

## TEMPERATURE DEPENDENCE OF SOME COBALT-SALTS/PEG SYSTEMS SPECTRA

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UV-VIS absorption spectra of Cobalt Chloride ( $\text{CoCl}_2$ ) and Cobalt Bromide ( $\text{CoBr}_2$ ) in Poly(Ethylene Glycol) (PEG) were measured and analyzed at different temperatures. Five different PEG average molecular weights (chain lengths) have been used. Two pseudo-tetrahedral Co-complexes have been identified. The formation of these complex-types is explained by studying the temperature behavior of such systems.

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### 1. Introduction

The UV-VIS spectroscopy has been used in the past to obtain information about the local environment of the transition-metal ions [1,2]. The Co-salt/polymer systems have been studied extensively in the last decade [3-5] because of their numerous applications. In spite of considerable developments in the field, the interactions between transition-metal ion and polymeric chain are not completely understood. In this paper it is studied the spectral behavior of  $\text{CoCl}_2$ /PEG and  $\text{CoBr}_2$ /PEG systems as a function of (at and above room) temperature. The UV-VIS spectroscopy measurements were performed in systems prepared with PEGs of different chain length. The Co-complex types existing in such systems were identified.

### 2. Experimental

Cobalt salts and PEG with average molecular weights of 200, 400, 600 and 1000 supplied by Aldrich, and PEG-4000 by Scientific Polymer Products have been used. Co-salts were dried at 120°C for 3 hours in a vacuum oven before use, to eliminate the moisture.

The spectra were recorded in the visible domain (500 – 800 nm) using a Varian, dual beam, Cary Model 118 spectrophotometer. A 2 nm/s scan speed and 1 nm recording steps were used. All samples were measured in a 2 mm path length glass cell.

To heat the samples we used an oven that has been introduced into the spectrometer sample's compartment. The power supply of the oven had an adjustable voltage (d.c.) device. A Chromel-Alumel thermocouple was used to monitor the temperature.

The-cobalt salt was directly dissolved in polymer at room temperature for PEG –200, -400 and -600 (liquids at room temperature) and at a little higher temperature than PEG's melting point for PEG -1000 and -4000 (solids at room temperature). The spectra were recorded at different temperatures to around 120 °C.

### 3. Results and discussion

Fig. 1 and Fig. 2 show the spectra of the  $\text{CoCl}_2$ /PEG-200 and  $\text{CoCl}_2$ /PEG-400, respectively, at different temperatures.

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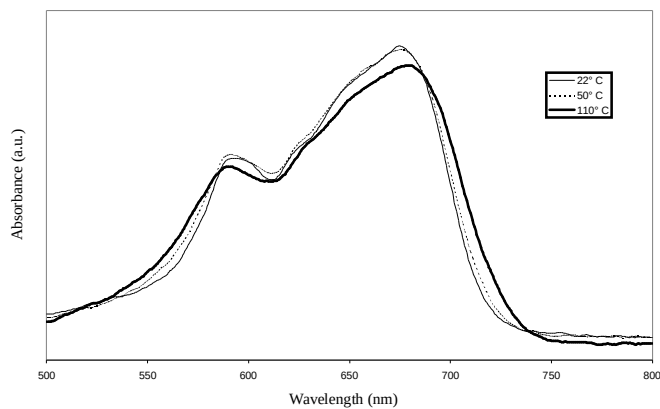


Fig. 1. Absorption spectra of the CoCl<sub>2</sub>/PEG-200 system as a function of temperature.

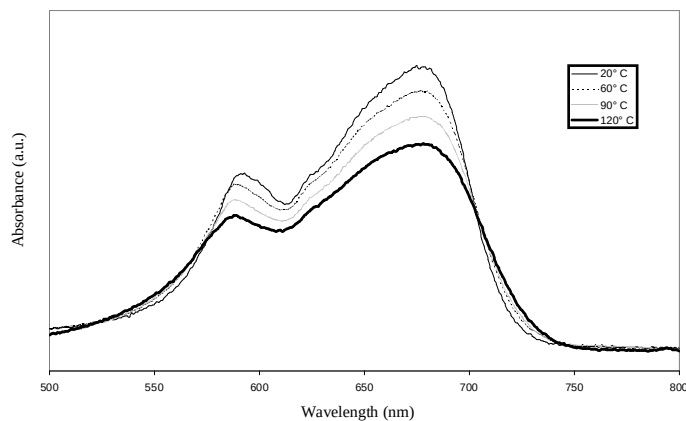


Fig. 2. Absorption spectra of the CoCl<sub>2</sub>/PEG-400 system as a function of temperature.

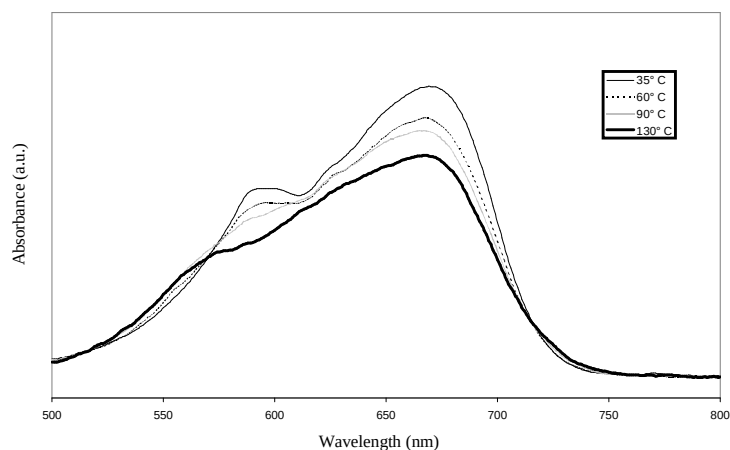


Fig. 3. The temperature dependence of the CoCl<sub>2</sub>/PEG-600 system spectra.

As can be seen, the general aspect of the spectra presented in Fig. 1 and Fig. 2 is similar. Comparing with literature data [1,2,6] concerning chloride-complexes of the cobalt in acetone solutions it is obvious that all the spectra presented in Fig. 1 and Fig. 2 belong to the tetrahedral [CoCl<sub>3</sub>L]<sup>-</sup> complex (where L is a ligand from polymer in our case). Based on the general (predominant) spectra aspect, we can say that, by increasing the temperature, the spectra do not present major changes.

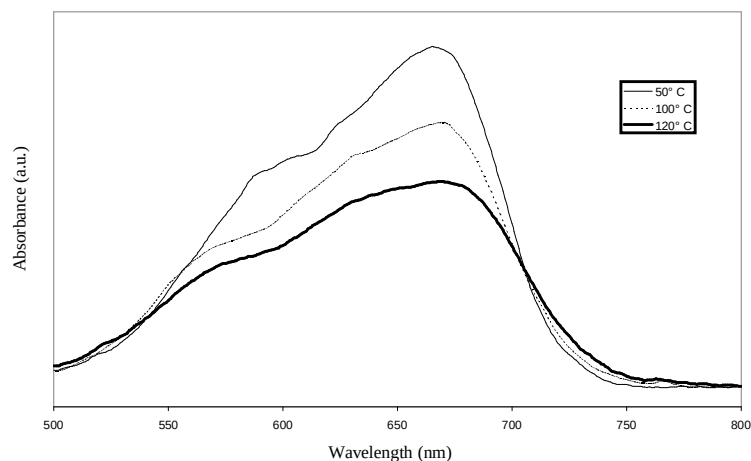


Fig. 4. Absorption spectra of the  $\text{CoCl}_2/\text{PEG-1000}$  system as a function of temperature.

In the same sense, we can observe that the  $[\text{CoCl}_3\text{L}]^-$  complex is preponderant at  $35^\circ\text{C}$  temperature (at room temperature PEG-600 is semi-liquid) and it is transformed into  $[\text{CoCl}_2\text{L}_2]$  complex at  $130^\circ\text{C}$ .

Fig. 4 and Fig. 5 show the spectra of  $\text{CoCl}_2/\text{PEG-1000}$  and  $\text{CoCl}_2/\text{PEG-4000}$  systems, respectively, at different temperatures.

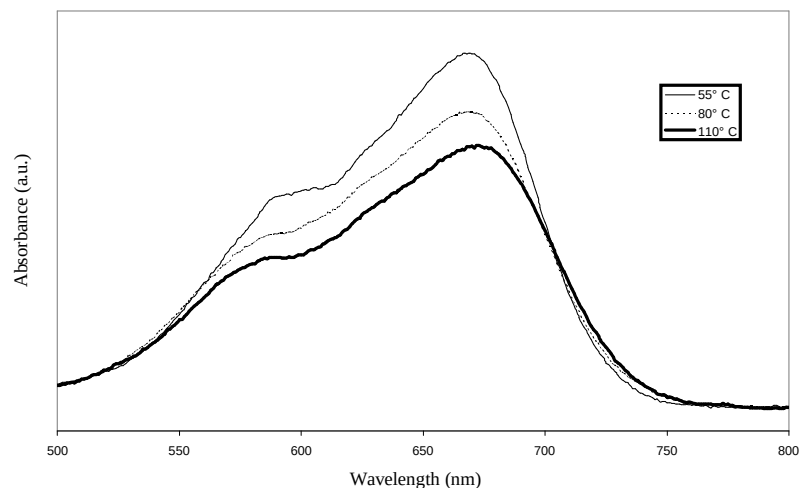


Fig. 5. Absorption spectra of the  $\text{CoCl}_2/\text{PEG-4000}$  system as a function of temperature.

One can also observe here a transformation from  $[\text{CoCl}_3\text{L}]^-$  complex type spectrum (though not so pure like the preceding cases) at low temperature to  $[\text{CoCl}_2\text{L}_2]$  complex spectrum at high temperature (similar with the  $\text{CoCl}_2/\text{PEG-600}$  system case).

The synopsis of these observations is presented in Table 1.

Table 1.

| Sample                          | Complex                           |                             |
|---------------------------------|-----------------------------------|-----------------------------|
|                                 | Low temp.                         | High temp.                  |
| $\text{CoCl}_2/\text{PEG-200}$  | $[\text{CoCl}_3\text{L}]^-$       | $[\text{CoCl}_3\text{L}]^-$ |
| $\text{CoCl}_2/\text{PEG-400}$  | $[\text{CoCl}_3\text{L}]^-$       | $[\text{CoCl}_3\text{L}]^-$ |
| $\text{CoCl}_2/\text{PEG-600}$  | $[\text{CoCl}_3\text{L}]^-$       | $[\text{CoCl}_2\text{L}_2]$ |
| $\text{CoCl}_2/\text{PEG-1000}$ | $[\text{CoCl}_3\text{L}]^-(\sim)$ | $[\text{CoCl}_2\text{L}_2]$ |
| $\text{CoCl}_2/\text{PEG-4000}$ | $[\text{CoCl}_3\text{L}]^-(\sim)$ | $[\text{CoCl}_2\text{L}_2]$ |

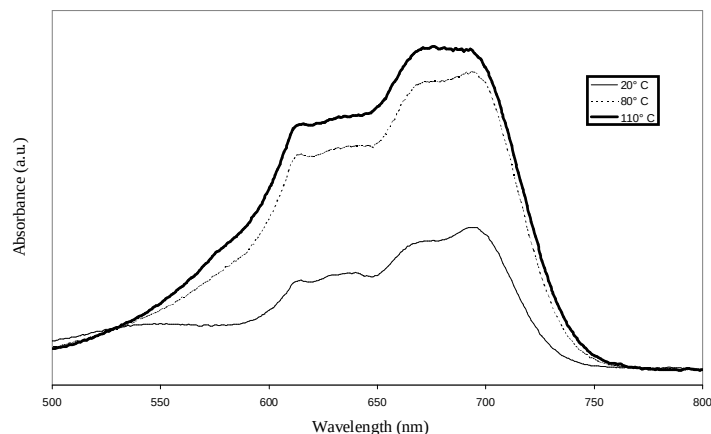


Fig. 6. Absorption spectra of the  $\text{CoBr}_2/\text{PEG-200}$  system as a function of temperature.

The mechanism that attempts to explain this behavior is the following. First, in all PEG's cases, the solvent produces some proportion of octahedral Co-complexes,  $[\text{CoCl}_5\text{L}]^-$  and  $[\text{CoL}_6]^{2+}$  complex types, where L is a ligand from the polymer,  $\text{OH}^-$  terminal group, which, like the water, prefers formation of the octahedral complexes. This fact is proven by exclusive octahedral type spectrum of the  $\text{CoCl}_2/\text{MEG}$  (MonoEthylene Glycol) system. The spectra of the octahedral complexes are harder detectable, because, as complexes with inversion centre, their absorption bands are lower (by about two orders of magnitude than those of the tetrahedral species). Free chlorine ions are produced when these octahedral complexes are formed. The  $T_d$ -like  $[\text{CoCl}_3\text{L}]^-$  complex (or sometimes, if  $\text{Cl}^-$  concentration is greater,  $[\text{CoCl}_4]^{2-}$  complex) are formed with these chlorine ions. The  $\text{CoCl}_2/\text{PEG}$  systems with longer polymeric chain length (PEG -600, -1000, -4000) are transformed, as seen from the spectra, at greater temperature from  $[\text{CoCl}_3\text{L}]^-$  into  $[\text{CoCl}_2\text{L}_2]$  complex. This means that the octahedral complexes formation is not favored at higher temperature. Therefore, the  $T_d$  – complexes with larger number of  $\text{Cl}^-$  ions are not formed anymore, because free chlorine ions are not enough. This phenomenon appears especially in cases with longer polymeric chain because there are fewer terminal  $\text{OH}^-$  - groups.

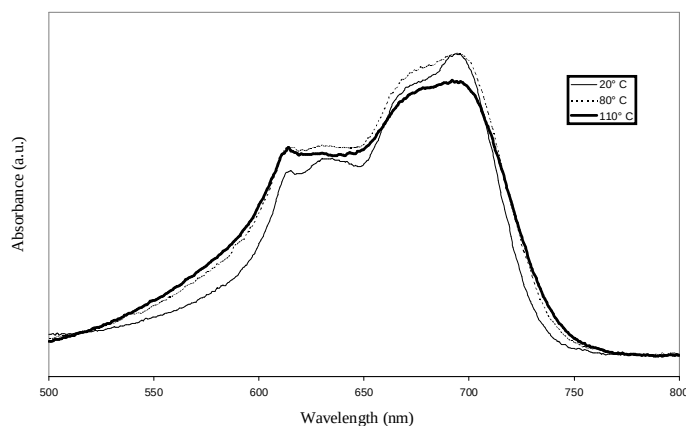


Fig. 7. Absorption spectra of the  $\text{CoBr}_2/\text{PEG-400}$  system as function of temperature.

To verify the proposed mechanism we performed similar experiments with  $\text{CoBr}_2/\text{PEG}$  systems. Fig. 6 – 10 show the spectra of  $\text{CoBr}_2/\text{PEG}$  –200, –400, –600, –1000 and –4000 systems, respectively, recorded at various temperatures in the same conditions as for the  $\text{CoCl}_2/\text{PEG}$  systems.

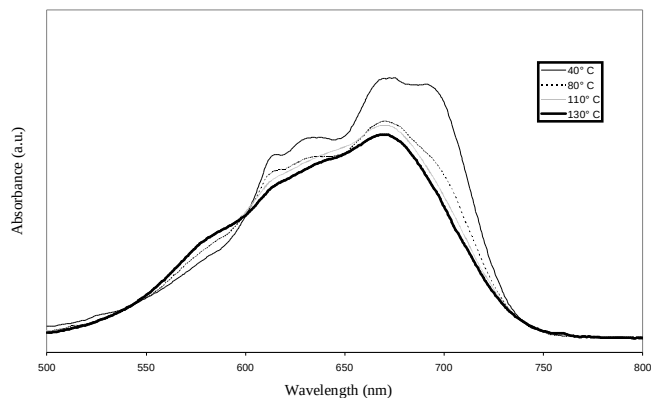


Fig. 8. Absorption spectra of the CoBr<sub>2</sub>/PEG-600 system as a function of temperature.

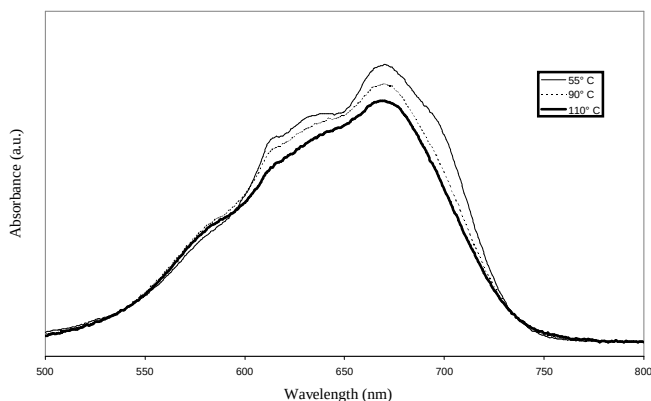


Fig. 9. Absorption spectra of the CoBr<sub>2</sub>/PEG-1000 system as a function of temperature.

Comparing with literature spectra [1,7] of tetrahedral bromo-complexes of cobalt, the predominant aspect of the spectra of CoBr<sub>2</sub>/PEG-200 (Fig. 6) and CoBr<sub>2</sub>/PEG-400 (Fig. 7) systems, at room temperature, show the presence of the [CoBr<sub>3</sub>L]<sup>-</sup> complex. At higher temperature the spectral data show that besides the [CoBr<sub>3</sub>L]<sup>-</sup> complex there is also the [CoBr<sub>2</sub>L<sub>2</sub>] complex. This is confirmed by the band at 580 nm belonging to a [CoBr<sub>2</sub>L<sub>2</sub>] type complex and by the flattening of the band at 634 nm belonging to a [CoBr<sub>3</sub>L]<sup>-</sup> type complex.

The case of CoBr<sub>2</sub>/PEG-600 system (Fig. 8) is rather clear. At lower temperature the predominant complex is [CoBr<sub>3</sub>L]<sup>-</sup> and at higher temperature the spectrum belongs to a [CoBr<sub>2</sub>L<sub>2</sub>] complex type.

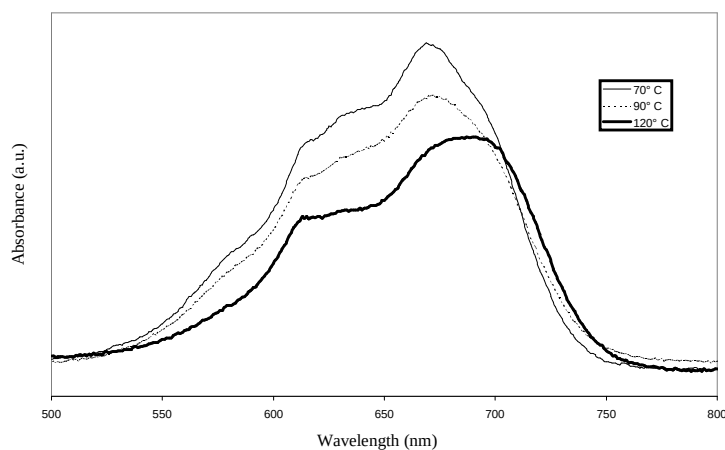


Fig. 10. Absorption spectra of the CoBr<sub>2</sub>/PEG-4000 system as a function of temperature.

For the  $\text{CoBr}_2/\text{PEG-1000}$  system, first we shall remark that the spectrum does not belong to a pure complex at low temperature, probably it is a mixture of  $[\text{CoBr}_3\text{L}]^-$  and  $[\text{CoBr}_2\text{L}_2]$  complexes (the first being predominant). At high temperature the concentration of  $[\text{CoBr}_2\text{L}_2]$  complex increases and the spectrum transforms into one of that type.

At lower temperature the spectrum of the  $\text{CoBr}_2/\text{PEG-4000}$  system is similar to that of  $\text{CoBr}_2/\text{PEG-1000}$  system, a predominant  $[\text{CoBr}_3\text{L}]^-$  complex, but also to some amount of  $[\text{CoBr}_2\text{L}_2]$  complex. At high temperature this system has a strange behavior because it transforms into  $[\text{CoBr}_3\text{L}]^-$  complex, contrary to  $\text{CoCl}_2/\text{PEG-4000}$  system.

Table 2 presents the main complex types appearing in the studied  $\text{CoBr}_2/\text{PEG}$  systems, at lowest and highest temperatures. The assignments have been indicated by the general spectra aspect, by comparing with literature data of tetrahedral bromo-complex of cobalt.

Table 2.

| Sample                          | Complex                                                        |                                                                   |
|---------------------------------|----------------------------------------------------------------|-------------------------------------------------------------------|
|                                 | Low temp.                                                      | High temp.                                                        |
| $\text{CoBr}_2/\text{PEG-200}$  | $[\text{CoBr}_3\text{L}]^-$                                    | $[\text{CoBr}_3\text{L}]^-$ ( $[\text{CoBr}_2\text{L}_2]$ appear) |
| $\text{CoBr}_2/\text{PEG-400}$  | $[\text{CoBr}_3\text{L}]^-$                                    | $[\text{CoBr}_3\text{L}]^-$ ( $[\text{CoBr}_2\text{L}_2]$ appear) |
| $\text{CoBr}_2/\text{PEG-600}$  | $[\text{CoBr}_3\text{L}]^-$                                    | $[\text{CoBr}_2\text{L}_2]$                                       |
| $\text{CoBr}_2/\text{PEG-1000}$ | $[\text{CoBr}_3\text{L}]^-$ (and $[\text{CoBr}_2\text{L}_2]$ ) | $[\text{CoBr}_2\text{L}_2]$                                       |
| $\text{CoBr}_2/\text{PEG-4000}$ | $[\text{CoBr}_3\text{L}]^-$ (and $[\text{CoBr}_2\text{L}_2]$ ) | $[\text{CoBr}_3\text{L}]^-$                                       |

The mechanism described above to explain the  $\text{CoCl}_2/\text{PEG}$  systems behavior at varying temperature is confirmed for the  $\text{CoBr}_2/\text{PEG}$  systems. It is observed that at high temperature for  $\text{CoBr}_2/\text{PEG-200}$  and  $\text{CoBr}_2/\text{PEG-400}$  systems the  $[\text{CoBr}_2\text{L}_2]$  complex appears as a consequence of octahedral links destruction at that temperature. Moreover, the spectrum at low temperature for systems with PEG-1000 and PEG-4000, which apparently does not belong to a unique complex, confirms the hypothesis that the octahedral complex formation for systems with longer polymeric chain is less probable because these complexes are formed with  $\text{OH}^-$  terminal groups, which are fewer. The behavior at high temperature of  $\text{CoBr}_2/\text{PEG-4000}$  system remains unexplained and further investigation must be done to understand it.

#### 4. Conclusions

The UV-VIS absorption spectra of the  $\text{CoCl}_2/\text{PEG}$  and  $\text{CoBr}_2/\text{PEG}$  systems with different polymeric chain length have been measured and analyzed. The temperature dependence of these spectra has been investigated. The tetrahedral-type Co-complexes that exist in such systems have been identified. The temperature dependence of the spectra of these systems shows Co-complexes transformation. A mechanism of the Co-complexes formation in Co-salts/PEG systems is proposed.

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