Thermodynamic Studies of Some Complexes of 2-benzoylpyridine 4-phenyl-3-thiosemicarbazone

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The stability constants of the Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2-benzoylpyridine 4-phenyl-3-thiosemicarbazone were determined using a spectrophotometric method at different temperatures (25, 30, 35 and 40 $\pm$ 0.1°C) and ionic strengths (0.05, 0.01 and 0.20 M KNO$_3$) in 50 % (v/v) aqueous ethanol. Plots of thermodynamic stability constants at zero ionic strength (ln K$^\circ$) versus T^{-1} gave linear curves and Δ H$^\circ$ and Δ S$^\circ$ were also calculated from these plots. Moreover, the changes in free energy for each metal-ligand system were calculated from the following equation.

Δ G$^\circ$ = -RT ln K$^\circ$

Keywords: Stability, thiosemicarbazone, ligand, thermodynamic, spectrophotometry

Introduction

Thiosemicarbazones are a class of compounds obtained by condensation of thiosemicarbazide with suitable aldehydes or ketones. In most complexes thiosemicarbazones behave as bidentate ligands because they can bond to metals through sulphur and the hydrazinic nitrogen atoms, although in a few cases they behave as unidentate ligands and bond through only sulphur atom[1−3].

Thiosemicarbazones find wide applications in biological and medical fields. Thiosemicarbazones have versatile pharmacological activities and these increase many-fold when thiosemicarbazones are complexed with metal ions[4−5].

Thiosemicarbazones act as chelating agents for metal ions, producing highly coloured complexes. These complexes are then used in selective and sensitive determinations of metal ions. From this standpoint, some transition metals have been determined by using thiosemicarbazones[3,6−12].

In the earlier thermodynamic studies of some metal complexes, potentiometric methods were used[13−17]. We have reported the thermodynamical studies on the transition metal ions complexes of some thiosemicarbazones using a spectrophotometric method[18−21]. In the present study, 2-benzoylpyridine 4-phenyl-3-thiosemicarbazone (BPPT) has been synthesized for the first time. The thermodynamic stability constants and thermodynamic parameters of the complexes of this ligand with Co(II), Ni(II), Cu(II) and Zn(II) were evaluated using a spectrophotometric method.

Experimental

Synthesis of BBPT

To a solution of 2-benzoylpyridine (0.6 g) (Aldrich), 4-phenyl-3-thiosemicarbazide (0.5 g) (Merck) in 30 ml ethanol, 70 ml of distilled water and conc. HCl (2 ml) were added. The mixture was refluxed for 3 h and then cooled to room temperature. The precipitated solid was filtered and dissolved in hot water. The solution neutralised with aq. Na_2CO_3, washed with hot water and recrystallised from water-ethanol (1:1) mixture. The structure of BPPT was identified by IR and ^1H NMR spectroscopy, elemental analysis (m.p 140-142°C, yield 65 %). Found 67.84 % C, 4.87 % H, 16.81 % N, 9.89 % S; calculated for $C_{19}H_{16}N_4S$: 68.65 % C, 4.85 % H, 16.85 % N, 9.65 % S. BPPT does dissolve in ethanol and N,N-dimethylformamide (DMF).

Reagents

Solutions of nickel sulphate, copper (II) sulphate, cobalt (II) nitrate and zinc (II) sulphate were prepared in distilled water and standardized according to known methods. The stock metal solution (0.001 M) was prepared from each standardized solution. Buffer solutions of sodium acetate-acetic acid (C_1 =0.209 M; pH 5.75), sodium carbonate-sodium bicarbonate (C_T = 0.5 M; pH 9.6) and potassium nitrate solution (1 M) were prepared in distilled water. The first buffer solution (pH 5.75) was used for the Zn and Ni experiments, the second buffer solution (pH 9.6) for the Cu and Co experiments. A 1 % (w/v) solution of BPPT in ethanol was used. All reagents and solvents were of analytical grade.

Apparatus

A Crison 2002 pH-ionmeter with a combined glass-calomel electrode and a Shimadzu UV-160 spectrophotometer with 1.0 cm quartz cells, equipped with a Lauda MT 3 circulating bath, were used.

Procedures

Determination of molar absorption coefficients: Into a 10 ml volumetric flask were introduced 2 ml of buffer solution, 2 ml of 1 M potassium nitrate solution, 3-3.5 ml of ethanol and X ml of BPPT solution (X=2 ml for Co; X = 1.5 ml for Zn, Ni and Cu. The X values are volumes sufficient to give the optimum ligand concentrations). This mixture was diluted with distilled water to 10 ml, and mixed thoroughly, then 3 ml of the mixture was transfered to a stoppered quartz cell. The cell was warmed for 15 min at 25 $\pm$ 0.1°C, then 20-60 μl of stock metal solution kept under the same conditions was added to the stoppered cell with a micropipette and the mixture was shaken (ionic strength I=0.2). Five mixtures with differing metal concentrations were prepared for each metal. The changes in absorbance at the wavelength of maximum absorption were recorded against a similar solution containing no metal ion until the reaction was complete (Table 1).

Determination of stability constants of the complexes: Into a 10 ml volumetric flask were placed 2 ml of buffer solution, 2 ml of 1 M potassium nitrate solution, 4.91-4.97 ml of ethanol and 0.03-0.09 ml of stock BPPT solution. This mixture was diluted with distilled water to 10 ml and mixed thoroughly; five mixtures with differing BPPT concentrations were prepared thus. A 3 ml portion of each mixture was transferred to a stoppered quartz cell. The cells were warmed for 15 min at 25 $\pm$ 0.1°C in the circulating bath. Keeping the ligand/metal mole ratio at $\approx$ 2, the reaction was initiated by adding the stock metal solution, kept under the same conditions, to each mixture (I=0.2). The changes in absorbance at the maximum wavelength were

recorded in the same way as for the determination of the molar absorption coefficients. Each experiment was repeated three times.

Table 1. Spectophotometric characteristics of the complexes

Complex	$\lambda_{\max}$(nm)	$\epsilon(dm^3mol^{-1}cm^{-1})$			Optimum pH
		I=0.05	I=0.10	I=0.20	
Zn-BPPT	401	34100	34400	35800	5.7
Ni-BPPT	388	43200	44000	45700	5.7
Cu-BPPT	404	22500	23500	24250	9.6
Co-BPPT	406	23500	24500	25250	9.6

At I=0.2, the experiments performed for the determination of the molar absorption coefficients and stability constants were repeated at 30, 35 and 40 $\pm$ 0.1°C by preparing the mixtures afresh.

The experiments were also performed at ionic strengths of 0.1 and 0.05 at each of the temperatures mentioned above.

Results and Discussions

The complexes of Co(II), Ni(II), Cu(II) and Zn(II) with BPPT are yellow-green in colour. The maximum absorption wavelengths ($\lambda_{\max}$), molar absorption coefficients (ϵ) at various ionic strengths. (I/mol dm^{-3}) and optimum pH values of these complexes are given in Table 1.

The effect of temperature and ionic strength on the molar absorption coefficients (ϵ) of the complexes were studied at different temperatures and ionic strengths. It was observed that the coefficients did not change with temperature but increased slightly with ionic strength as in our studies[18-21]. For this reason molar absorption coefficient were determined over the range of 0.05 to 0.2 in ionic strength. The maximum absorption wavelentgh ($\lambda_{\max}$) of each complex did not shift when ϵ's and stability constants were determined. So during experiments, absorption peak preserved its homogeneity. Solutions of metal ions and reagents in experimental range obey Beer's law.

Since optimum pH for the each complex was studied the influence of the pH on the ϵ was not investigated. The Ni(II) and Zn(II) complexes have a maximum absorption at pH values close to 5.7 and these complexes are formed rapidly. The formation of the Co(II) and Cu(II) complexes are very slow at pH 5.7. To increase the formation rate of these complexes, pH values were increased. As cobalt and copper hydroxides are precipitated at pH $\geq$ 10, cobalt and copper experiments were carried out at pH 9.6.

For all complexes, the metal/ligand mole ratio was found to be 1:2 using the method of continuous variations[22] (Job's method). This results shows that BPPT is a bidentate ligand.

M, L and ML$_2$ represent, respectively, the metal ion, the ligand and the complex.

$$M + 2L \rightleftharpoons ML_2$$
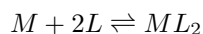
If the L/M ratio is very large, the equilibrium shifts completely to the right, and one can write

$$C_M \approx [ML_2],$$

were C_M is the analytical concentrations of metal. Using measured absorbances of the mixtures, the molar absorption coefficients are determined from Beer's law. Because the measured absorbances pertain only to the ML$_2$ complex[23], the following equation can be written for the stability constant of the complex:

$$K = \frac{[ML_2]}{[M][L]^2} = \frac{[ML_2]}{(C_M - [ML_2])(C_L - 2[ML_2])^2}$$

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In this equation, if A/ϵ is substituted for $[ML_2]$, the equation becomes

$$K = \frac{A/\epsilon}{(C_M - A/\epsilon)(C_L - 2A/\epsilon)^2}$$

where A is the measured absorbance and ϵ the molar absorption coefficient. K is calculated from this equation[24].

For each temperature, the average values of $\ln K$ were plotted againsts ionic strength for each metal-ligand system. Straight lines were obtained and the curves were extrapolated to zero ionic strength to give thermodynamic stability constant, $(\ln K^\circ)$[13-17].

For each metal-ligand system, values of $\ln K^\circ$ were plotted against T^{-1}. A straight line was obtained, showing that ΔH° and ΔS° are essentially independent of temperature over the temperature range considered. The slope of the line is $-\Delta H^\circ/R$, and the intecept at $T^{-1} = 0$ is $\Delta S^\circ/R$. The values of ΔH° and ΔS° may be calculated, respectively, from the slope and the intercept of plot. Using the equation $\Delta G^\circ = -RT\ln K^\circ$, the values of ΔG° for each metal-ligand were calculated.

The average values of the stability constants $(\ln K)$ of the metal complexes were found to be proportional to the ionic strength and inversely proportional to the temperature (Table 2).

Table 2. The stability constant $(\ln K)$ at different temperatures and ionic strength (I, mol dm^{-3}), and the thermodynamic parameters.

System	Temp.	$\ln K$			$\ln K^\circ$	$-\Delta G^\circ$	$-\Delta H^\circ$	$+\Delta S^\circ$
	(°C)	I=0.20	I=0.10	I=0.05		(kJ mol^{-1})	(kJ mol^{-1})	(J mol^{-1}K^{-1})
Cu-BPPT	25	26.03	25.98	25.89	25.86	64.10	24.40	133.23
	30	25.86	25.82	25.75	25.72	64.82		
	35	25.71	25.63	25.58	25.54	65.63		
	40	25.6	25.47	25.40	25.33	65.92		
Co-BPPT	25	24.11	24.06	24.03	24.00	59.49	12.20	158.65
	30	24.05	23.99	23.96	23.93	60.31		
	35	23.99	23.91	23.88	23.84	61.08		
	40	23.93	23.84	23.81	23.78	61.86		
Zn-BPPT	25	25.93	25.91	25.84	25.77	63.88	12.96	170.83
	30	25.83	25.78	25.73	25.70	64.47		
	35	25.73	25.66	25.63	25.50	65.59		
	40	25.63	25.54	25.52	25.47	66.28		
Ni-BPPT	25	23.61	23.58	23.53	23.51	58.28	10.69	159.69
	30	23.55	23.52	23.46	23.45	59.10		
	35	23.47	23.45	23.38	23.37	59.87		
	40	23.40	23.38	23.31	23.29	60.60		

The data in Table 2 showed that spontaneity of these metal-ligand reaction increased with temperature however stabilities of resulting complexes decreased. The values of ΔG° follow the order Cu(II) $\geq$ Zn(II) > Co(II) > Ni(II). The ΔS° values are all positive indicating that change in entropy favours complex

formation. Further negative values of ΔH° predicts the exothermic nature of the complex reactions. In comparison to $\Delta S^{\circ}, \Delta H^{\circ}$ is very large and is mainly responsible for the complexation.

Acknowledgement

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