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# Thermodynamic Studies of 5-(P-Bromophenylazo)-3 Phenylrhodanine and Its Metal Complexes.

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# THERMODYNAMIC STUDIES OF 5-(P-BROMOPHENYLAZO)-3-PHENYLRHODANINE AND ITS METAL COMPLEXES

# دراسات الديناميكا الحرارية للمركب ٥-(بارا-بروموفينيل آزو ) - ٣ - فينيل رودانين ومتراكباته مع العناصر

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## خلاصة

تم حساب ثابت التكسير لمركب ٥-(بارا-بروموفينيل آزو ) - ٣ - فينيل رودانين وكذلك حساب درجة الثبات لمتراكباته مع بعض العناصر الانتقالية الثنائية التكافؤ $(Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+})$ باستخدام طريقة معايرة الجهد في وسط يحتوي على ١, ٠ مولر كلوريد بوتاسيوم وكذلك محلول الإيثانول في الماء بنسبة ٤٠ % ، وقد وجد أن درجة ثبات المتراكبات تكون في $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$ .

وكذلك تم دراسة تأثير درجة الحرارة وبالتالي حساب ثوابت الديناميكا الحرارية ، وقد وجد ان عملية تكسير المركب تكون غير تلقائية وماصة للحرارة والإنتروبيا غير مرغوبة ، وقد كانت عملية تكوين المتراكبات تلقائية وطاردة للحرارة والإنتروبيا مرغوبة .

## ABSTRACT

The dissociation constant of 5-(p-bromophenylazo)-3-phenylrhodanine (HL) and metal-ligand stability constants of its complexes with bivalent ($Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$) metal ions have been determined potentiometrically in 0.1 M KCl and 40% (v/v) ethanol-water mixture. The order of the stability constants of the formed complexes was found to be $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$. The effect of temperature was studied and the corresponding thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) were derived and discussed. The dissociation process is nonspontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, exothermic and entropically favorable.

**Key Words:** 5-(p-bromophenylazo)-3-phenylrhodanine, potentiometry and thermodynamics.

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## INTRODUCTION

Azo compounds based on rhodanine play a central role as chelating agents for a large number of metal ions. They form a stable six-membered ring after complexation with the metal ions and can also be used as analytical reagents[1]. Rhodanine derivatives have been used in treatment of cancer turberculosis and malaria [2].

The synthesis of 5-(p-bromophenylazo)-3-phenylrhodanine (HL) has been reported elsewhere [3,4]. The dissociation and the stability constants of $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ complexes with HL are determined potentiometrically, herein, at different temperatures. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

## EXPERIMENTAL

### Preparation of HL

The 5-(p-bromophenylazo)-3-phenylrhodanine (HL) was prepared [5] by dissolving p-bromoaniline (0.1 mole) in conc. hydrochloric acid. The hydrochloric compound was diazotized below –5°C with a solution of sodium nitrite (0.1 mole, 30 ml distilled $H_2O$). The diazonium chloride was coupled with an alkaline solution of 3-phenylrhodanine (0.1 mole) in 20 ml of pyridine. The crude dye was collected by filtration and crystallized from ethanol, then dried in a vacuum desiccator over anhydrous $CaCl_2$.

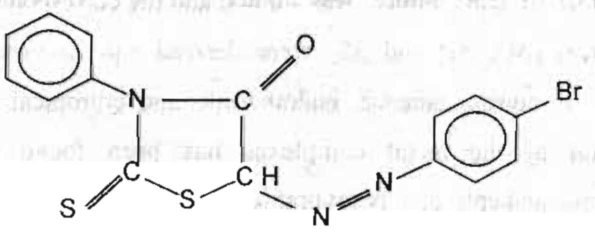

Fig. 1. Structure of the ligand (HL)

### Reagents and materials

Metal ion solutions (0.001 M) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA [6]. The ligand solutions (0.01 M) were prepared by dissolving the accurate weight of the solid in ethanol (Analar). Solutions of 0.005 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 40% (v/v) ethanol-water mixture was used as titrant and standardized against oxalic acid (Analar).

### Potentiometric measurements

The apparatus, general conditions and methods of calculation were the same as in the previous work [3]. The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.02 M NaOH in 40% (v/v) ethanol-water mixture:

(i) 5 ml 0.005 M HCl + 5 ml 1 M KCl + 20 ml ethanol;

(ii) 5 ml 0.005 M HCl + 5 ml 1 M KCl + 15 ml ethanol + 5 ml 0.01 M ligand;

(iii) 5 ml 0.005 M HCl + 5 ml 1 M KCl + 15 ml ethanol + 5 ml 0.01 M ligand + 5 ml 0.001 M metal chloride.

For each mixture, the volume was made up to 50 ml with bidistilled water before the titration. These titrations were repeated for temperatures of 303, 308 ,313 and 318 K. A constant temperature was maintained by using an ultrathermostat (Neslab 2 RTE 220). The pH-meter readings in 40% (v/v) ethanol-water mixture are corrected according to the Van Uitert and Hass relation [7].

## RESULTS AND DISCUSSION

### Proton-ligand dissociation constants

The number of protons associated with the compound at different pH values, $\bar{n}_A$, were calculated from the titration curves of the acid in the absence and presence of a ligand. Thus, the formation curves ( $\bar{n}_A$ vs. pH ) for the proton-ligand systems were constructed and found to extend between 0 and 1 in the $\bar{n}_A$ scale. This means that ligands have one ionizable proton (the hydrogen ion of the hydroxyl group in the rhodanine moiety). It can be seen that for the same volume of NaOH added the ligand titration curves had a lower pH value than the acid titration curve. The displacement of a ligand titration curve along the volume axis with respect to the acid titration curve is an indication of proton dissociation. The proton-ligand stability constants (Table 1) were calculated using the method of Irving and Rossotti [8].

**Metal-ligand stability constants**

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions ( $\bar{n}$ ) versus the free ligand exponent (pL), according to Irving and Rossotti [9]. These curves were analyzed and the successive stability constants were determined using different computational methods [10, 11] which agree within 1% error. Accordingly the average values are represented in Table 2.

The following general remarks can be pointed out:

(i) The maximum value of $\bar{n}$ was ≈ 2 indicating the formation of 1:1 and 1:2 {metal:ligand} complexes only.

(ii) The metal ion solution used in the present study was very dilute (10$^{-4}$ M), hence there was no possibility of formation of polynuclear complexes [12].

(iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves point to the formation of strong metal complexes [13].

(iv) In most cases, the colour of the solution after complex formation was observed to be different from the colour of the ligand at the same pH.

(v) For the same ligand at constant temperature. the stability of the chelates increases in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$ [14].

**Effect of temperature**

The average dissociation constants ($pK^H$) for HL, as well as the stability constants of its complexes with $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ have been evaluated at 298, 308 and 318 K, (Tables 1 and 2). The enthalpy change ($\Delta H$) for the dissociation and complexation processes were calculated from the slope of the plot $pK^H$ or log K vs. $^1/_T$ (Figure 1) using the graphical representation of Van't Hoff equation:

$$-2.303\ RT \log K = \Delta H - T\,\Delta S \quad \ldots\ldots\ldots\ldots (1)$$

or

$$\log K = \frac{-\Delta H}{2.303R}\left(\frac{1}{T}\right) + \frac{\Delta S}{2.303R} \quad \ldots\ldots\ldots\ldots (2)$$

From the free energy change ($\Delta G$) and ($\Delta H$) values one can deduce the entropy changes ($\Delta S$) using the well known relationships (3) and (4) :

$$\Delta G = -2.303\ RT \log K \ldots\ldots\ldots\ldots (3)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad \ldots\ldots\ldots\ldots (4)$$

where:

R: gas constant = 8.314 $JK^{-1}mole^{-1}$

K: dissociation constant for the ligand or stability constant of the complex.

T: absolute temperature.

All thermodynamic parameters of the dissociation process of HL are recorded in Table 1. From these results the following conclusions can be made:

(i) The $pK^H$ values decrease with increasing temperature, i.e., the acidity of the ligands increases[15].

(ii) A positive value of $\Delta H$ indicates that the process is endothermic.

(iii) A large positive value of ΔG indicates that the dissociation process is nonspontaneous.

(iv) The dissociation processes for HL have negative values of ΔS as a result of the solvation processes which is accompanied with a decrease in disorder, so confirmation of nonspontaneous reaction.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions : (a) release of $H_2O$ molecules, and (b) metal-ligand bond formation. Examination of these values shows that:

(i) The stepwise stability constants (log $K_1$ and log $K_2$) for ligand complexes decrease with increasing temperature, i.e., its stability constants increase with decreasing the temperature.

(ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process.[16]

(iii) The ΔH values are negative, meaning that these processes are exothermic and favorable at lower temperature.

(iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favorable.

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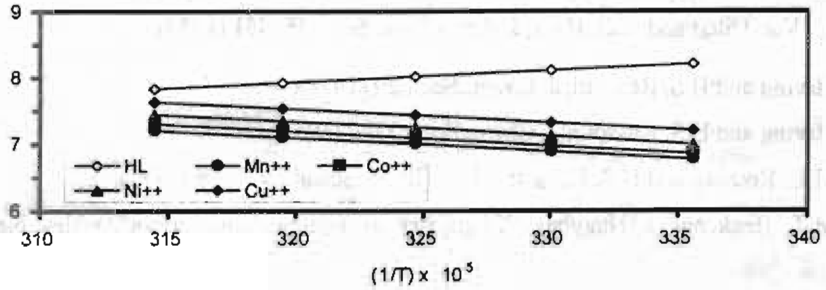

Fig. 2: pK $^H$ of HL and log K $_1$ of metal-HL complexes vs. 1/T.

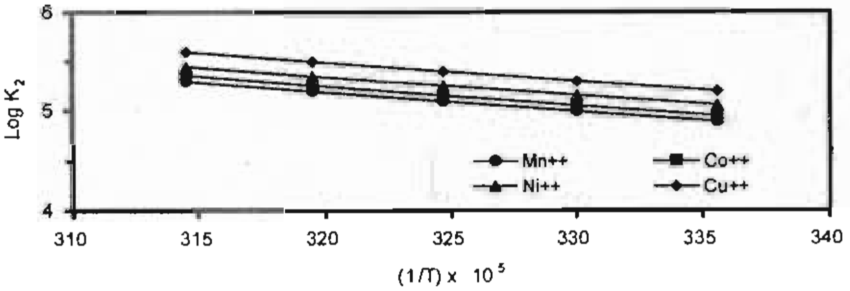

Fig. 3: Log K $_2$ of metal-HL complexes vs. 1/T.

**Table 1.** Thermodynamic functions for the dissociation of HL in 40% (v/v) ethanol - water mixture and 0.1 M KCl at different temperatures.

| Temp. K | Dissociation constant $pK^H$ | Free energy change ($kJmol^{-1}$) $\Delta G$ | Enthalpy change ($kJmol^{-1}$) $\Delta H$ | Entorpy change ($Jmol^{-1} K^{-1}$) $-\Delta S$ |
|---|---|---|---|---|
| 298 | 7.85 | 44.79 | 26.309 | 62.017 |
| 303 | 7.78 | 45.10 | | 62.0165 |
| 308 | 7.70 | 45.41 | | 62.016 |
| 313 | 7.63 | 45.72 | | 62.0155 |
| 318 | 7.56 | 46.03 | | 62.015 |

**Table 2.** Stepwise stability constants for ML and $ML_2$ complexes of HL in 40% (v/v) ethanol -water mixture and 0.1 M KCl at different temperatures.

| $M^{n+}$ | 298 K | | 303 K | | 308 K | | 313 K | | 318 K | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\log K_1$ | $\log K_2$ | $\log K_1$ | $\log K_2$ | $\log K_1$ | $\log K_2$ | $\log K_1$ | $\log K_2$ | $\log K_1$ | $\log K_2$ |
| $Mn^{2+}$ | 6.20 | 5.08 | 6.125 | 5.01 | 6.05 | 4.94 | 5.98 | 4.865 | 5.91 | 4.79 |
| $Co^{2+}$ | 6.98 | 5.85 | 6.905 | 5.78 | 6.83 | 5.71 | 6.76 | 5.635 | 6.69 | 5.56 |
| $Ni^{2+}$ | 7.36 | 6.20 | 7.29 | 6.12 | 7.22 | 6.04 | 7.155 | 5.97 | 7.09 | 5.90 |
| $Cu^{2+}$ | 8.52 | 7.15 | 8.45 | 7.07 | 8.38 | 6.99 | 8.305 | 6.915 | 8.23 | 6.84 |

**Table 3.** Thermodynamic functions for ML and $ML_2$ complexes of HL in 40% (v/v) ethanol-water mixture in the presence of 0.1 M KCl.

| $M^{n+}$ | Temp. (K) | Free energy change ($kJmol^{-1}$) | | Enthalpy change ($kJmol^{-1}$) | | Entorpy change ($Jmol^{-1} K^{-1}$) | |
|---|---|---|---|---|---|---|---|
| | | $-\Delta G_1$ | $-\Delta G_2$ | $\Delta H_1$ | $\Delta H_2$ | $\Delta S_1$ | $\Delta S_2$ |
| $Mn^{2+}$ | 298 | 35.38 | 28.99 | 26.31 | 26.31 | 30.437 | 8.994 |
| | 303 | 35.53 | 29.06 | | | 30.43 | 9.076 |
| | 308 | 35.68 | 29.13 | | | 30.423 | 9.157 |
| | 313 | 35.83 | 29.15 | | | 30.416 | 9.076 |
| | 318 | 35.98 | 29.17 | | | 30.409 | 8.995 |
| $Co^{2+}$ | 298 | 39.83 | 33.38 | 26.31 | 26.31 | 45.37 | 23.726 |
| | 303 | 40.055 | 33.525 | | | 45.365 | 23.8115 |
| | 308 | 40.28 | 33.67 | | | 45.36 | 23.812 |
| | 313 | 40.505 | 33.76 | | | 45.355 | 23.805 |
| | 318 | 40.73 | 33.85 | | | 45.35 | 23.712 |
| $Ni^{2+}$ | 298 | 41.99 | 35.38 | 24.495 | 27.217 | 58.708 | 27.393 |
| | 303 | 42.285 | 35.5 | | | 58.713 | 27.338 |
| | 308 | 42.58 | 35.50 | | | 58.718 | 27.282 |
| | 313 | 42.875 | 35.77 | | | 58.722 | 27.325 |
| | 318 | 43.17 | 35.92 | | | 58.726 | 27.368 |
| $Cu^{2+}$ | 298 | 48.61 | 40.80 | 26.31 | 28.124 | 74.833 | 42.537 |
| | 303 | 49.015 | 41.01 | | | 74.933 | 42.528 |
| | 308 | 49.42 | 41.22 | | | 75.033 | 42.519 |
| | 313 | 49.765 | 41.435 | | | 74.939 | 42.527 |
| | 318 | 50.11 | 41.65 | | | 74.844 | 42.535 |