- IQ (—) solutions.



**Figure 2.** The continuous variation plot for Zn<sup>2+</sup>-IQ in DMF solutions.



**Figure 3.** The molar - ratio method. [IQ] = 0.5 mM and [Zn<sup>2+</sup>] = 5 m M.

The formation of a 1:1 complex between a ligand (L) and cation (M) can be described by:



The corresponding stability constant is defined as:

$$K_f = \frac{[ML]}{[M][L]} = \frac{[ML]}{([M]_i - [ML])([L]_i - [ML])} \tag{2}$$

That [ML] = complex concentration, [M] = equilibrium concentration of cation, [L] = equilibrium concentration of ligand, [M]<sub>i</sub> = initial concentration of cation and [L]<sub>i</sub> = initial concentration of ligand. If only the complex forming complex has an absorption at a certain wavelength, the experimentally measured absorptivity is given by the equation (3):

$$A = \epsilon b[ML] \tag{3}$$

If [M]<sub>i</sub> >> [L]<sub>i</sub>, the equation (2) can be transformed in to the equation (4) (with b = 1)

$$K_f = \frac{\frac{A}{\epsilon}}{[M]_i \left( [L]_i - \frac{A}{\epsilon} \right)} \tag{4}$$

With some changing, the equation (4) will be transformed in to the equation (5)

$$\frac{[M]_i [L]_i}{A} = \frac{[M]_i}{\epsilon} + \frac{1}{\epsilon K_f} \tag{5}$$

The plotting of  $\frac{[M]_i [L]_i}{A}$  as a function of [M]<sub>i</sub> gets a straight line with the slope of  $\frac{1}{\epsilon}$ . From

this slope the molar absorptivity ( $\epsilon$ ) of the complex can be calculated. The intercept of this straight line will be equal to  $\frac{1}{\epsilon K_f}$  which gives the formation constant of the complex.

The stability constants of the 1:1 metal ion-IQ complexes in different water-DMF solvent mixtures were obtained at room temperature by measuring the absorbance of the complexes at  $\lambda_{max}$  of the complexes. During the experiments the solution of the metal cations with concentration (1-3 mM) were added to the solution of IQ in a separate steps.

The data given in Table 1 clearly indicate the effect of the solvent properties on the stability of complexes. In the all cases of this study there is an reverse relationship between

the stabilities of complexes and the amount of water in the binary mixed solvents. The stability of complexes of the metal cations with IQ in the most cases decrease in the order of  $Zn^{2+} > Co^{2+} > Pb^{2+} > Cd^{2+} > Mn^{2+}$ .

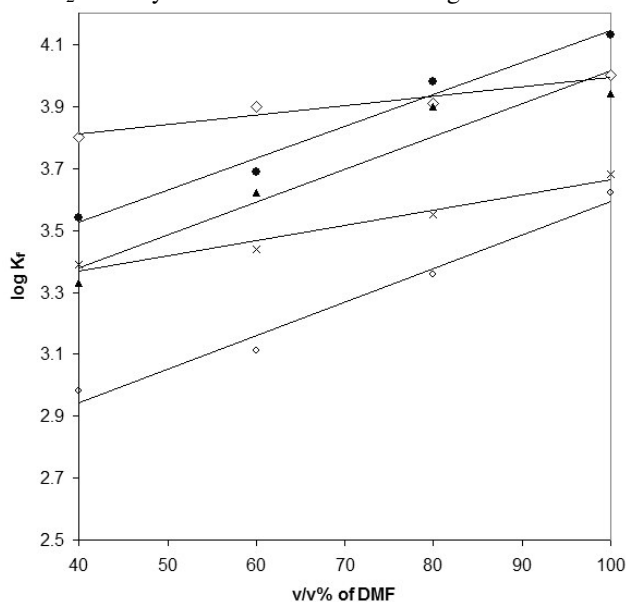
**Table 1.** The results of stability constants for the complexation reactions of  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  ions with IQ in various DMF/ $H_2O$  binary mixtures.

v/v% DMF	Log $K_f \pm S^a$				
	$Zn^{2+}$	$Co^{2+}$	$Pb^{2+}$	$Cd^{2+}$	$Mn^{2+}$
100	4.13± 0.01	4.00± 0.01	3.94± 0.01	3.68± 0.07	3.62± 0.02
80	3.98± 0.01	3.91± 0.08	3.90± 0.02	3.55± 0.01	3.36± 0.03
60	3.69± 0.01	3.90± 0.08	3.62± 0.00	3.44± 0.03	3.11± 0.09
40	3.54± 0.01	3.80± 0.09	3.33± 0.01	3.39± 0.08	2.98± 0.03
20 <sup>b</sup>	<sub>b</sub>	<sub>b</sub>	<sub>b</sub>	<sub>b</sub>	<sub>b</sub>

<sup>a</sup> standard deviation (n = 3).

<sup>b</sup> At this composition of binary mixed solvents( also less than 20%), during the complexation experiments, we observed a precipitation in the solutions.

The stability of a complex formed in a solution strongly depends on the nature of the solvent medium<sup>25</sup>. During the complexation, the ligand should be able to replace the solvent molecules as completely as possible in the first solvation shell of the cation, or the cation should be able to replace the solvent molecule with the ligand. Therefore, the variation of the solvent produces a significant change in the binding properties and selectivity of the ligand for a certain cation over the others. Very few data about the complexation reactions between IQ and metal cations in binary systems as well as mixed solvents are available in literature. The variation of the formation constants of IQ complexes with  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  ions with solvent compositions in DMF/ $H_2O$  binary mixture are illustrated in Figure 4.



**Figure 4.** The variation of stability constants of the different metal ion complexes of IQ in DMF/ $H_2O$  binary systems. The curves show: (▲)  $Pb^{2+}$ -IQ ; (○)  $Mn^{2+}$ - IQ ; (\*)  $Zn^{2+}$ - IQ ; (◇)  $Co^{2+}$ -IQ and (×)  $Cd^{2+}$ - IQ.

As it is shown in Figure 4, the stability constants of all complexes increase with increasing the amount of DMF in the DMF/H<sub>2</sub>O binary mixtures. In a weak solvating solvent system such as DMF, which has a low donor number (DN=26.2), the solvating of the metal cations and the ligand should be less than H<sub>2</sub>O with bigger donor number (DN=33)<sup>25</sup>. Therefore, less energy is need at the desolvation step of Co<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> cations and IQ during the complex formation in DMF than in H<sub>2</sub>O.

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