

Colorimetric Detection of Cobalt in Different Solvents by Using Their Solvatochromic Properties

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Abstract

Cobalt chloride solutions exhibit different colours in different solvents thus displaying solvatochromic behaviour. This study reports spectrophotometric investigation of solvatochromic behavior of cobalt chloride solutions in different polar protic and aprotic solvents. The results are discussed in correlation with solvent properties such as dielectric constant, hydrogen bonding ability of solvent, ratio between hydrocarbon chain length and number of polar groups. Spectrophotometric analysis of solutions was carried out to understand interaction between solvent and cobalt salt as well as probable molecular structure of salt-solvent complex. The results showed that most of the polar protic solvents displayed pink color and polar aprotic ones showed blue colour. When the results with a series of alcoholic solvents were compared it was found that colour is not only a function of hydrogen bonding ability of solvent but also depends on hydrocarbon chain length.

Index Headings: Solvatochromism, spectrophotometry, aprotic, protic, polar, solvent.

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INTRODUCTION

Cobalt chloride solvent systems have been a matter of interest and curiosity for the scientific community worldwide due to their colorful solvatochromic behavior. A number of investigators have studied the absorption spectra of cobalt chloride solutions in hydrochloric acid [1-4]. The focus of most of the studies was directed towards analysis of absorption bands and prediction of structure of coloured complexes. The absorption spectra of solutions of cobalt chloride, cobalt bromide and cobalt iodide in concentrated hydrochloric, hydrobromic and hydriodic acids was studied by Wallace R. Brode *et al.*, [5]. The change in absorption spectrum of cobalt chloride in aqueous solution with increasing concentration of hydrochloric acid was studied by Albert Jackson *et al.*, [6].

Katzin *et al.*, carried out spectrophotometric studies of cobaltous chloride in different solvent systems [7]. He was the first researcher who used optical spectroscopic data to analyze cobalt salt structures. Fine and Trutia in subsequent studies revealed the presence of several types of complexes in cobalt chloride solvent systems [8, 9]. The absorption spectra of cobalt chloride in concentrated perchlorate

solution was studied by K. Mizutani *et al.*, [10]. He mentioned that the colour change of cobalt chloride from pink to reddish violet on addition of large amount of sodium perchlorate was due to decrease of water activity caused by the added inert salt which favours the formation of chloro complexes. The colour of transition metal compounds particularly solvatochromic behavior of cobalt (II) chloride was studied by M. Raczko *et al.*, [11]. Absorption spectra of $\text{CoCl}_2/\text{Acetone}$ systems was again studied by A. Trutia *et al.*, [12] Selective solvation of Co^{2+} in aqueous ethanol was studied by Hafiz ur Rehman [13] and behavior of cobalt cations in aqueous and alcoholic solutions of cobalt chloride hexahydrate was also investigated by P. Petkova *et al.*, [14]. Cobalt chloride based humidity sensor attached to sol-gel modified cellulosic material was studied by R. Tessadri *et al.*, [15]. Recently P. Zielonka *et al.*, studied visualization of wood humidity using cobalt chloride during microwave drying [16]. They proposed a simple method using cobalt chloride solution which on drying changes its colour from transparent through light pink up to deep blue thus allowing for visualization of moisture content in wood sample.

Hence it is observed that Cobalt chloride solutions have been extensively studied since nineteenth century for their colorful solvatochromic behavior and sensing property especially for their application as humidity sensor. However till date no such study has been carried out where cobalt chloride solvent interaction has been spectroscopically investigated with respect to solvent properties such as dielectric constant, hydrogen bonding ability of solvent especially ratio between hydrocarbon chain length and number of polar hydroxyl groups. Hence spectrophotometric analysis of cobalt chloride solutions in different types of protic and aprotic solvents with varying chain lengths and number of polar hydroxyl groups was carried out to understand interaction between solvent and cobalt salt as well as resulting solvatochromic response.

MATERIALS AND METHODS

Cobalt salt ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was supplied by Aldrich and was used as received. Spectroscopic grade solvents (HPLC grade Fluka) used in the study were of highest available purity. Deionized water and borosil glasswares were used for preparation of solutions. UV-Visible spectra were recorded by using instrument Analytikjena SPECORD 205 in the wavelength range 190-1100nm. A 50 nm/sec scan speed and 1nm recording steps were used. All samples were measured in a 1cm path length quartz cuvette.

The cobalt salt was directly dissolved in 5ml of each solvent and the developed colour was recorded and spectra of solutions were measured by using UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Table-1 shows details of the solvents properties used in the study such as molecular formula, molecular weight, boiling point, density, water solubility and dielectric constant. The color of cobalt chloride solutions in each solvent is also mentioned. It is observed that cobalt chloride solutions displayed different colors in different solvents as shown in Fig-1. In addition to well reported two colors i.e. blue in acetone and pink in water some mixed colors were also observed. In this study two different categories of solvents were selected. Chloroform, acetonitrile, DMF, NMP and acetone being polar aprotic whereas methanol, ethanol, isopropanol, butanol, ethylene glycol, diethylene glycol, glycerol and water being polar protic. From Fig-1 it is observed that all the polar aprotic solvents showed blue colour, but few polar protic solvents i.e. isopropanol, butanol and diethylene glycol also showed blue color. Ethanol and chloroform showed pink colour with a slight bluish tinge. Rest of the solutions showed pink colour.

It has been reported in previous studies that cobalt chloride in aqueous solutions exist in the form of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ having octahedral configuration and displaying pink colour which consists of a Co^{2+} ion surrounded by six water molecules in an octahedral arrangement as shown in Fig-2a. The electronegative oxygen atoms are positioned toward the positively charged Co^{2+} ion. On the other hand in DMF or acetone solutions the configuration is tetrahedral as shown in Fig-2b due to the presence of $[\text{CoCl}_4]^{2-}$ ions exhibiting blue color. The equilibrium can be shifted from octahedral pink to tetrahedral blue by adding either HCl or chloride salts to aqueous solutions of cobalt chloride or in reverse direction that is from tetrahedral blue to octahedral pink by adding water as shown by equations 1 and 2 below:

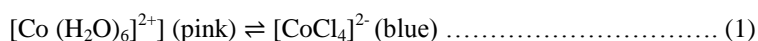


Table-1: Solvent properties, colour and absorbance of CoCl_2 solutions

S.L No	Solvent	Formula	Molecular weight	Boiling point ($^{\circ}\text{C}$)	Density (g/ml)	Solubility in H_2O (g/100g)	Dielectric constant	Colour	UV-Vis Abs (nm)
1.	Chloroform	CHCl_3	119.38	61.7	1.498	0.795	4.81	Bluish pink	520 670
2.	Acetonitrile (MeCN)	$\text{CH}_3\text{C}\equiv\text{N}$	41.05	81.16	0.786	Miscible	37.5	Blue	590 680
3.	Dimethylformamide (DMF)	$\text{H}-\text{C}(=\text{O})\text{N}(\text{CH}_3)_2$	73.09	153	0.944	Miscible	36.7	Blue	610 670
4.	N-methyl-2-pyrrolidinone (NMP)	$\text{CH}_5\text{H}_9\text{NO}$	99.13	202	1.033	10	32	Blue	580 660
5.	Methanol	CH_3OH	32.04	64.6	0.791	Miscible	32.6	Light pink	520
6.	Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	46.07	78.5	0.789	Miscible	24.6	Pink	520
7.	Butanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	74.12	117.6	0.81	6.3	17.8	Blue	670
8.	Isopropanol	$\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_3$	88.15	82.4	0.785	Miscible	18.3	Blue	570 610 660

9.	Ethylene glycol	HOCH ₂ CH ₂ OH	62.07	195	1.115	Miscible	37.7	Light pink	525
10.	Diethylene glycol	C ₄ H ₁₀ O ₃	106.12	245	1.118	10	31.7	Blue	550 590 680
11.	Glycerol	C ₃ H ₈ O ₃	92.09	290	1.261	Miscible	42.5	Pink	525
12.	Acetone	C ₃ H ₆ O	58.08	56.2	0.786	Miscible	20.7	Blue	590 695
13.	Water	H-O-H	18.02	100	0.998	-	78.54	Light pink	520

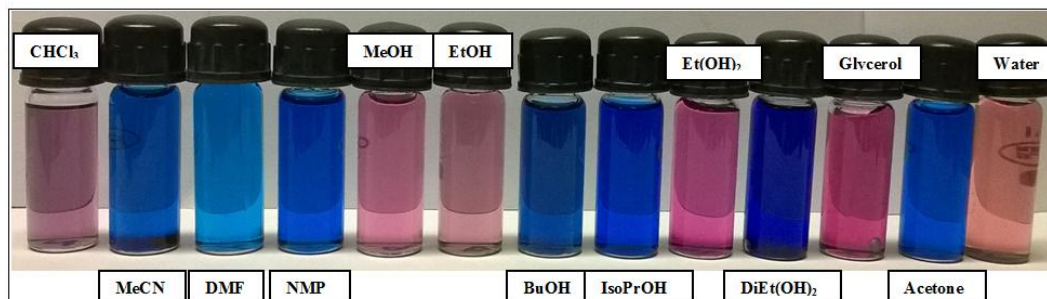


Fig-1: Colors of cobalt chloride solutions in different solvents

UV-Vis Spectral Results

The UV-Vis spectroscopic absorption bands of different cobalt chloride solutions are mentioned in Table-1. The absorption spectra of cobalt chloride solutions in polar aprotic solvents as acetonitrile, DMF, NMP and acetone displaying blue colour showed two absorption bands at 580-610nm and 660-700nm. Slight shifts in the peak positions were observed depending on the nature of solvent as noticed in the UV-Vis absorption spectrum of DMF and acetone shown in Fig 3 and 4 respectively. In DMF, two peaks one small at 610nm and one broad at 670nm is observed. Acetone system also shows multiple peaks from 590 to 695nm range with broadening of peaks. Similar type of spectra of CoCl₂/Acetone systems were reported by A. Trutia *et al.*, [9] where it was stated that acetone acts as a ligand due to oxygen atom and forms complex with CoCl₂ showing absorption peaks in same region. On the other hand methanol, ethylene glycol, glycerol and water, showed pink color as shown in Fig-1. UV-Vis spectra of methanol and water are shown in Fig 5 and 6. Both solutions showed one very strong absorption band at 520-525nm. When small molecular size solvents such as water and methanol is used as a solvent, CoCl₂ complexes with six total molecules to form pink octahedral complex ion. Strong solvation of Co²⁺ by water makes it difficult to form tetrahedral complex in aqueous solution. But ethylene glycol and glycerol also displayed pink colour and similar absorption band at 530nm observed for glycerol (Fig-7) proves that although bigger in molecular size compared to water and methanol but these two solvents are also able to form octahedral complexes. This result shows that in these two cases steric factors are overpowered by ion solvent interaction. This may be due to the presence of two and three hydroxyl groups respectively leading to greater chances for hydrogen bonding. Chloroform and ethanol solutions displayed pink color with slight bluish

tinge (Fig-1). The UV-Vis absorption spectrum of CHCl₃ solution is shown in Fig 8 which shows absorption spectra at 520nm with a small hump at 670nm. The appearance of additional small hump shows partial formation of tetrahedral complex structures also in addition to formation of octahedral structures which is in correlation with slight bluish tinge in their solutions.

The solutions for large alcoholic solvents as isopropanol, butanol, diethylene glycol etc showed several peaks in the range of 500-700nm. With these alcohols it is observed that tetrahedral complex formation is preferred (blue color) rather than octahedral (pink color) to minimize repulsive forces and steric hinderance. Hence it can be stated that here steric factors play a dominant role in comparison to ion solvent interaction.

One of the important solvent property is dielectric constant (ϵ'), which is related to polarity of solvent. Higher the ϵ' of any solvent higher the polarity. Generally high ϵ' solvents like water, dissolves inorganic salts due to solvation of ions by H⁺ and OH⁻ ions. From the Table I it is observed that only ϵ' is not the deciding parameter for color of CoCl₂ solvent systems, as it is clearly seen that solvents having nearly similar ϵ' {CH₃CN(37.5), ethylene glycol (37.7) & CH₃OH (32.6), Diethylene glycol (31.7), NMP (32)} showed different colours of CoCl₂ solutions.

In addition to this observation, a very interesting phenomenon has also been observed where butanol a primary alcohol with 4 carbon atoms and one hydroxyl functional group shows blue colour whereas glycerol comparatively bulky triol with three carbon atoms and three hydroxyl functional groups showed pink colour. Similar phenomenon has been observed

with ethanol and ethylene glycol. Here both solvent molecules possess two carbon atoms but ethylene glycol with one extra hydroxyl group compared to ethanol showed pink colour in comparison to ethanol which showed bluish pink colour. The UV-Vis spectra of ethanol and ethylene glycol also show similarities with spectra of complexes having a mixture of both octahedral and tetrahedral complexes as well as only octahedral complexes respectively.

These observations show that number of polar hydroxyl groups plays a major role in deciding configurational structure of CoCl_2 -solvent complex system as well as color generated. More the number of polar OH groups more the probability of formation of

octahedral complexes irrespective of other solvent properties.

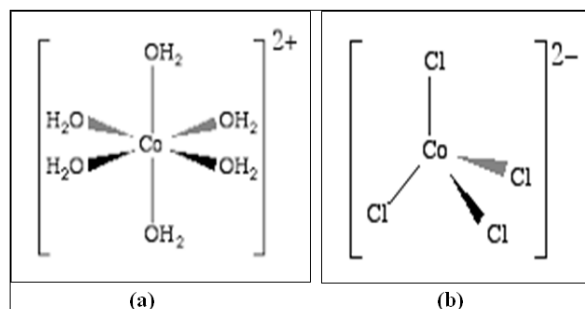


Fig-2(a): Octahedral configuration of cobalt hexahydrate ion and (b) Tetrahedral configuration of cobalt tetrachloride ion

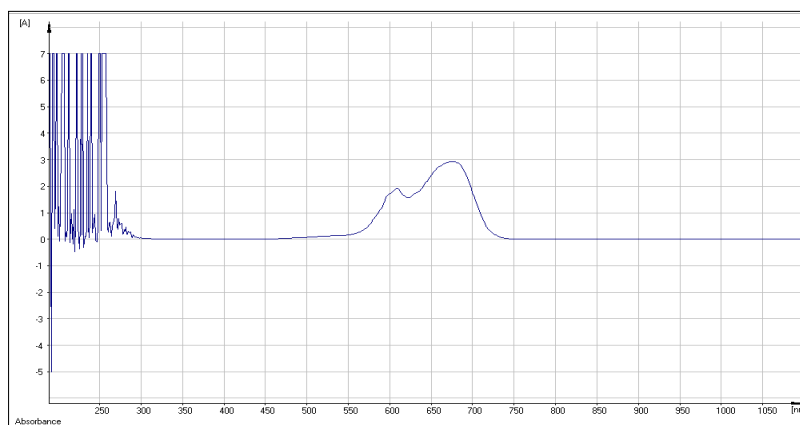


Fig-3: Absorption spectrum of blue colored CoCl_2 -DMF complex

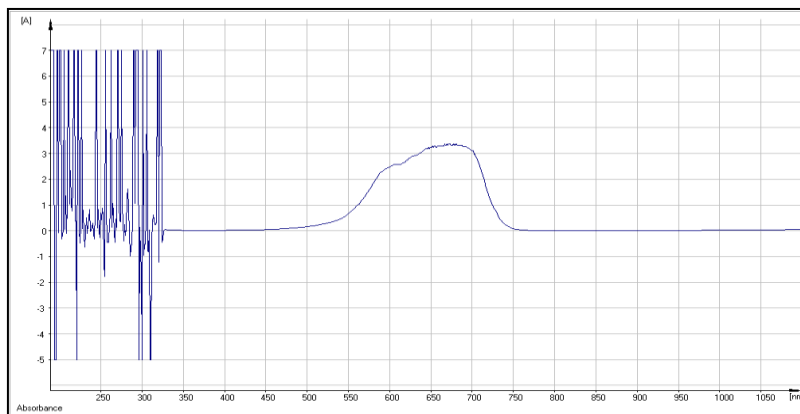


Fig-4: Absorption spectrum of blue colored CoCl_2 -acetone complex

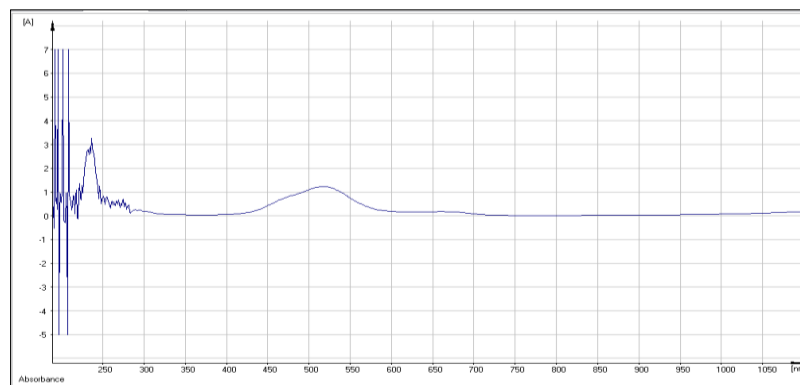
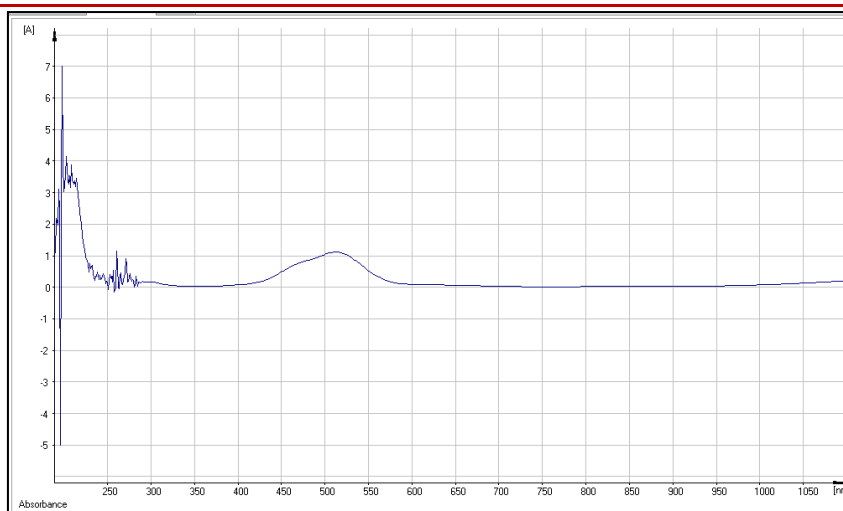
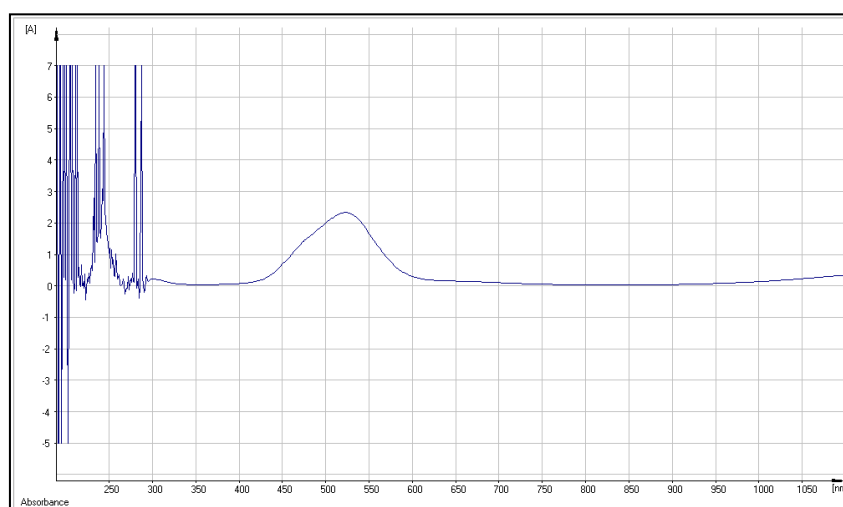
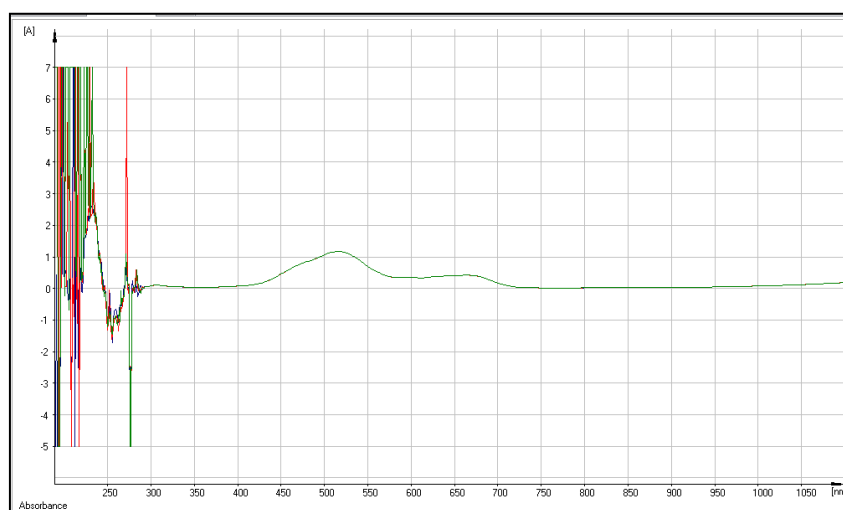


Fig-5: Absorption spectrum of pink colored CoCl_2 -methanol complex

Fig-6: Absorption spectrum of pink colored CoCl_2 -water complexFig-7: Absorption spectrum of pink colored CoCl_2 -glycerol complexFig-8: Absorption spectrum of bluish pink colored CoCl_2 - CHCl_3 complex

CONCLUSION

In the present work, spectrophotometric analysis of solvatochromic behavior of cobalt chloride solutions in different polar protic and aprotic solvents was carried out by using UV-Vis spectroscopy. The

results showed that most of the polar protic solvents displayed pink color and polar aprotic ones showed blue colour. The dielectric constant of solvents does not play major role in deciding the configuration and hence color of CoCl_2 -solvent complex system. When the results

with a series of alcoholic solvents with increasing chain length, branching and number of hydroxyl functional groups were compared it was found that colour is not only a function of hydrogen bonding ability of solvent due to the presence of polar hydroxyl groups but also depends on hydrocarbon chain length. Less the hydrocarbon chain length and more the number of hydroxyl groups, higher the probability of formation of pink octahedral complex and vice versa.

REFERENCES

1. Russell, W. J. (1881). Proceedings of the Royal Society of London, 32:258.
2. Hartley, W. N. (1903). XLV.—On colour changes observed in some cobalt salts. *Journal of the Chemical Society, Transactions*, 83, 401-405.
3. Jones, H. C., Getman, F. H., Bassett, H. P., McMaster, L., & Uhler, H. S. (1907). Hydrates in aqueous solution. *American Chemical Journal*, 37:126.
4. Hill, R., & Howell, O. R. (1924). LXXXI. Crystal structure and absorption spectra.—The cobaltous compounds. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 48(287), 833-847.
5. Brode, W. R., & Morton, R. A. (1928). The absorption spectra of solutions of cobalt chloride, cobalt bromide, and cobalt iodide in concentrated hydrochloric, hydrobromic, and hydriodic acids. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 120(784), 21-33.
6. Howell, O. R., & Jackson, A. (1933). The change in the absorption spectrum of cobalt chloride in aqueous solution with increasing concentration of hydrochloric acid. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 142(847), 587-597.
7. Katzin, L. I., & Gebert, E. (1950). Spectrophotometric Studies of Cobaltous Chloride. *Journal of the American Chemical Society*, 72(12), 5464-5471.
8. Fine, D. A. (1962). Halide complexes of cobalt (II) in acetone solution. *Journal of the American Chemical Society*, 84(7), 1139-1144.
9. Trutia, A., & Musa, M. (1966). Absorption spectra of divalent cobalt halides in ethanol and acetone. *Revue Roumaine de Chimie*, 11(8), 927.
10. Mizutani, K., & Sone, K. (1967). Absorption Spectra of Cobalt (II) Chloride in concentrated perchlorate solutions. *Zeitschrift für anorganische und allgemeine Chemie*, 350(3-4), 216-224.
11. Bartecki, A., Tłczal, T., & Raczko, M. (1991). The color of transition metal compounds. II. Solvatochromism of Cobalt (II) chloride. *Spectroscopy letters*, 24(4), 559-575.
12. Stanescu, G., & Trutia, A. (2005). On absorption spectra of CoCl₂/acetone systems. *Journal of optoelectronics and advanced materials*, 7(2), 1009-1015.
13. Phonphuak, N. (2013). Effects of additive on the physical and thermal conductivity of fired clay brick. *Journal of Chemical Science and Technology*, 2(1), 95-99.
14. Petkova, P., & Nedkov, V. (2013). Behavior of Co²⁺ cations in the aqueous and alcoholic solution of CoCl₂ · 6H₂O. *Acta Physica Polonica A*, 123(2), 207-208.
15. Schramm, C., Kitzke, A., & Tessadri, R. (2017). Cobalt chloride-based humidity sensor attached to sol-gel modified cellulosic material. *Cellulose Chemistry and Technology*, 51:273.
16. Zielonka, P., Jarzabek, W. A., Ksiazka, P., & Dolowy, K. (2015). Annals of Warsaw University of Life Sciences-SGGW, *Forestry and Wood Technology*, 92:489.