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Study of Kinetics of Complexation Reaction of Co²⁺ with 2-benzoylpyridine-4-phenyl-3-thiosemicarbazone and Kinetic-spectrophotometric Determination of Cobalt

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Abstract Kinetics of complexation reaction of Co²⁺ with 2-benzoylpyridine-4-phenyl-3-thiosemicarbazone (BPPT) was spectrophotometrically examined at 421 nm. The ligand that is developed for a simple kinetic-spectrophotometric determination of Co²⁺ is based on 1:2 complex formation between Co²⁺ and BPPT. The complexation reaction was carried out in ethanol-water medium at 25 °C. Kinetic and activation parameters of the complexation reaction were calculated, and the rate equation and the reaction mechanism were proposed. The calibration graph is linear in the concentration range of 0.10~2.91 mg·L⁻¹ for the tangent method. The species that caused interference were investigated.

Keywords: Cobalt, Thiosemicarbazone, Kinetic study, Kinetic-spectrophotometric determination

Thiosemicarbazones and phenylthiosemicarbazones are interesting ligands because of their ability to form highly stable and intensely colored complexes, which is attributed to the formation of bond between sulfur and hydrazino nitrogen atoms, and these colored complexes are ideally suited for spectrophotometric detection. In most complexes, thiosemicarbazones behave as bidentate ligands because they can bond to metals through sulfur and the hydrazinic nitrogen atoms, whereas in certain cases they behave as unidentate ligands^[1-2]. Different thiosemicarbazones and phenylthiosemicarbazones were reported as spectrophotometric^[3-6], spectrofluorimetric^[7], and voltammetric^[8] ligands for metal ions^[9]. Moreover, thiosemicarbazones and their metal complexes exhibit a wide range of biological properties such as antitumoral, antifungal, antibacterial, anti-inflammatory, and anti-HIV^[10-15]. They have been used for applications in devices related to telecommunications, optical computing, optical storage, and optical information processing^[13]. Therefore, numerous studies on the metal complexes of thiosemicarbazones have been reported^[1, 13-18].

Even though cobalt is not considered to be as toxic as most of the heavy metals, it has hazardous effects on human being and animals^[19]. The determination of trace amounts of cobalt in natural water is of considerable interest because cobalt is important for living species for it forms complexes with vitamin B12. The deficiency of cobalt in ruminants usually results in different

types of anemia. Large amounts of cobalt lead to toxicological effects such as vasodilatation, flushing, and cardiomyopathy in human being and animals^[20].

The principal aim of this study was to elucidate the kinetics and the mechanism of complexation between Co²⁺ and 2-benzoylpyridine-4-phenyl-3-thiosemicarbazone (BPPT). Moreover, BPPT molecule was used as a spectrophotometric ligand for the kinetic-spectrophotometric determination of Co²⁺. BPPT form colored complexes with Cd²⁺, Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Hg²⁺, and Ag⁺ over the pH range of 4.0~9.0, whereas it forms only colored complexes with Fe²⁺, Co²⁺, Cu²⁺, and Hg²⁺ over the pH range of 1.0~3.0. Because Fe²⁺, Cu²⁺, and Hg²⁺ metal cations rapidly form complexes with this ligand under experimental conditions (especially in the pH range of 1.0~3.0), these cations cannot be determined by kinetic analysis. If a sample does not contain Fe²⁺, Cu²⁺, and Hg²⁺, the kinetic determination of cobalt may be realized.

1 Experimental

1.1 Chemicals

All reagents were purchased from the Aldrich Chemical Company and used as received. Cobalt solution: cobalt nitrate was dissolved in distilled water and standardized volumetrically; it was then diluted as required before use (app. 1.0×10⁻³ mol·L⁻¹). BPPT solution: a 0.1% (w/V) solution of BPPT in ethanol was

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Table 1 Preparation of HCl/KCl buffer solution

pH	1.00	1.20	1.40	1.60	1.80	2.00	2.20
<i>x</i>	67.00	42.50	26.60	16.20	10.20	6.50	3.90

25 mL 0.2 mol·L⁻¹ KCl+*x* mL 0.2 mol·L⁻¹ HCl (dilution to 100 mL)

prepared. Buffer solution: HCl/KCl (pH 1.00~2.20) buffer solutions were prepared as shown in Table 1^[21] and were controlled using a pH meter. The mixture was also used for the control of ionic strength in kinetic study. Solutions of ions: solutions of different ions used for interference studies were prepared by dissolving the calculated amounts of each compound in distilled water.

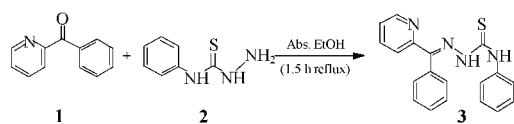
1.2 Instrumentation

A Shimadzu 160 UV-Vis spectrophotometer with 10 mm matched quartz cells with a stopper and a digital Crison 2002 pH meter with a combined glass electrode assembly were used for the absorbance and pH measurements, respectively. Moreover, the spectrophotometer was equipped with a Lauda MT3 circulating thermostatic bath for maintaining constant temperature.

¹H NMR and infrared spectra were recorded on a Bruker 400 MHz ¹H-NMR spectrometer and on a Perkin Elmer Model 1605 FT-IR spectrophotometer, respectively.

1.3 Synthesis of BPPT

Synthesis of the BPPT was carried out using different methods^[22] described in the published reports^[23]. The ligand was obtained in absolute ethanol in the presence of catalytic amounts of acid (Scheme 1). The equimolecular solutions of 2-benzoylpyridine (**1**) (1.5 g) in 30 mL of absolute EtOH and 4-phenyl-3-thiosemicarbazone (**2**) in 20 mL of warm absolute EtOH were placed in a 100-mL flask, and then 2~3 drops of concentrated H₂SO₄ were added. The mixture was stirred for 1.5 h at room temperature. After one day, the resultant cooled solution was filtered. The precipitate was neutralized with 0.5% sodium carbonate, washed with H₂O and Et₂O, and dried in vacuum, which resulted in the formation of a yellow-brown product (67% yield). BPPT (**3**) dissolves in ethanol and *N,N*-dimethylformamide (DMF). All analytical and spectroscopic data were in good agreement with the expected values. The melting point of the BPPT was 141~143 °C (lit. 140~142 °C). Analytical calculation for (C₁₉H₁₆N₄S)(%): C 68.65, H 4.85, N 16.85, S 9.65; found(%): C 68.95, H 4.89, N 16.89, S 9.76. ¹H NMR (400 MHz, CDCl₃) δ 13.1 (s, 1H, —NNH), 10.31 (s, 1H, NH), 8.02 (t, 2H, Ar—H), 7.73 (d, 2H, Ar—H), 7.57~7.62 (m, 4H, Ar—H), 7.48 (d, 2H, Ar—H), 7.39 (q, 2H, Ar—H), 7.21 (q, 2H, Ar—H).

**Scheme 1** Synthesis of BPPT

1.4 Procedures

The kinetic studies have been evaluated by monitoring the absorbance corresponding to the formation of the Co²⁺ complex as a function of time at 421 nm on the spectrophotometer. To a 10-mL volumetric flask, 4.4 mL of EtOH, 2 mL of HCl/KCl buffer solution (pH 1.2), and 0.6 mL of 0.1% (*w/V*) BPPT solution were added, which was diluted to the mark using distilled water and mixed thoroughly. 3 mL of this mixture was transferred to the stoppered quartz cell. The cell was warmed in the thermostatic bath at (25.0±0.1) °C for 15 min. Following this, 5~100 μL of 1.06×10⁻³ mol·L⁻¹ of Co²⁺ solution was added and was stored in the thermostatic bath for 15 min. A calculated quantity of the solution was then transferred into a 10-mm quartz cell within 15 s for the absorbance measurements. The changes in absorbance were recorded against a similar solution but without Co²⁺; the changes were recorded until the reaction was complete (5~6 min). The initial rate (tanα) was determined using the first straight part of the run (usually the 3%~5% of the reaction) and curve-fitting analysis was applied. The temperature was varied between 15 and 35 °C, the pH between 1.0 and 2.5, the amount of buffer solution between 1.00 mL and 3.00 mL, the added BPPT concentration between 0.60×10⁻⁴ mol·L⁻¹ and 5.42×10⁻⁴ mol·L⁻¹, the percentage of EtOH between 0.20% and 0.80%, and the initial Co²⁺ concentration between 1.76×10⁻⁶ and 3.52×10⁻⁵ mol·L⁻¹. With the exception of the variable studied, the initial conditions were as: *c*_{BPPT}=1.81×10⁻⁴ mol·L⁻¹; pH=1.2; *T*=(25.0±0.1) °C; φ(EtOH)=0.50%, and *c*_{Co²⁺}=1.41×10⁻⁵ mol·L⁻¹.

In a 25-mL standard flask, 5 mL of HCl/KCl buffer solution (pH 1.2 and for controlling ionic strength), 11 mL of EtOH, and 1.5 mL of 0.1% (*w/V*) BPPT solution were added. The solution was made up to the mark with distilled water and mixed thoroughly. 3 mL of the solution was accurately measured and transferred into a cuvette and was left to stand for 15 min in the controlled temperature cell holder of the spectrophotometer. The sample solution (several microliters of the 1.06×10⁻³ mol·L⁻¹ of Co²⁺) was carefully added to avoid mixing. The lid was closed and the cell was inverted twice or thrice (this point was taken as zero time). The absorbance-time data were obtained. To obtain the calibration graphs, tangent, fixed-time, and fixed-time methods were used.

2 Results and discussion

2.1 Spectral data and stoichiometry

The absorption spectrum of the brownish Co²⁺-BPPT complex showed a maximum at 421 nm (Fig.1). The intensity of the brownish color increased with time. Pure BPPT in ethanol had maxima at ca 356 nm; a shift in maxima was attained after the

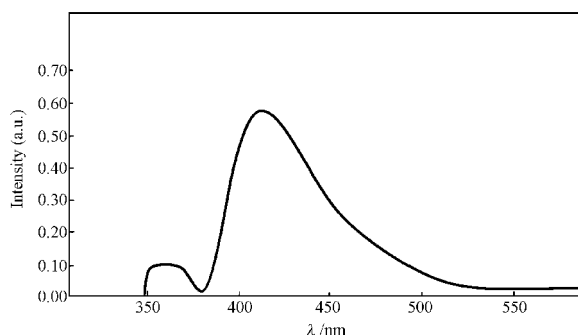


Fig.1 Absorption spectra of the Co^{2+} -BPPT complex against a ligand blank

addition of cobalt. The stoichiometric ratio ($n(\text{metal}):n(\text{ligand})=1:2$)^[23] of the Co^{2+} -BPPT complex was verified using Job's continuous variation method.

2.2 Determination of reaction order and conditional rate constant

The determination of the rate law was simplified using the isolation method where the concentrations of all the reactants except one are in large excess. Under experimental conditions, which are constant pH and a large excess of BPPT concentration with respect to that of the metal ion, the reaction is pseudo-first order with respect to the metal ion. Thus, the integrated equation in terms of absorbance can be written as^[24]

$$\ln(A_{\infty}-A_t)=\ln A_{\infty}-k_{\text{Co}}t$$

where k_{Co} is the conditional (or pseudo) rate constant, and A_t is the absorbance at any time t and A_{∞} is the final absorbance. A graph of $\ln(A_{\infty}-A_t)$ against time is a straight line; its slope allows the determination of the conditional rate constant of the complex formation reaction, and average value of this constant obtained for nine different determinations is given as

$$k_{\text{Co}}=(1.28\pm 0.05)\times 10^{-2} \text{ s}^{-1}$$

2.3 Effect of reaction variables

To determine the optimum conditions for the complexation reaction between Co^{2+} and BPPT, the effects of pH, ionic strength, temperature, and reactant concentrations were examined. To determine the effect of the amount of buffer on the complexation reaction, various volumes of buffer solutions were added. Changes in the amount of buffer had little influence on the reaction rate, and so the amount of buffer was fixed at 2 mL HCl/KCl buffer solution for a total 10 mL solution ($[\text{K}^+]=0.01 \text{ mol}\cdot\text{L}^{-1}$ and $[\text{Cl}^-]=0.017 \text{ mol}\cdot\text{L}^{-1}$).

On one hand, the reaction rate increased appreciably with the increase in the percentage of ethanol in mixed solvent. On the other hand, when there was less than 35% of ethanol, the reaction rate was very low. In practice, 50% of EtOH- H_2O mixed solvent was chosen because this percentage of mixed solvent was suitable for use with 40%~60% of EtOH.

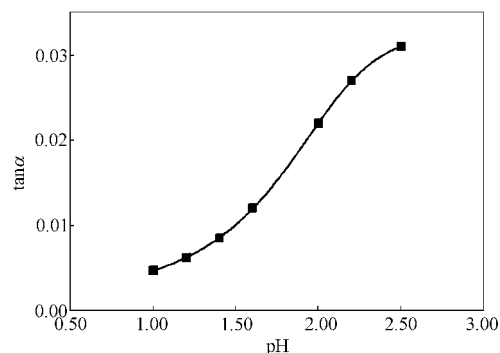


Fig.2 Dependence of the reaction rate on pH

$1.41\times 10^{-5} \text{ mol}\cdot\text{L}^{-1} \text{ Co}^{2+}$, other conditions as in procedure

The reaction proceeded most favorably in the pH range of 1.0~2.5, because the reaction did not take place practically at $\text{pH}<1.0$ and was very rapid at $\text{pH}>2.5$. For this reason, HCl/KCl buffer solution of pH 1.2 was selected. The effect of pH on the reaction rate was examined over the range (Fig.2). Hence, when $\ln[\tan\alpha]$ was plotted against $\ln[\text{H}^+]$, a partial order of pH was obtained as -1 .

2.4 Effect of BPPT concentration

The influence of the ligand concentration on the reaction rate was studied over the range of 6.02×10^{-5} to $5.42\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$. From Fig.3, the rate of complexation reaction increases with increasing ligand concentration up to $5.42\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ and remains nearly constant at higher concentrations. Therefore, a $1.81\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ of the ligand (1.5 mL of 0.1% BPPT solution for the total 25 mL of the solution) was chosen. To establish the partial orders of reaction with respect to ligand concentration, the logarithm of the ligand concentration was plotted against $\ln k_{\text{Co}}$ (Fig.4). The plot has a slope of 1.01; therefore, the reaction rate of complex formation is pseudo-first order with respect to the ligand concentration.

2.5 Effect of temperature

The effect of temperature on the complexation reaction was studied over the range of 10 to 35 °C (Fig.5). Because the reaction progressed at a faster rate at higher temperatures, the room

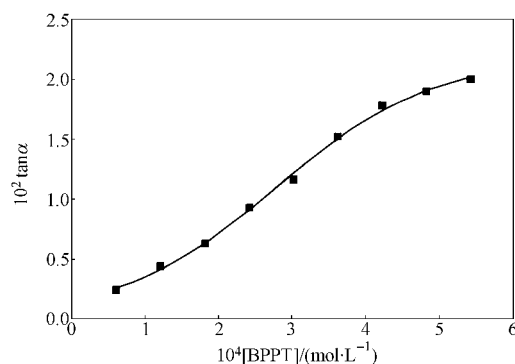


Fig.3 Effect of ligand concentration on the reaction rate

$1.41\times 10^{-5} \text{ mol}\cdot\text{L}^{-1} \text{ Co}^{2+}$

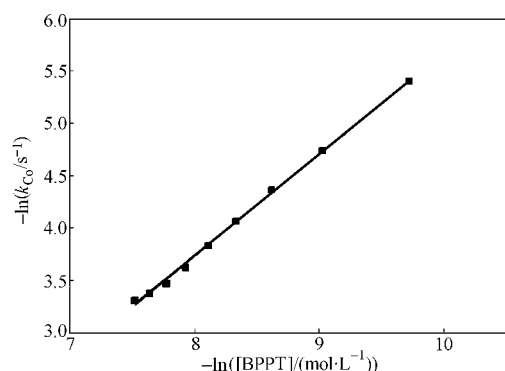


Fig.4 Effect on pseudo-first order rate constant of varying ligand concentration

$1.41 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \text{ Co}^{2+}$, other conditions as in procedure

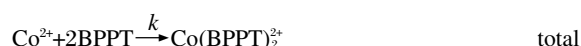
temperature (25 °C) was selected as the optimum temperature.

2.6 Determination of activation parameters

The reaction rate constants of nine different concentrations of Co²⁺ were determined at five different temperatures. $\ln k$ versus $1/T$ plot gave a straight line, from which the energy of activation (E_a) was calculated according to Arrhenius equation^[25-26]. The other activation thermodynamic parameters were calculated at 25 °C. The results are shown in Table 2.

2.7 Reaction mechanism and rate equation

From the above-mentioned results, the reaction mechanism can be written as follows:



Finally,

$$\frac{d[\text{Co}(\text{BPPT})_2^+]}{dt} = \frac{d[\text{CoBPPT}(\text{OH})^+]}{dt} = k'' \cdot [\text{Co}(\text{OH})^+] [\text{BPPT}] = k'' \cdot K \cdot [\text{Co}^{2+}] [\text{OH}^-] [\text{BPPT}]$$

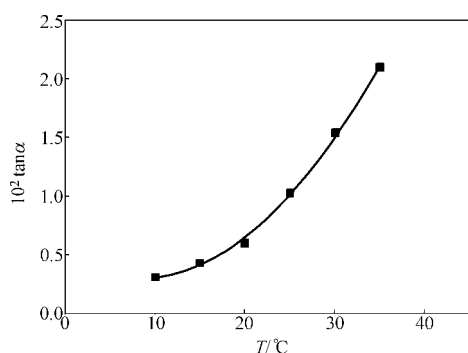


Fig.5 Influence of temperature on the reaction rate

$1.41 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \text{ Co}^{2+}$, $[\text{BPPT}] = 1.81 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $\text{pH} = 1.2$, $[\text{KCl}] = 0.027 \text{ mol} \cdot \text{L}^{-1}$, $\varphi(\text{EtOH}) = 0.50\%$

Table 2 Activation thermodynamic parameters for the Co²⁺-BPPT complexation reaction at 25 °C

A	E_a	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger
($\text{mol}^{1/2} \cdot \text{L}^{-1/2} \cdot \text{s}^{-1}$)	($\text{kJ} \cdot \text{mol}^{-1}$)	($\text{kJ} \cdot \text{mol}^{-1}$)	($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	($\text{kJ} \cdot \text{mol}^{-1}$)
$(3.23 \pm 0.19) \times 10^{10}$	56.15 ± 1.20	53.67 ± 0.98	-52.04 ± 1.09	69.19 ± 1.02

$$= k'' K [\text{Co}^{2+}] \frac{K_{\text{H}_2\text{O}}}{[\text{H}^+]} [\text{BPPT}]$$

$$= k'' K K_{\text{H}_2\text{O}} \frac{[\text{Co}^{2+}] [\text{BPPT}]}{[\text{H}^+]}$$

$$= k \frac{[\text{Co}^{2+}] [\text{BPPT}]}{[\text{H}^+]}$$

K is complexation constant of $[\text{Co}(\text{OH})]^+$.

The above-mentioned kinetic data suggest that the rate equation for the formation of the Co²⁺-BPPT complex in a HCl/KCl buffer medium is as follows:

$$\frac{d[\text{Co}(\text{BPPT})_2^+]}{dt} = k \frac{[\text{BPPT}] [\text{Co}^{2+}]}{[\text{H}^+]}$$

2.8 Kinetic-spectrophotometric determination of cobalt

Calibration graphs were obtained by applying the tangent, the fixed-time, and the fixed-absorbance methods^[27].

The tangent method has been applied and the calibration graph is linear over the concentration range $0.1038 \sim 2.9064 \text{ mg} \cdot \text{L}^{-1} \text{ Co}^{2+}$. The following equation of the calibration graph was obtained:

$$\tan \alpha (\Delta A / \Delta t) = 9.00 \times 10^{-4} + 6.60 \times 10^{-3} C \quad (R = 0.9960)$$

where C is the Co²⁺ concentration in $\text{mg} \cdot \text{L}^{-1}$.

For the fixed-time method, the calibration graph is linear over the concentration range $0.1038 \sim 2.0760 \text{ mg} \cdot \text{L}^{-1} \text{ Co}^{2+}$. Analysis of the data gave the calibration graph:

$$\Delta A = 2.56 \times 10^{-2} + 0.338 C \quad (R = 0.9967)$$

where ΔA (for 2 min) is the change of absorbance at 421 nm.

For the fixed absorbance methods, the time necessary to obtain an absorbance of 0.200 was plotted against the Co²⁺ concentration. Using this method, the calibration graph is linear over the concentration range of $0.8304 \sim 2.0760 \text{ mg} \cdot \text{L}^{-1} \text{ Co}^{2+}$ with this method. The reciprocal of time ($1/\Delta t$) versus the initial concentration of cobalt was plotted, and the following equation was obtained.

$$1/\Delta t = 5.72 \times 10^{-3} + 5.31 \times 10^{-2} C \quad (R = 0.9973)$$

where Δt is the necessary time.

Interferences were investigated using a standard $0.8302 \text{ mg} \cdot \text{L}^{-1} \text{ Co}^{2+}$ solution with varying concentrations of other species according to the tangent method. The tolerance amount of an ion was taken as the amount that caused an error of not more than 2% in the determination of Co²⁺ (Table 3). BPPT does not form a complex with the metals except for Co²⁺, Fe²⁺, Cu²⁺, and Hg²⁺ under the experimental conditions. Thus, Fe²⁺, Cu²⁺, and Hg²⁺ interfered positively due to the complex formation with BPPT.

Table 3 Tolerance limits of foreign ions for the kinetic determination of Co²⁺ (0.8302 mg·L⁻¹) using the tangent method at 25 °C

Ion	Added as	Amount tolerated (mg·L ⁻¹)
Ni ²⁺	NiSO ₄ ·7H ₂ O	2.3477
Al ³⁺	Al(NO ₃) ₃	9.8934
Zn ²⁺	ZnSO ₄ ·7H ₂ O	1.7437
Cr ³⁺	CrCl ₃ ·6H ₂ O	13.8701
Mg ²⁺	MgSO ₄	12.1550
Ca ²⁺	CaCl ₂	10.6912
Ba ²⁺	BaCl ₂ ·2H ₂ O	54.9320
Sb ³⁺	Sb ₂ (SO ₄) ₃	81.1705
Cd ²⁺	CdSO ₄	2.2482
cyanide	KSCN	27.0600
tartarate	tartaric acid	15.1963
citrate	citric acid	6.4968
bromide	NaBr	22.8960
fluoride	NaF	5.8990

3 Conclusions

For the reaction of 2-benzoylpyridine-4-phenyl-3-thiosemicarbazone (BPPT) with Co²⁺, the order of the reaction was determined using the initial rate method. BPPT forms highly stable 1:2 metal-ligand complexes with Co²⁺. Although certain other transition metal ions form complexes with this reagent, their absorbance maxima are significantly different from the one formed with Co²⁺ ($\lambda_{\max}=421$ nm, $\epsilon_{\max}=2.01 \times 10^{-4}$ L·mol⁻¹·cm⁻¹). An HCl/KCl solution of pH 1.2 was selected as the buffer solution. Formation of this complex is completed at approximately 6 min under the experimental conditions. The activation parameters were calculated. The absorbance-time curves for solutions containing different amounts of Co²⁺ were recorded against a similar solution without Co²⁺. Different methods were established to determine Co²⁺ kinetically; the tangent, fixed-time, and fixed-absorbance methods. However, in general, the tangent method is recommended.

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