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Potentiometric studies of metal Complexes of 4-(4-nitrophenylazo) resorcinol (magneson) with Co(II), Cu(II), and Zn(II) ions in mixed solvent

Nabil Bader[a], Tagdida Hiba, Younis Ben Amer[b], Zainab Al borki, and Aziza Ahmida

Department of Chemistry, Faculty of Science, University of Benghazi, Benghazi, Libya

A B S T R A C T

In this research work, the acid dissociation constants of 4-(4-nitrophenylazo) resorcinol = **L1** and the formation constant of the metal chelates formed by this ligand with Co(II), Cu(II), and Zn (II) have been determined Potentiometrically at 288K in 75% ethanol-water mixture at 0.1M KNO$_3$ ionic strength against 0.1 M KOH. The stability constants of metal complexes were detected at different temperatures.

The thermodynamics parameters such as ΔG, ΔH and ΔS of binary complexes were determined using the Vant-Hoff equations to measure the effect of temperature on the stability of **4-(4-nitrophenylazo) resorcinol** complexes with metal ion. The influence of solvents on the free ligand and their metal complexes have been determined and discussed.

Introduction

O-Hydroxydiarylazo compounds, like 4-(4-nitrophenylazo) resorcinol (magneson) have attracted much attention, as they are very weak acids that exist in solution as an equilibrium mixture of strongly hydrogen-bonded azo and hydrazone forms [1,2].

They have been used in dyestuffs, as spectrophotometric and titrimetric reagents, and in solvent extraction studies [3]. Also in many other uses in the industry of color and pigments, food colorant, pesticides and in the medical and pharmaceuticals [4].

They have been studied widely because of their excellent thermal and optical properties in applications [2,5], they have reactive groups (heterocyclic nitrogen azo, and *o*-hydroxy groups which can potentially coordinate to metal ions.

However , 4-(4-Nitrophenylazo) resorcinol also known as azo violet or magneson I. it is a red colour powder, it is used as a spot test reagent and forms blue lake on reaction with Mg(OH)$_2$ in alkaline solution. It is mainly used for determining the presence of magnesium in the solution of 4-(4-Nitrophenylazo) resorcinol. It is act as a pH indicator.

O-Hydroxydiarylazo reagent like 4-(2-thiazolylazo) resorcinol form metal complexes with Co(II), Cu(II), and Zn (II) and others metals [6-8].

In addition to the utilization of azo compounds in the analytical chemistry fields due to their abilities to coordinate with different ions and detected them in trace amounts due to their sensing to these trace amounts of metal ions, using different techniques of analysis. [1]

This study is focusing on the synthesis of metal complexes of Co(II), Cu(II), and Zn(II) with 4-(4-nitrophenylazo) resorcinol (magneson) in mixed solvent system (Ethanol-Water) at different conditions and their stability constant and formation constant of metal complexes have been determined by by potentiometric method. More ever the thermodynamics of binary complexes were determined using the Vant-Hoff equation to measure the effect of temperature on the stability of 4-(4-nitrophenylazo) resorcinol complexes with metal ion. recorded at room temperature (25˚C) by using a conductivity meter, Mod CMD 750 WPA. A jenway pH- meter has been used for potentiometric measurements

Experimental

Materials and Methods:

All materials and reagents used in the work were of the highest available purity. Mixtures were titrated against standard 0.1M- KOH in vol. 75% ethanol-water mixture at 288, 298 and 308K respectively. The Conductivity measurements of metal complexes were recorded at room temperature (25˚C) by using a conductivity meter, Mod CMD 750 WPA. A jenway pH- meter has been used for potentiometric measurements.
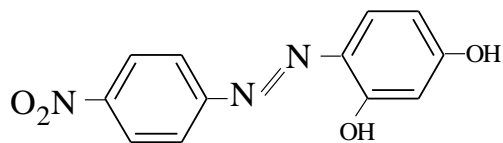
Preparation of the 4-(4-Nitrophenylazo) resorcinol (magnasone) (L₁) .

The Magnesone ligand (**L₁**) was prepared by dissolving (3ml, 25mmol) in absolute ethanol and distilled water to give a solution of 0.01M concentration at room temperature. The chemical structure of L1 are shown in Scheme1

O_2N — ... — $N=N$ — ... — OH / OH

Log K

	288 (K)	298 (K)	308 (K)
Free ligand	4.53	4.58	4.43
Co(II)	4.85	4.88	4.87
Cu(II)	5.80	5.52	4.92
Zn(II)	5.00	4.97	4.90

Schem 1. Chemical structure of 4-(4-nitrophenylazo) resorcinol. (**L₁**)

KOH solution

0.1M solution of potassium hydroxide was prepared by dissolving the amount of KOH in 75% (v/v) ethanol-water.

Metal Ion Solutions

0.10 M solutions of the metal ions were prepared by dissolving the appropriate masses of the metal nitrate salt in total volume of 250 mL. distilled water.

Results and discussion

Potentiometric titration curves of the free ligand and mixtures of (metal ion–ligand) with KOH solution are shown in Fig.1. The complexation process occur as the pH value decreases in case of presence of metal ions, which indicates the formation of complexes which represent the equilibrium in the solution, the bonding may occur through oxygen atom of the hydroxyl group by displacement of protons and the lone pair electrons of the azo nitrogen atom. Potentiometric titration curves of the free ligand and mixtures of (metal ion–ligand) with KOH solution are shown in Fig.1. The complexation process occur as the pH value decreases in case of presence of metal ions, which indicates the formation of complexes which represent the equilibrium in the solution, the bonding may occur through oxygen atom of the hydroxyl group by displacement of protons and the lone pair electrons of the azo nitrogen atom.
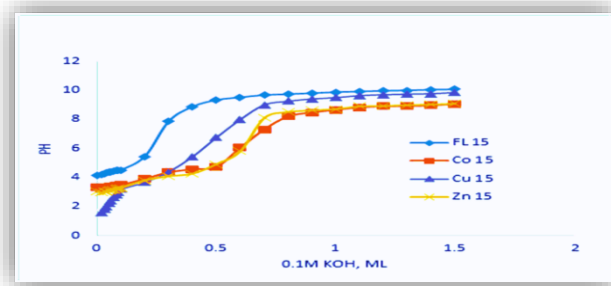

Figure (1): Titration curves of magneson (L1) at the presence and absence of metal ions at 15°C and 0.1 M KNO₃ ionic strength.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions($\bar{n}$) vs. the free ligand exponent (pL) according to Irving and Rossotti equation (1)[10].

$$Log[\bar{n}/(1-\bar{n})] = logK - pL \qquad (eq.1)$$

Even more, The influence of temperatures on the dissociation constant and their stability constants L1 drived for Co(II), Cu(II), and Zn (II) in 75% (v/v) ethanol-water have been measured at three different temperatures 288, 298, 308 K at constant ionic strength (0.1M KNO₃) and, the data are listed in Table 1, in order to calculate the thermodynamical parameters, ΔH, ΔS, and ΔG.

Table1: Stability constants of L₁ and their metal complexes with Co(II), Cu(II), and Zn(II) metal ions at different temperatures

The results in Table 1 shows that the dissociation

constant values increase with increase in temperature and this indicates that, the acidity of the ligand increases with increasing of temperature. Also the stability constant log K for the complexes decrease with increasing temperature which means that complexation process favors the lower temperatures.

The increasing order of stability constant with respect to the metal ions were found to be Cu > Zn > Co which is also in agreement with that of Irving and Williams order [9].

Copper complex is more stable than Zn and Co due to the tetragonal distortion of the octahedral symmetry in the coordination sphere [10-15]. Copper can form square planar complex while Co(II) and Zn(II) form octahedral or tetrahedral complex.

All thermodynamic parameters of the complexation process for the ligand with metal ions, ΔG°, ΔH° and ΔS° were determined and summarized in Tables 2.

The values of ΔG° at 25°C of the complexes have been calculated using the formula

$$\Delta G° = -2.303RT \, logK \qquad (eq. 2)$$

Were T= absolute temperature in kelvin and R= ideal gas constant and log K = stability constant of complex.

The enthalpy (ΔH°) for the complexation process was calculated from the slope of log K versus 1/T using the graphical representation extracted from *vant's Hoff* equation [16].

$$lnK = (-\Delta H° / RT) + (\Delta S° / R) \qquad (eq. 3)$$

ΔS has been calculated from the following equation, $\Delta S° = (\Delta H° - \Delta G°)/T \qquad (eq. 4).$

Table 2: Thermodynamic parameters of complexes formation L₁ with transition metal ions at 1.0 M. KNO₃ in 75% ethanol-water mixture.

Metal ion	-(ΔG) kJ/mol	(ΔH) kJ/mol	(ΔS) J/mol.K
Co(II)	-93.43	-0.01915	87.46414
Cu(II)	-105.69	-0.84247	354.8348
Zn(II)	-95.16	-0.09574	123.4493

All values of ΔG for complexation are negative, indicating the spontaneity of the complexation process. The negative values of ΔH° show that the coordination process is exothermic, indicating that the complexation reactions favor the low temperatures [17]. The positive values ΔS° for all investigated complexes indicate that the increase in entropy by the release of bound solvent molecules on coordination is greater than the decrease resulting from the coordination process itself. The obtained values of ΔH and ΔS° can be considered as the sum of two contributions: (a) release of H_2O molecules attached to the divalent metal ion and (b) formation of metal-ligand bond. The obtained results confirm the formation of the complexes in the system. [18-22]

Effect of Ethanol-water ratio

 The effect of ethanol-water ratios on the dissociation of the organic ligand **L1** and its chelate compounds are present in Table 3. The results showed that the complexation is affected by the composition of the mixed solvents. The order of dissociation of Magneson and its complexes stability was in order of 75% > 50%. The values of Log K increase with increase of the values of mole fraction of the solvent mixture, the values of pKₐ for the free ligand and Log K for metal complexes increase with decrease of dielectric constant or when the proportion of organic solvent increases from 50 to 75%. This is can be attributed to the increase in strength of electrostatic bond between azo group in the ligand and the metal cation, as solute– solvent interaction decrease by the increase of solvent contents [23]. This trend of increasing *PKa* values with an increase in organic solvent content of mixed solvents is consistent with many previous studies [24].

Table 3: Effect of ethanol-water percent on the stability constant of metal complexes at 25˚C.

Log *K*

	50%	75%
Free ligand	2.31	4.58
Co	3.61	4.88
Cu	3.79	5.52
Zn	3.60	4.97

Effect of solvents on the free ligand and their metal complexes

The effect of solvents on the organic ligand (magneson) and their metal complexes are measured by two mixed solvents systems, 75% (v/v) Ethanol–water and 75% (v/v) Acetone-water. The measurements were performed by pH –metric technique at 25˚C and 0.1M KNO₃ ionic strength. The results are shows in Table 4. The values show that the order of the basicity of the ligand in different mixed solvents was higher for acetone than Ethanol. Protonation constant in mixed aqueous solvents decreases with three factors: a) Increase of dielectric constant of the solvent (The values of dielectric constants μ is 2.85, and 1.69 for acetone and ethanol at 25 ºC) , b) Decrease of the extent of hydrogen bonding in water by the organic solvent and, c) Increasing the proton solvent ion by the organic solvent.[25] The values of stability constants of complexes of the ligand with divalent metal ions are higher in case of acetone than in ethanol [26] .

Table 4: Stability Constants for free ligand and It's Chelates In 75% Organic- Aqueous Solvents at 25˚C and 0.1 M KNO₃.

	Log *K*	
	Ethanol-water	Acetone- water
Free ligand	4.58	8.19
Co	4.88	6.73
Cu	5.52	8.17
Zn	4.97	7.69

Conclusion

In this present study, the acid dissociation constant of -(4-nitrophenylazo) resorcinol and its complexes were studied using the potentiometric techniques in 75% v/v ethanol-water medium by using pH titration techniques. The order of stability constant of metal complexes were found in the following order Cu(II) > Zn(II) > Co(II).

The negative free energy change for the complexes indicates the spontaneity of the complex formation process. The complexation of 4-(4-nitrophenylazo) resorcinol with metal ions is affected with the type and the ratio of the organic solvent. The entropy values indicate the complexation is favoured by entropy factors. The negative value of ΔH indicate the exothermic nature of reaction process with increasing stability suggesting lower temperature favours the chelation process.

Acknowledgments

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