NOTE

Stability Studies of Some Transition Metal Chelates of α-Benzilmonoximethiosemicarbazone

Dilip C. Sawant, Satish G. Pingale and R.G. Deshmukh*†
Department of Chemistry, K.T.S.P. Mandal's K.M.C. College, Khopoli-410 203, India
E-mail: ravideshmukh@vsnl.net

Stability constant values of Co(II), Ni(II) and Cu(II) chelates of α-benzilmonoximethiosemicarbazone have been determined pH-metrically at temperature 28 ± 0.5 ℃ and at different ionic strengths (0.050, 0.075 and 0.100 M) in 60.40 (v/v) dioxane-water medium. The formation constants have been calculated using the Bjerrum half ñ integral and graphical method.

Key Words: Stability constant, Transition metal chelates, α-Benzilmonoximethiosemicarbazone.

Metal complexes of schiff base are studied extensively due to their chelating ability with metal ions[1,2]. Many attempts have been made to evaluate different factors affecting the stability of metal chelates along with their stability constants[3-5].

Thiosemicarbazones are good chelating agents and their biological as well as analytical applications are well known[2,6,7]. With a view to investigate the formation of Co(II), Ni(II) and Cu(II) chelates of α-benzilmonoximethio-semicarbazone in solution state, the formation constants have been determined.

The pH titrations were carried out on an expanded scale pH-meter model No. EQ-615 supplied by equiptronics with a combined glass electrode. The smallest scale division on the expanded scale is 0.01 pH units.

Standardization of the instrument was carried out by means of buffer of 0.050 M potassium hydrogen phthalate (pH - 4.00) and 0.010 M borax (pH -9.18) before performing titrations.

Ligand solution was prepared in dioxane. All the metal salt solutions were prepared and standardized by conventional procedures[8]. A solution of KOH was prepared 0.100 M in double distilled carbonate free water and standardized with standard solution of succinic acid.

All chemicals used were of analytical reagent grade. The titration's were carried out in an inert atmosphere of nitrogen, which was presaturated with double distilled carbonate free water. All measurements were carried

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†Department of Chemistry, Kokan Gyanpeeth Karjat College of A.S.C., Karjat-410 201, India.

out at temperature 28 ± 0.5 ºC. The method of Bjerrum and Calvin as modified by Irving and Rossotti[9] was used to determine ñ and pL values.

Synthesis of α-benzilmonoximethiosemicarbazone: In 1 L round bottom flask was placed 23 g (0.102 mol) α-benzilmonoxime dissolved in 250 cm^3 ethanol. To this solution was added 10 g (0.109 mol) of thiosemicarbazide in 250 cm^3 ethanol and the reaction mixture was refluxed for 10 h in presence of 5 cm^3 of concentrated hydrochloric acid. The reaction mixture was cooled to the room temperature. The white crystalline product so formed was separated by filtration and recrystallized from methanol. The product was dried at 110 ºC in an hot air oven and weighed, purity was checked by TLC (m.p. 183 ºC, Yield: 20.5 g or 67 % of theoretical for α-benzilmonoxime).

pH Titration: The following solutions were titrated pH metrically against standard carbonate free potassium hydroxide (0.100 M) solution keeping the total volume 30 cm^3 (V$_o$). All the titrations carried out in 60:40 (v/v) dioxane:water and at 0.050, 0.075 and 0.100 M KCl ionic strengths to determine ñ and pL values of the complexes.

Set-I:

For μ = 0.050:

(i) 3.00 cm^3 HCl (0.100 M) + 1.20 cm^3 KCl (1.000 M) + 7.80 cm^3 distilled water + 18.00 cm^3 dioxane.

(ii) 3.00 cm^3 HCl (0.100M) + 1.20 cm^3 KCl (1.000M) + 3.00 cm^3 ligand (0.050 M) + 7.80 cm^3 distilled water + 15.00 cm^3 dioxane.

(iii) 3.00 cm^3 HCl (0.100 M) + 1.11 cm^3 KCl (1.000 M) + 3.00 cm^3 ligand (0.050 M) + 4.89 cm^3 distilled water + 3.00 cm^3 of metal chloride solution (0.010 M) + 15.00 cm^3 dioxane.

Set-II:

For μ = 0.075:

(i) 3 cm^3 HCl (0.10 M) + 1.95 cm^3 KCl (1 M) + 7.05 cm^3 distilled water + 18 cm^3 dioxane.

(ii) 3 cm^3 HCl (0.10 M) + 1.95 cm^3 KCl (1 M) + 3 cm^3 ligand (0.05 M) + 7.05 cm^3 distilled water + 15 cm^3 dioxane.

(iii) 3 cm^3 HCl (0.10 M) + 1.86 cm^3 KCl (1 M) + 3 cm^3 ligand (0.05 M) + 4.14 cm^3 distilled water + 3 cm^3 of metal chloride solution (0.01 M) + 15 cm^3 dioxane.

Set-III:

For μ = 0.100:

(i) 3 cm^3 HCl (0.10 M) + 2.70 cm^3 KCl (1 M) + 6.30 cm^3 distilled water + 18 cm^3 dioxane.

(ii) 3 cm^3 HCl (0.10 M) + 2.70 cm^3 KCl (1 M) + 3 cm^3 ligand (0.05 M) + 6.30 cm^3 distilled water + 15 cm^3 dioxane.

(iii) 3 cm^3 HCl (0.1 M) + 2.61 cm^3 KCl (1 M) + 3 cm^3 ligand (0.05 M) + 3.39 cm^3 distilled water + 3 cm^3 of metal chloride solution (0.01 M) + 15 cm^3 dioxane.

The pH meter readings were plotted against the volume of KOH used for each titration.

Protonation constants: The ligand remains in the protonated (or undissociated) form at least up to pH 2.70. The dissociation begins at around pH 2.75 and completed around pH 11.27. The values ñ range from 0 to 1 indicating the monobasic nature of the ligand.The pKa value obtained for the ligand by plotting $ñ_A$ *vs.* pH revels that the ligand is weakly acidic.

Stability constants of the metal complexes: Complexation in all cases of transition metals was uniformly well below the dissociation of the ligand. This means that formation of hydroxides or hydrolysis of metal ions is not interfering in the process of complexation. The observed ñ values which are ranging from 0 to 2 for a bivalent metal ions reveal the formation of ML_2 complexes for these metal ions (Table-1).

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS AND METAL-LIGAND
STABILITY CONSTANTS

Compound	K_1		K_2	$\log \beta$ $(K_1 + K_2)$
	Half integral method	Graphical method	Half integral method	
$\mu = 0.050$				
Ligand	11.21	11.190	-	-
Co(II)	7.48	7.480	6.63	14.11
Ni(II)	7.53	7.530	6.94	14.47
Cu(II)	12.62	12.625	9.48	22.10
$\mu = 0.075$				
Ligand	11.19	11.19	-	-
Co(II)	8.06	8.06	5.87	13.93
Ni(II)	7.41	7.40	6.68	14.09
Cu(II)	12.57	12.57	9.48	22.05
$\mu = 0.100$				
Ligand	11.17	11.170	-	-
Co(II)	6.87	6.876	6.45	13.32
Ni(II)	7.42	7.420	6.77	14.19
Cu(II)	12.62	12.625	9.48	22.10

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