

## THE STUDY OF THE COMPLEX FORMATION OF THE COPPER(II) ION WITH SALICYLIC ACID BY MEANS OF THE EPR AND UV-VIS SPECTROSCOPY METHODS WITHIN WIDE RANGE OF AQUEOUS MEDIUM'S pH VALUES

S. K. GRIGORYAN<sup>1\*</sup>, G. S. GRIGORYAN<sup>2\*\*</sup>, A. I. MARTIRYAN<sup>1\*\*\*</sup>, L. G. TADEVOSYAN<sup>1\*\*\*\*</sup><sup>1</sup>Chair of Inorganic and Analytical Chemistry, YSU, Armenia<sup>2</sup>Chair of Physical and Colloids Chemistry, YSU, Armenia

The complex formation of the copper(II) ion with salicylic acid by means of the EPR and UV-Vis spectroscopy methods has been studied under standard conditions within pH 4.0–10.2 values. It has been shown that in the pH 4.0–5.5 acidic media the I type complex is formed, in which the Cu<sup>2+</sup> ion is connected with two salicylic acid ligands H<sub>2</sub>Sal and two water molecules, when in the pH 7.5–10 alkaline media the type II complex is formed, in which the Cu<sup>2+</sup> ion is connected only with two salicylic acid anions Sal<sup>2-</sup>. By means of the EPR and UV-Vis spectroscopy methods it has been also estimated that the ligand field of the type I complexes is stronger than that of the type II complexes.

**Keywords:** copper(II) ion, salicylic acid, complex formation.

**Introduction.** In the present article the complex formation of the copper(II) ion with salicylic (2-hydroxybenzoic) acid by means of the EPR and UV-Vis spectroscopy methods has been studied in an aqueous medium within wide range of the pH values. The copper(II) ion as well as salicylic acid C<sub>6</sub>H<sub>4</sub>(OH)COOH (H<sub>2</sub>Sal) are essential compounds for the human organism, fulfilling numerous biochemical roles [1–3]. Salicylic acid itself and substituted salicylic acids – compounds with mixed function, cause great interest owing to their ability to form various complexes with metal ions (especially d-elements ions), which retrieve wide application in different fields of industry and medicine [4–7]. Issuing from this aspect the modeling of these two substances for the synthesis of complexes in aqueous medium within wide range of the pH values as well as the determination of their structures were the goal of our study.

The salicylic acid, being dibasic acid, in the acidic and neutral aqueous solutions is present in the molecular state H<sub>2</sub>Sal. In alkaline medium the hydrogen atoms of carboxyl and phenolic groups segregate and double charged anion [C<sub>6</sub>H<sub>4</sub>OCOO]<sup>2-</sup>(Sal<sup>2-</sup>) is formed. Metal salicylates of the M(HSal)<sup>-</sup><sub>n</sub> coordination types will be formed in neutral and weak acidic media, and correspondingly M(Sal<sup>2-</sup>)<sub>n</sub> will be formed in alkaline solutions [5].

\* E-mail: [anorgkim@ysu.am](mailto:anorgkim@ysu.am)\*\* E-mail: [gevsgrig@ysu.am](mailto:gevsgrig@ysu.am)\*\*\* E-mail: [armart@ysu.am](mailto:armart@ysu.am)\*\*\*\* E-mail: [lusinet@ysu.am](mailto:lusinet@ysu.am)

Note that the studies on complex formation of different “vital metal” ions, including also copper(II), especially with organic and biological ligands (including salicylic acid and its derivatives) were carried out for a long time [3–5, 8, 9]. The appearance of various spectroscopic methods of investigation in chemistry fostered rapid and accurate revealing of the composition and structure of intermediate and complex compounds of different donor-acceptor systems. We had also carried and carry now the studies of the complex formation in aqueous and mixed aqueous-organic media between metal(II) ions of first transition row ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  et al.) and ligands of the different composition and structure (amines, aminoalcohols, aminoacids, aromatic oxyacids) [10–12]. Aiming to receive new comparative data we have performed the study of the complex formation of the  $\text{Cu}^{2+}$  with salicylic acid in an aqueous medium within pH range 4.0–10.2 by means of EPR and UV-Vis spectroscopy methods.

**Experimental Part.** “Pure for analysis” grade  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and “chemically pure” salicylic acid were used to prepare aqueous solutions. The studies were carried out at standard temperature and within pH 4.0–10.2 range. The acidity of the solutions has been regulated by adding required quantities of potassium hydroxide. The pH values of aqueous solutions have been measured using JENWAY 4330 instrument.

EPR-spectra have been registered by PЭ-1301 (Russia) instrument within 3 cm wavelength range using 100 KHz high frequency modulation. Relative concentrations of copper(II) ions have been determined by means of double integration of EPR spectra.

UV-Vis spectra have been registered by SPECORD M40 and Analytic Jena SPECORD 50 spectrometers. Quartz cuvettes (1 cm in thickness) were used for measurements, twice-distilled water was used as reference solution. The cuvette temperature was maintained stable – temperature deviations did not exceed  $\pm 0.1^\circ\text{C}$ .

**Results and Discussion.** EPR spectra of  $\text{Cu}^{2+}$ –salicylic acid complexes in the aqueous media pH 4.0–10.2 range are presented in Figs. 1 and 2.

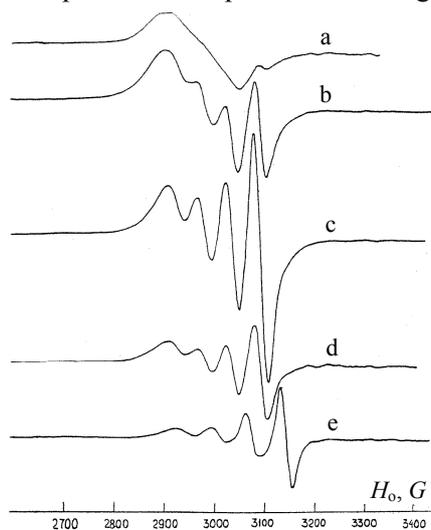


Fig. 1. EPR spectra of  $\text{Cu}^{2+}$ –salicylic acid complexes at different pH values: a – 4; b – 4.5; c – 5.5; d – 6.0; e – 6.5.

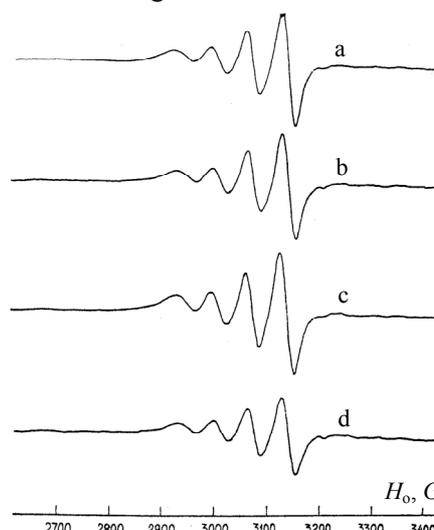


Fig. 2. EPR spectra of  $\text{Cu}^{2+}$ –salicylic acid complexes at different pH values: a – 7.5; b – 8.5; c – 9.5; d – 10.2.

Fig. 1,a is control EPR signal of the hydrated  $\text{Cu}^{2+}$  without salicylic acid at pH 4.0, the rest spectra (b–e) are with ligands. Fig. 1,a presents by itself mainly the singlet, arising from unpaired electron  $3d^9$  configuration. At pH 4.5 (Fig. 1,b) ultra-thin structure (UTS) arises, due to the interaction of an unpaired electron with its nucleus, which spin ( $I$ ) equals  $3/2$ . And since the number of ultra-thin interactions equals  $2nI + 1$  (in our case  $n = 1$ ), so their number must equal 4. Really just four UTS components were observed in EPR spectrum (Fig 1, b–e), which is connected with formation of the  $\text{Cu}^{2+}$ –salicylic acid complexes. A detailed analysis of the data obtained, carried by means of double integration method shows that with increase of pH values from 4.0 to 5.5 the relative concentration of copper(II) ions as well as complexes formed in the system increases almost linearly (Fig. 3), and further increase in pH higher that 5.5 leads to decrease in their relative concentrations and causes the changes of EPR spectra shape (Figs. 1 and 2). At pH 7.5–10.2 the shape of EPR spectra does not change, as well as do not change the relative concentrations of  $\text{Cu}^{2+}$  ions (Fig. 3).

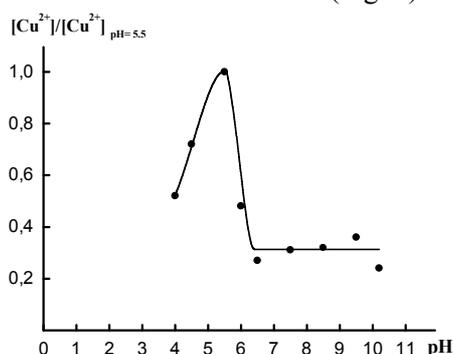


Fig 3. The dependence of relative concentration of  $\text{Cu}^{2+}$ –salicylic acid complexes on the pH values according to the EPR spectroscopy data.

Issuing from the experimental results obtained by us and accounting also literary data [8, 9], it has been stated the formation of the two types of complexes: type I within pH 4.0–5.5 range and type II within pH 7.5–10.2 (Fig. 4).

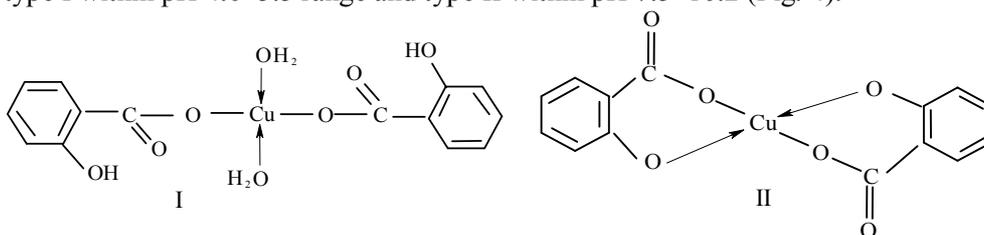


Fig. 4. The structures of  $\text{Cu}^{2+}$ –salicylic acid complexes of types I and II.

The values of UTS constants in EPR spectra in the studied pH range also indicate the formation of the two types – I and II, at the given pH 4.0–5.5 and pH 7.5–10.2 ranges, i.e. in the acidic and alkaline media (Fig. 5).

As it is evident from the Fig. 6, at 4.0–5.5 the value of UTS constant is approximately  $56 G$ , and at  $\text{pH} \geq 7.5$  it is correspondingly  $68 G$ . Such changes in the values of UTS constant depending on the medium pH values, which are in correlation with the relative concentrations of the studied complexes, approve the formation of I and II type complexes. In the type I complex  $\text{Cu}^{2+}$  ion coordinates with two  $\text{HSa}^-$  anions and two  $\text{H}_2\text{O}$  molecules (Fig. 4). In the alkaline medium

(pH 7.5–10.2), owing to lack of free orbitals in the  $\text{Cu}^{2+}$  ion, water molecules do not enter into the first coordination sphere of the complex, though the removal of the water molecule proton increases together with increase of pH values. Connected with the stated, the structure of the type II complex may be presented as a result of coordination of  $\text{Cu}^{2+}$  ions with two anion ligands of salicylic acid  $\text{Sal}^{2-}$  (Fig. 4).

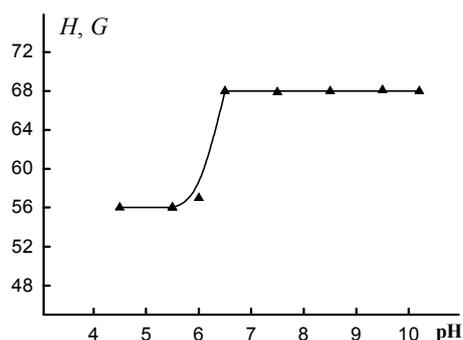


Fig. 5. The dependence of UTS constant of EPR spectra of  $\text{Cu}^{2+}$ -salicylic complexes on the pH values of the aqueous medium.

The circumstance that ligand field in the type II complex is more powerful than that in the type I complex serves as additional proof which witnesses for benefit of suggested interpretation of the structures of obtained I and II type complexes. It has been estimated by EPR and UV-Vis spectral data, presented in Fig. 6, a and b.

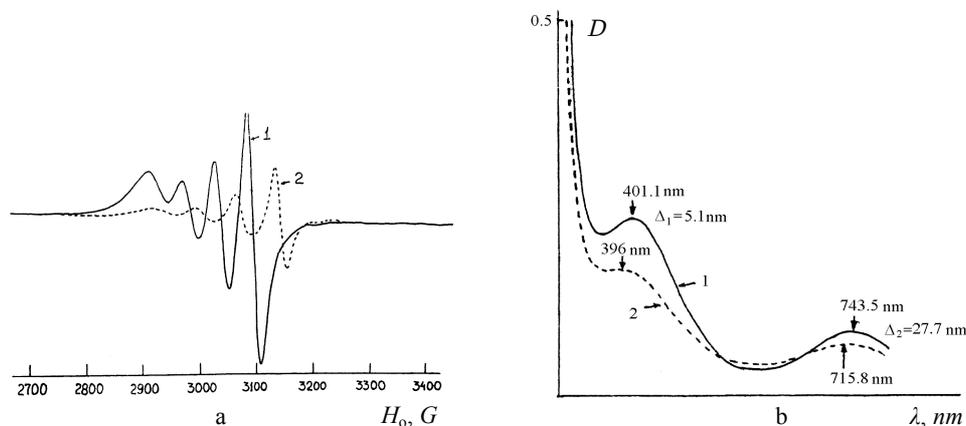


Fig. 6. EPR (a) and UV-Vis (b) spectra of the  $\text{Cu}^{2+}$ -salicylic acid complexes at pH 5.5 (1) and 7.5 (2).

The imposed EPR spectra of the complexes investigated under pH 5.5 (1) and pH 7.5 (2) are presented in Fig. 6,a. One can see that the EPR signal of the type II complex (pH 7.5) is shifted to the right, to the higher values of magnetic field compared with the type I complex (pH 5.5). Besides, it is evident that the value of UTS constant for the type II complex is higher than that for the type I complex.

A special investigation has been carried out by means of UV-Vis spectroscopy method aiming to obtain additional approval witnessing about the increasing of ligand field in the type II complexes. The UV-Vis spectra of  $\text{Cu}^{2+}$ -salicylic acid complexes of both types are presented in Fig. 6,b. One can mark that for the type II complex (pH 7.5) compared with the type I (pH 5.5) a short-wavelength shift of the absorption maximum exists. If for the sample with

pH value 5.5 the main adsorption maximum corresponds to the  $\lambda=401.1\text{ nm}$ , the same maximum for the pH 7.5 sample is shifted to the left by  $5.1\text{ nm}$  and equals  $\lambda=396.0\text{ nm}$ . In the visible part of the spectrum the short-wavelength shift can be observed more legible: for the sample under pH 5.5 absorption maximum is observed at  $\lambda=743.5\text{ nm}$ , while for the sample under pH 7.5 it is shifted to the left by  $27.7\text{ nm}$  ( $\lambda=715.8\text{ nm}$ ).

Thus, the results obtained by means of EPR and UV-Vis spectroscopy methods witness that the ligand field in the type II complexes is more powerful compared with the type I complexes. At the same time these results approve the correctness of our interpretation about the composition and structure of the obtained type I and type II complexes between copper(II) ions and salicylic acid in aqueous medium under various pH values.

Received 21.06.2019

Reviewed 02.12.2019

Accepted 16.12.2019

#### REFERENCES

1. Chirkin A.A., Danchenko E.O. *Biochemistry*. Medical literature (2010), 624 p. (in Russian).
2. Elliot W., Elliot D. *Biochemistry and Molecular Biology*. Nauka/Interperiodika (2010), 444 p. (in Russian).
3. Walche J.M. Wilson's Disease. *Biochem. J.*, **111** : 3 (1969), 8–9.
4. Sorenson J.R.J. Cooper Chelates as Possible Active Forms of the Anti-arthritis Agents. *J. Med. Chem.*, **19** : 1 (1976), 135–140.
5. Telzhenskaya P.N., Schwartz E.M. Complex Compounds of Salicylic Acid and Its Derivatives. *Coord. Chemistry*, **3** : 9 (1977), 1279–1295 (in Russian).
6. Mentasti E., Secco F., Venturini M. Complex Formation between Ni(II) and Co(II) with Salicylic Acids. Equilibria and Reaction Mechanisms. *Inorg. Chem.*, **19** : 11 (1980), 3528–3531.
7. Kharitonov Yu.Ya., Tuyebakhova Z.K. Salicylate Complexes of Cobalt(II), Nickel(II), Zinc and Cadmium. *Coord. Chemistry*, **9** : 11 (1983), 1512–1527 (in Russian).
8. Gorinchoy V.V., Simonov Yu.A., Shova S.G., Schofranski V.N., Turte K.I. Crystal and Molecular Structures of Cu–M (M=Cu, Sr, Ba) Binuclear Complexes Based on Salicylic Acid. *Journal of Structural Chemistry*, **50** : 6 (2009), 1196–1202 (in Russian).
9. Sharma G., Narula A.K.  $\text{Eu}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Eu}^{3+}$ – $\text{Yb}^{3+}$  Complexes with Salicylic Acid and 1,10-Phenanthroline: Synthesis, Photoluminescent Properties and Energy Transfer. *Journal of Fluorescence*, **25** : 2 (2015), 355–360.
10. Grigoryan S.K. Reactions of Hydroperoxides with Amines and Aminoalcohols in Aqueous Solutions in the Presence and Absence of Metal Ions. *RUSS CHEM REV*, **52** : 6 (1983), 936–952.
11. Grigoryan S.K., Petrosyan G.G., Grigoryan G.S., Vardanyan E.Ya. Complex Formation of Lysine with Metal(II) Ions and the Action of Complexes on Cumene Hydroperoxide Decomposition in Aqueous Solution. *Chem. Journal of Armenia*, **58** : 4 (2005), 12–20 (in Russian).
12. Grigoryan G.S., Harutyunyan M.G., Grigoryan S.K. Catalytic Activity of Co(II) Ion and Isoleucine Complex on Decay of Cumene Hydroperoxide in Aqueous Solution. *Proceedings of YSU. Chemical and Biological Sciences*, **1** (2014), 15–19.