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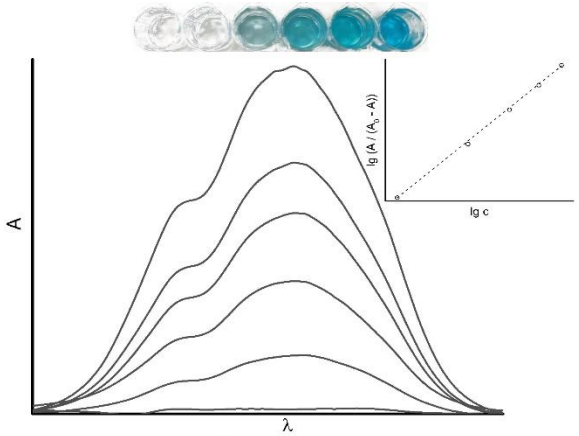
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Determination of the average ligand number and the equilibrium constant for the complexation reaction of Co^{2+} and SCN^- in water-organic solvent mixtures: A physical chemistry laboratory experiment for undergraduate students

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Abstract

In the present study, the suitability of the complexation reaction between Co^{2+} and SCN^- in water-organic solvent mixtures for the development of a laboratory experiment for undergraduate students was examined. From the measurement of absorbances of a series of solutions containing equal quantities of the metal (Co^{2+}) but different quantities of the ligand (SCN^-), the average ligand number and the equilibrium constant for the complex formation reaction are estimated using a Bent–French method. The students derive an expression for the relation between the experimentally determined values of the equilibrium constants and the stability constants of two adjacent complexes and estimate these stability constants. The experimental conditions and the used instrumentation drastically affect the measured average ligand number and equilibrium constant, and the calculated stability constants. However, the results are illustrative, suitable for educational purposes and reproducible by the various groups of students. The instructions for the students and the example data processing are provided.



$$\lg \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+})} = \lg K_{exp} + n \cdot \lg c(SCN^-)$$

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Highlights

- The reaction between Co^{2+} and SCN– in water organic medium forms tetrahedral complex.
- The reactions are suitable for laboratory practice teaching chemical equilibrium.
- The average ligands and equilibrium constant determined by the Bent-French method.
- Experiments can be performed using different instruments found in the laboratory.
- The stability constants of two complex forms are evaluated from the experiment.

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1. Introduction

Laboratory experiments are a significant part of physical chemistry teaching because they present real examples of the physical chemistry concepts encountered by the students in lectures. However, the processes and reactions suitable for student laboratory experiments must provide quantitatively acceptable results in a finite time, and the methods should be as simple as possible (Halpern and Reeves, 1988). For the teaching of the concept of chemical equilibrium, often a reaction with the formation of a colored product that could be followed colorimetrically is employed (DeGrand *et al.,* 2011; de Morais *et al.,* 2016; Rodríguez and Mirenda, 2012; Samayoa-Oviedo, 2022). In the present study, an experiment with the complexation reaction between the cobalt and thiocyanate ions in a water-organic solvent mixture is developed to teach the topics of chemical equilibria and stability constants.

In different organic solvents cobalt (II) forms a series of tetrahedral complex ions with thiocyanate with ligand number up to 4 (Dickinson *et al.,* 1975; Katzin and Gebert, 1950; Pilarczyk *et al.,* 1987; Silber and Murguia, 1985), whereas in water and methanol octahedral complex ions with ligand number up to 6 are formed (Senise and Perrier, 1958; Velloso *et al.,* 1985). The tetrahedral complex ions are formed fast, they are stable and have a clear blue color, and this reaction is even used for the spectrophotometric determination of cobalt (Brown and Steinbach, 1959; Lundquist *et al.,* 1955; Reddy, 2004; Singh *et al.,* 1985; Wilson and McFarland, 1963). The formation of these complexes is also not dependent on pH in the pH range where the aqueous Co^{2+} ion is stable. This eliminates the necessity of strict pH control and simplifies the experiment (Belyaev *et al.,* 2002).

Although Ren *et al.* (2019) already developed a laboratory experiment utilizing the complexation of cobalt with thiocyanate in alcoholic solution, it was devoted to the study of the shift of the equilibrium between octa- and tetrahedral cobalt complexes by varying the alcohol ratio in the solution. Suppose many students attend the physical chemistry course. In that case, giving each student a different variant of the laboratory exercise is always advisable, so that every student may work with their unique problem. It is well known that the stability constants of cobalt-thiocyanate complexes significantly vary with both solvent composition, and alteration of the mole fraction of organic solvent in the medium (Silber and Murguia, 1985), which provides the instructor the unlimited possibility to vary the solvent composition and to give a unique dataset for each student. However, the experiment should also strictly control the water-organic solvent ratio to avoid significant systematic errors.

The aim of this work is to develop a laboratory experiment for the undergraduate students on the topic of chemical equilibria and stability constants of complex ions, to test the experiment with the students and to provide methodical recommendations for students and instructors on how to run the experiment.

In the present study, a simple laboratory experiment aimed at the survey of cobalt-thiocyanate complexation in the water-organic solvent mixtures, in which students determine the average ligand number and the equilibrium constant of the reaction, and based on their data, the stability constants are evaluated. The experiment implements the Bent-French method (Bent and French, 1941), which is very easy for undergraduate students to understand and use. This method was first proposed for the determination of stability constants in the system Fe^{3+}–SCN^-, but it also works with thiocyanate complexes of other methods. The method is well suited for the situation when several complex ions with different metal-to-ligand ratios might form. In this case both the experimental equilibrium constant and the average ligand number might be determined and based on this data the stability constants of two adjacent species might be evaluated. The theoretical background of the method in relation to the studying system Co^{2+}–SCN^- is presented in **Section 2.5**.

2. Experimental

2.1. Reagents and solutions

Reagents and solutions used for research were cobalt(II) chloride hexahydrate (pure grade, 97%), potassium thiocyanate (pure for analysis, 98%), acetone (pure grade, 99%), acetonitrile (pure grade, 99%), methanol (pure grade, 99%), ethanol (pure grade, 99%), and propan-2-ol (pure grade, 99%) were purchased from Lenreactiv (St. Petersburg, Russia).

2.2. Instrumentation

The analytical balance VLA-220S-O produced by Gosmetr (St. Petersburg, Russia) was used for weighing. The spectrophotometer SF-2000 produced by OKB Spektr (St. Petersburg, Russia), the photoelectrocolorimeter KFK-2 produced by Zagorskij optiko-mehaničeskij zavod (Sergiev Posad, Russia), and the digital colorimeter equipped with laser diode light emitters produced by Relab Ltd (Moscow, Russia) were used for colorimetric measurements. The distiller DÈ-4M produced by Èlektromedoborudovanie (St. Petersburg, Russia) produced distilled water for solution preparations. The 2nd-grade glassware was used in the laboratory.

2.3. Preparation of solutions

The solutions of $CoCl_2$ with the concentration of 0.005 mol/L and KSCN with the concentration of 0.5 mol/L are prepared by students directly before the start of the experiment by dissolving appropriate weightings in distilled water, transferring the solutions into the 50 mL volumetric flasks and diluting them to the mark with distilled water. The solution of KSCN with a concentration of 0.25 mol/L is prepared by placing 25 mL of the prepared 0.5 mol/L solution into the 50 mL volumetric flask and diluting to the mark by distilled water. Each student prepared a specific mixture of organic solvents according to the instructor's recommendation.

2.4. General procedure

Students prepare two series of solutions with the same amount of Co^{2+} but with different amounts of SCN^-. For this the aliquots of 0.005 mol/L $CoCl_2$, 0.5 mol/L or 0.25 mol/L KSCN solutions and water as described in **Table 1** were placed in the series of 25 mL volumetric flasks, 10 mL of chosen organic solvent or mixture of solvents was added to each flask, the solutions are vortex-mixed and thermostated at the room temperature over 10 min, completed to the mark by the same mixture of organic solvents, well shaken and thermostated over 10 min again. Then, the solutions' absorbances were measured against distilled water in the optical glass cuvettes, using the chosen path length at the chosen wavelength. The selection of the path length and the wavelength (or optical filter) is the part of the student exercise, and they depend on the composition of the solvent and concentrations of the reagents. The instruction for the students on how to perform the experiment is in **Appendix**.

Table 1. Solution series for the laboratory experiment.

No of solution	1	2	3	4	5	6
V ($CoCl_2$, 0.005 mol/L), mL	2.0	2.0	2.0	2.0	2.0	2.0
V (KSCN, 0.25 mol/L), mL	0.5	1.0	1.5	2.0	2.5	8.0
V (H_2O), mL	7.5	7.0	6.5	6.0	5.5	–
No of solution	**7**	**8**	**9**	**10**	**11**	**12**
V ($CoCl_2$, 0.005 mol/L), mL	2.0	2.0	2.0	2.0	2.0	2.0
V (KSCN, 0.5 mol/L), mL	0.5	1.0	1.5	2.0	2.5	8.0
V (H_2O), mL	7.5	7.0	6.5	6.0	5.5	–

Source: Elaborated by the authors.

2.5. Experimental data processing

The average ligand number in the complex and the experimentally determined equilibrium constant for each solution series (1–6 and 7–12) are calculated according to the Bent-French method (Bent and French, 1941).

Depending on the initial concentrations of both Co^{2+} and SCN^- ions the complexes of different composition might be formed in a solution. In the general case the equation of the complex formation reaction is presented by **Eq. 1**:

$$Co^{2+} + n\ SCN^- \rightleftharpoons [Co(SCN)_n]^{2-n} \quad (1)$$

where $0 \leqslant n \leqslant 4$ is the average number of ligands bound to a single metal atom. The value of n is determined by **Eq. 2**:

$$n = \frac{c_0(SCN^-) - c(SCN^-)}{c_0(Co^{2+})} \quad (2)$$

where $c_0(SCN^-)$ and $c_0(Co^{2+})$ are the initial concentrations of thiocyanate and cobalt ions in a solution, respectively (mol/L), $c(SCN^-)$ is the equilibrium concentration of free thiocyanate ions (mol/L). The equilibrium concentrations of the various complex ions in a solution are related to each other by the material balance equations shown by **Eq. 3**:

$$\begin{cases} c_0(Co^{2+}) = c(Co^{2+}) + \sum_{i=1}^{4} c\left([Co(SCN)_i]^{2-i}\right), \\ c_0(SCN^-) = c(SCN^-) + \sum_{i=1}^{4} i \cdot c\left([Co(SCN)_i]^{2-i}\right) \end{cases} \quad (3)$$

The equilibrium constant of the reaction (1) might be expressed as **Eq. 4**:

$$K_{exp} = \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+}) \cdot c^n(SCN^-)} \quad (4)$$

Taking logarithm of the **Eq. 4** and rearranging yields **Eq. 5**:

$$\lg \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+})} = \lg K_{exp} + n \cdot \lg c(SCN^-) \quad (5)$$

The **Eq. 5** presents a linear dependency of $\lg \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+})} = f\left(\lg c(SCN^-)\right)$. If the initial ligand concentration exceeds the initial metal concentration several times, then the difference of the ligand concentration during the complexation reaction might be neglected, and it could be assumed that the equilibrium concentration of ligand equals its initial concentration. This way, by performing the experiment series with equal initial concentrations of the metal and different initial concentrations of the ligand, one can determine the equilibrium concentrations of free metal and complex ions, plot the graph of the linear dependency $\lg \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+})} = f\left(\lg c(SCN^-)\right)$ and estimate the average ligand number n as its slope, and the value of experimentally determined equilibrium constant $\lg K_{exp}$ as its intercept.

The cobalt-thiocyanate complexes in a water-organic medium have a characteristic blue color, which makes it possible to perform a colorimetric measurement of their concentration. If one assumes that all complex ions with different numbers of ligands have equal molar attenuation coefficients, then the **Eq. 5** transforms into **Eq. 6**:

$$\lg \frac{A}{A_0 - A} = \lg K_{exp} + n \cdot \lg c(SCN^-) \quad (6)$$

where A is the absorbance of the solution of the complex ion (the solutions 1–5 and 7–11 in **Table 1**), A_0 is the absorbance of the solution, in which all cobalt ions are bound to the complex, and there are no free metal ions (the solutions 6 and 12 in **Table 1**).

From two series of solutions (namely, the solutions 1–6 and 7–12 in **Table 1**) two different values of average ligand number (n_1 and n_2) and two different experimental equilibrium constants ($K_{exp,1}$ and $K_{exp,2}$) are obtained. If one assumes that that at the experimental conditions only two adjacent complex ions $[Co(SCN)_x]^{2-x}$ and $[Co(SCN)_{x+1}]^{1-x}$ so that $x < n_1$, $n_2 < x+1$ are present in a solution, and the mole fractions of the other complexes are negligible, then the stability constants of the ions $[Co(SCN)_x]^{2-x}$ and $[Co(SCN)_{x+1}]^{1-x}$ could be estimated as it is presented in **Eqs. 7–10**:

$$\begin{cases} Co^{2+} + x\ SCN^- \rightleftharpoons [Co(SCN)_x]^{2-x} \\ \beta_x = \frac{c([Co(SCN)_x]^{2-x})}{c(Co^{2+}) \cdot c^x(SCN^-)} \end{cases} \quad (7)$$

$$\begin{cases} Co^{2+} + (x+1)\ SCN^- \rightleftharpoons [Co(SCN)_{x+1}]^{1-x} \\ \beta_{x+1} = \frac{c([Co(SCN)_{x+1}]^{1-x})}{c(Co^{2+}) \cdot c^{x+1}(SCN^-)} \end{cases} \quad (8)$$

$$\begin{cases} Co^{2+} + n_1\ SCN^- \rightleftharpoons (x+1-n_1)[Co(SCN)_x]^{2-x} + (n_1-x)[Co(SCN)_{x+1}]^{1-x} \\ K_{exp,1} = \frac{c^{x+1-n_1}([Co(SCN)_x]^{2-x})\cdot c^{n_1-x}([Co(SCN)_{x+1}]^{1-x})}{c(Co^{2+})\cdot c^{n_1}(SCN^-)} \end{cases} \quad (9)$$

$$\begin{cases} Co^{2+} + n_2\ SCN^- \rightleftharpoons (x+1-n_2)[Co(SCN)_x]^{2-x} + (n_2-x)[Co(SCN)_{x+1}]^{1-x} \\ K_{exp,2} = \frac{c^{x+1-n_2}([Co(SCN)_x]^{2-x})\cdot c^{n_2-x}([Co(SCN)_{x+1}]^{1-x})}{c(Co^{2+})\cdot c^{n_2}(SCN^-)} \end{cases} \quad (10)$$

By combining Eqs. 7–10, one could express the relationship between the experimental equilibrium constants and the stability constants according to Eq. 11:

$$\begin{cases} \lg K_{exp,1} = (x+1-n_1)\cdot \lg \beta_x + (n_1-x)\cdot \lg \beta_{x+1} \\ \lg K_{exp,2} = (x+1-n_2)\cdot \lg \beta_x + (n_2-x)\cdot \lg \beta_{x+1} \end{cases} \quad (11)$$

By solving the Eq. 11, one could estimate the stability constants β_x and β_{x+1}.

3. Results and discussion

3.1. Absorption spectrum of the complex

An absorption spectrum of the blue tetrahedral cobalt–thiocyanate complex exhibits a single peak. The wavelength corresponding to the absorption maximum ranges from 620 to 650 nm depending on the organic solvent or mixture used. For example, the spectra of two complexes in a mixture containing (by volume) 40% water, 20% acetone, and 40% propan-2-ol, and 40% water, 30% acetone, and 30% propan-2-ol, are shown in Fig. 1 together with the corresponding maximum wavelengths and absorbances. The choice of mixture composition was arbitrary.

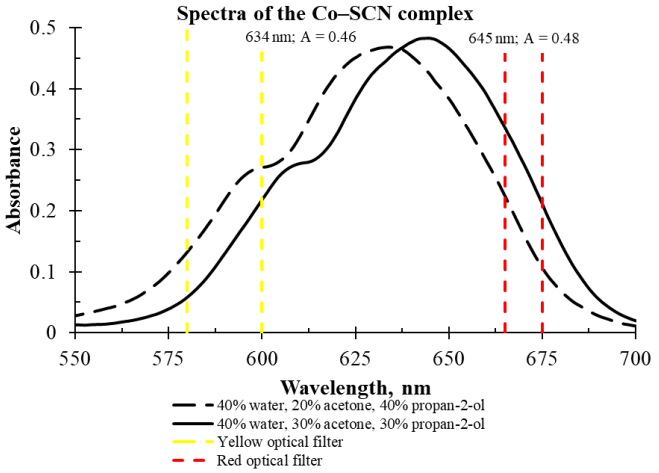


Figure 1. The absorption spectra of the solutions containing 400 μmol/L Co^{2+} and 0.16 mol/L SCN^- in different mixtures of water, acetone and propan-2-ol, and the wavelength ranges of yellow and red optical filters of photocolorimeter.
Source: Elaborated by the authors.

Suppose the laboratory experiment is performed using a spectrophotometer. In that case, the students are asked to record the UV-spectrum of the solution 12 from Table 1 in a water-organic solvent medium and make other subsequent measurements on the wavelength of the absorption maximum. However, the experiment might be also run using a photocolorimeter with the set of optical filters or a digital colorimeter with the set of light-diode emitter. In that case, the students are asked to measure the absorbance of the solution 9 from Table 1 at all available wavelengths and choose one that gives the absorbance value close to 0.4.

3.2. Example of experimental data processing

An example of experimental data obtained by the students revealing the cobalt–thiocyanate complexation in a mixture containing (by volume) 40% water, 30% acetone and 30% propan-2-ol are presented in Table 2.

The experimental dependencies of $\lg \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+})} = f(\lg\ c(SCN^-))$ are shown in Fig. 2.

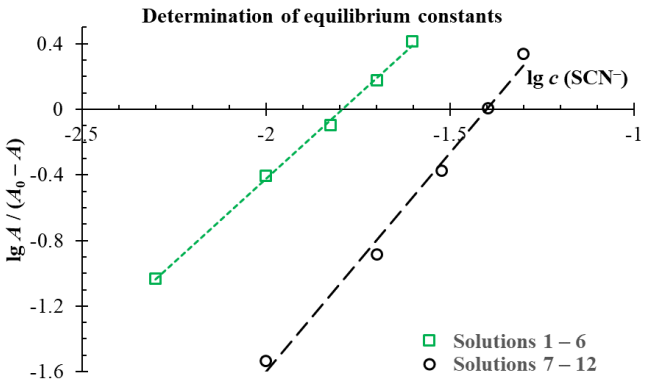


Figure 2. Typical dependencies of $\lg \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+})} = f(\lg\ c(SCN^-))$ in a mixture of 40 vol.% water, 30 vol.% acetone and 30 vol.% propan-2-ol: □ – solutions 1–6 from Table 1, ○ – solutions 7–12 from Table 1.
Source: Elaborated by the authors.

Table 2. Typical results obtained by students in a mixture of 40 vol.% water, 30 vol.% acetone and 30 vol.% propan-2-ol and the processing of experimental data.

No of solution from Table 1	1	2	3	4	5	6	7	8	9	10	11	12
c (SCN^-), mol/L	0.005	0.01	0.015	0.02	0.025	–	0.01	0.02	0.03	0.04	0.05	–
lg c (SCN^-)	−2.301	−2.00	−1.824	−1.699	−1.602	–	−2.00	−1.699	−1.523	−1.398	−1.301	–
A	0.0155	0.0514	0.0812	0.1095	0.1318	0.1824 ([A] = [A_0])	0.0137	0.0555	0.1437	0.2432	0.3302	0.4822 ([A] = [A_0])
$\frac{A}{A_0 - A}$	0.093	0.392	0.803	1.502	2.605	–	0.029	0.130	0.425	1.017	2.172	–
lg $\frac{A}{A_0 - A}$	−1.032	−0.406	−0.095	0.177	0.416	–	−1.534	−0.886	−0.372	0.008	0.337	–

Source: Elaborated by the authors.

By processing the experimental data from **Table 2** using the least squares technique, the following parameters of **Eq. 6** might be obtained: $n_1 = 2.04 \pm 0.05$, lg $K_{exp,1} = 3.65 \pm 0.09$, $n_2 = 2.7 \pm 0.1$, lg $K_{exp,2} = 3.7 \pm 0.2$. Since $2 < n_1, n_2 < 3$, by substituting these values into **Eq. 11**, one might obtain **Eq. 12**:

$$\begin{cases} (0.96 \pm 0.05) \cdot \lg \beta_2 + (0.04 \pm 0.05) \cdot \lg \beta_3 = 3.65 \pm 0.09 \\ (0.3 \pm 0.1) \cdot \lg \beta_2 + (0.7 \pm 0.1) \cdot \lg \beta_3 = 3.7 \pm 0.2 \end{cases} \quad (12)$$

By solving **Eq. 12**, one might estimate the values of stability constants β_2 and β_3 as is demonstrated by **Eq. 13**:

$$\begin{cases} \lg \beta_2 = \frac{(0.96 \pm 0.05) \cdot 17.5 - (0.3 \pm 0.1)}{(3.65 \pm 0.09) \cdot 17.5 - (3.7 \pm 0.2)} = \frac{60 \pm 1}{16.5 \pm 0.8} = 3.6 \pm 0.2 \\ \lg \beta_3 = \frac{(0.3 \pm 0.1) \cdot (3.6 \pm 0.2)}{0.7 \pm 0.1} = \frac{1.1 \pm 0.4}{0.7 \pm 0.1} = 1.6 \pm 0.8 \end{cases} \quad (13)$$

The presented example shows how students derive the expressions for stability constants of the cobalt–thiocyanate complex in water–organic medium and estimate the constants from their experimental data. This way, students obtain practical experience in the spectroscopic methods of studying chemical equilibria.

3.3. Replicability of data obtained by different students

To study the experiment's replicability, seven students performed the measurements in the same mixture of solvents in different days. The precision test results are presented in **Table 3**.

One might see that the results obtained by different students agree satisfactorily with each other, and the relative standard deviation of the results does not exceed 13%. This is a reasonably fair precision for the student laboratory exercise, which means that the experiment's replicability is sufficient to introduce it to the students.

Table 3. Inter-day precision test of results obtained by students in a mixture of 40 vol.% water, 30 vol.% acetone and 30 vol.% propan-2-ol.

No of solutions from Table 1	1	2	3	4	5	6	7	8	9	10	11	12
Absorbances of the solutions obtained by the different students in different days	0.0133	0.0520	0.0822	0.1165	0.1351	0.1749	0.0141	0.0631	0.1425	0.2519	0.3223	0.4820
	0.0169	0.0522	0.0891	0.1080	0.1396	0.1851	0.0114	0.0623	0.1499	0.2372	0.3357	0.4808
	0.0174	0.0424	0.0729	0.1004	0.1231	0.1801	0.0131	0.0566	0.1373	0.2527	0.3317	0.4840
	0.0192	0.0564	0.0796	0.1142	0.1323	0.1876	0.0107	0.0482	0.1477	0.2383	0.3298	0.4810
	0.0171	0.0451	0.0780	0.1087	0.1293	0.1802	0.0130	0.0612	0.1380	0.2390	0.3278	0.4821
	0.0168	0.0521	0.0746	0.1091	0.1262	0.1914	0.0114	0.0614	0.1350	0.2459	0.3286	0.4909
	0.0198	0.05034	0.0880	0.1159	0.1322	0.1763	0.0146	0.0601	0.1424	0.2486	0.3202	0.4799
Mean value	0.0172	0.05012	0.0807	0.1104	0.1311	0.1822	0.0126	0.0590	0.1419	0.2448	0.3280	0.4830
Standard deviation	0.0020	0.0047	0.0062	0.0056	0.0055	0.0060	0.0014	0.0052	0.0054	0.0066	0.0053	0.0037
Relative standard deviation, %	12.05	9.49	7.69	5.12	4.20	3.31	11.80	8.81	3.86	2.69	1.62	0.77

Source: Elaborated by the authors.

3.4. Experimenting using different instrumentation

When the spectrophotometer is not available in an educational laboratory, the experiment might be performed using simpler instrumentation, such as photocolorimeter with a set of optical filters, or a digital colorimeter with a set of diode-light emitters. In both cases, the incident light becomes not strictly monochromatic but covers a narrow interval of wavelengths. As one might see from **Fig. 1**, neither yellow nor red optical filter (or diode-light emitter) overlaps with the interval 620–650 nm, where the absorption maximum of the complex ion is usually present. Consequently, the absorbances measured with both these instruments are lower than those obtained with spectrophotometer. The results of the estimation of the average ligand numbers, experimental equilibrium constants and calculation of stability constants of complexes are presented in **Table 4**.

Table 4. Average ligand number, experimental equilibrium constants and estimated stability constants of cobalt–thiocyanate complexes in a mixture of 40 vol.% water, 30 vol.% acetone and 30 vol.% propan-2-ol obtained by different instrumentations.

Instrumentation	Wavelength, nm	n_1	n_2	lg $K_{exp,1}$	lg $K_{exp,2}$	lg β_2	lg β_3
Spectrophoto-meter	645	2.04 ± 0.05	2.7 ± 0.1	3.65 ± 0.09	3.7 ± 0.2	3.6 ± 0.2	1.6 ± 0.8
Photocolori-meter with yellow optical filter	590 ± 10	2.1 ± 0.1	2.6 ± 0.2	3.2 ± 0.2	4.5 ± 0.3	0.33 ± 0.08	0.2 ± 0.2
Photocolorimeter with red optical filter	670 ± 5	2.21 ± 0.08	2.5 ± 0.1	3.07 ± 0.07	3.56 ± 0.08	0.4 ± 0.1	0.4 ± 0.3
Digital colorimeter with yellow optical filter	590 ± 10	2.1 ± 0.1	2.6 ± 0.1	3.3 ± 0.1	4.6 ± 0.2	0.33 ± 0.06	0.2 ± 0.2
Digital colori-meter with red optical filter	670 ± 5	2.24 ± 0.09	2.6 ± 0.1	3.1 ± 0.1	3.54 ± 0.09	0.4 ± 0.1	0.5 ± 0.4

Source: elaborated by the author.

As one might see from Table 4, the values of average ligand numbers obtained using different instrumentation coincide well within the ranges of their uncertainties. The values of experimental equilibrium constants are also reasonably close to each other. However, the estimated values of the stability constants of two adjacent complex forms estimated from the absorbance maximum significantly differ from those calculated from the absorbances of yellow or red optical filters or diode-light emitters. The reason for these discrepancies is lower precision of these instruments, larger uncertainty intervals of the average ligand numbers and experimental equilibrium constants measured not in the actual absorbance maximum, and, consequently, larger errors of algebraic calculations. Regardless of this, the usage of a photocolorimeter or a digital colorimeter still provides representative results that are suitable for laboratory experiments.

3.5. Implementation of the experiment in the Physical Chemistry curriculum

This laboratory experiment was tested in the laboratory practical course on Physical Chemistry of Novosibirsk State University.

First, the description of the work and the methodological instructions for students were reviewed and evaluated by the instructors conducting the practical course, and their questions and comments were considered. After approval, instructors conducted test experiments with students and participated in obtaining and processing the data. Then the work was included in the general schedule of the laboratory practical course.

The work is carried out by one academic group (15 people). Undergraduate students (more specifically, of 3rd year of study) carry out the experiment in pairs. Before starting the work, they discuss with the instructor the general theory, order and rationale of actions when performing the experiment. If the students demonstrate knowledge and readiness to work, they are allowed to perform the experiment. Upon its completion, the teacher checks and agrees on the data they have obtained.

Then the students write a report on the work done, indicating a brief theory, the order of the experiment, the experimental data obtained and their processing. Finally, the students discuss the results with the instructor.

Even if the results obtained by various students on the same day using the same reagents look pretty similar, the low precision of highly colored solutions leads to different slopes of the regression lines. Therefore, the calculated average numbers of ligands and experimental equilibrium constants, and consequently, the estimated stability constants of two adjacent complex ions, are significantly scattered. Moreover, the solutions are thermostated at the room temperature, which could vary day by day, and consequently, the inter-day precision of the results is even lower. In addition, the assumption of the Bent-French method that all complex ions absorb light similarly and have equal attenuation coefficients makes the obtained results completely non-rigorous.

As a result, the results obtained are not academic but only educational in importance. However, it was found that this reaction is very suitable for teaching complexation equilibria in the physical chemistry course because the experiment is simple and inexpensive, works well, and gives quantitatively acceptable and representative results for students. Therefore, this laboratory experiment is well-suited for undergraduate physical chemistry students.

The difference between the present experiment and several other published laboratory experiments on chemical equilibria (DeGrand *et al.,* 2011; de Morais *et al.,* 2016; Rodríguez and Mirenda, 2012; Samayoa-Oviedo, 2022) is that most of these experiments focus on a single reaction, whereas in the present study, cobalt and thiocyanate ions might form multiple complex ions simultaneously, allowing for speciation to occur. Thus, the considered situation is more complex, and the students are tasked not only to estimate a single equilibrium constant, but also to determine the average metal-to-ligand ratio in the experimental conditions and to estimate the stability constant of two adjacent complex forms.

4. Conclusions

The laboratory experiment for the physical chemistry course for undergraduate students has been developed. In this experiment, students determine the average number of ligands in the cobalt–thiocyanate complex in water-organic solvent medium and the experimental equilibrium constant and then evaluate the stability constants of two adjacent complex ions in a solution. The reaction was found to be suitable for this experiment.

The formation equilibria of tetrahedral cobalt–thiocyanate complex ions are heavily affected by the organic solvent used and the organic-to-aqueous ratio. By varying the ratio of organic solvents and the quantity of water in a solvent mixture, the instructor has a nearly unlimited possibility of giving different variations of this experiment to different groups of students. The students could compare the results obtained with those obtained in different solvent mixtures.

The experiment was tested with the students and implemented in the Physical Chemistry laboratory course for undergraduates. The methodical recommendations on how to perform the experiment and process the experimental data were provided.

Conflict of interest

The authors declare that there is no conflict of interest.

Data availability statement

Data sharing is not applicable.

Artificial Intelligence usage statement

The authors declare that they did not use Artificial Intelligence tools at any stage of the preparation, correction, or evaluation of this work.

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Appendix

Instruction for the students on how to perform the experiment

1. Calculate the weighting of $CoCl_2 \cdot 6H_2O$ and KSCN that are needed for the preparation of 50 mL of 0.005 mol/L solution of $CoCl_2$ and 0.05 mol/L solution of KSCN. Take these weightings with the analytical balance, place them into glass beakers, dissolve in distilled water, place the solutions into the corresponding 50 ml volumetric flasks and complete the mark with distilled water. Take 25 mL of the freshly prepared 0.5 M KSCN solution, place it in another 50 mL volumetric flask and complete the mark with distilled water.

2. Prepare two series of solutions, containing equal amount of the cobalt ions and different amounts of the thiocyanate ions. To do it, take the aliquots of the prepared solutions of 0.005 mol/L $CoCl_2$, 0.5 mol/L or 0.25 mol/L KSCN, and water presented in **Table 1** into a series of 25 mL volumetric flasks using graduated pipettes, add 10 mL of chosen organic solvent or mixture of solvents to each flask, mix the solutions thoroughly, allow to stand at the room temperature for 10 min, complete to the mark by the same organic solvent, mix thoroughly and allow to stand at the room temperature for 10 min again.

3. Record the UV-spectrum of the prepared solution against the distilled water and determine the wavelength of absorption maximum. Measure the absorbances of the prepared solutions against the distilled water at the chosen wavelength.

4. For each solution calculate the concentration of thiocyanate ions.

5. Place the experimental results and the calculated values in **Table 2**.

6. For two series of solutions perform the linear regression of the dependencies $\lg \frac{c([Co(SCN)_n]^{2-n})}{c(Co^{2+})} = f(\lg\ c(SCN^-))$. Evaluate the average ligand numbers as the slopes of these dependencies, and the logarithms of the experimental equilibrium constants $K_{exp,1}$ and $K_{exp,2}$ as the intercepts.

7. Make a conclusion about the complex ions present in a solution and evaluate their stability constants by writing and solving the appropriate system of equations.