The composition and structure of iron(III) complex compounds with salicylic acid in ethanol solution and in the solid thin film state

Olga Khalipova, Svetlana Kuznetsova, and Vladimir Kozik

The Composition and Structure of Iron(III) Complex Compounds With Salicylic Acid in Ethanol Solution and in The Solid Thin Film State

Olga Khalipova[a], Svetlana Kuznetsova[b] and Vladimir Kozik [c]

Tomsk State University, 36 Lenina Avenue, Tomsk 634050 Russian Federation

[a]corresponding author: chalipova@mail.ru
[b]onm@xf.tsu.ru
[c]vkozik@mail.ru

Abstract. Owing to their properties iron(III) salicylate complexes are interest of for application in biomedicine and environmental monitoring. Recently this complex compounds also are investigated as a potential candidate for preparing Fe_2O_3 films by sol-gel method from ethanol film-forming solution. Relevance of the work was caused by necessity to determine the structure and composition of iron(III) salicylate complexes in ethanol solution and in the solid film state, which influence on film properties. Nowadays this information is absence in the literature. UV spectroscopy, NMR measurement, methods of isomolar series and thermal analysis were used to analyze the composition of complex in ethanol solution and in the solid state. It was found, that salicylic acid interacts with iron(III) chloride in ethanol solution promotes the formation of $[FeC_6H_4OCOO]^+$ complex, where salicylate ligand behaves as bidentate ligand. After removal of the solvent from solution iron(III) chloride salicylate crystal hydrate complex of 1:1 stoichiometry was formed in solid state. Thermal decomposition of this compound led to formation $\alpha–Fe_2O_3$.

INTRODUCTION

There is currently much interest in iron(III) salicylate complexes, which has arisen due to the wide scope of applications of these compounds, namely, in biomedicine and environmental monitoring [1–4]. In recent years complexes of metal salts with salicylic acid have also been intensively investigated for applications in manufacturing oxide film materials by sol–gel method [5–7]. These oxide films are very useful material for the decision of problems of material science in the field of microelectronics and solar energy. For example, iron oxide thin films are suitable materials for photoelectrochemical solar cell for solar energy conversion, for microelectronic circuits as capacitors, for rechargeable batteries as negative electrode, for smart windows devices as electrochromic materials, for interference filters [8–11].

Fabrication of films from film-forming solutions (FFSs) based on complex compounds (sol-gel method) is the most promising method, since in this case there is no need for using expensive equipment and preparing precursor materials. The most important technological step of this method is FFSs ripening for few days, during which complexes are formed by reaction between the metal salts and organic ligands in solution. The formation of metal salicylate complexes directly in the solution ensures uniformity of oxide coatings and increases adhesion of FFSs to substrate [5–7]. For example, the using of FFS based on cerium(III) salicylate increases the adhesion and uniformity of the resulting $CeO_2–SnO_2$ films [6].

In a great number of works [1–4, 12] studied the complexation between iron(III) salts and salicylic acid in aqueous medium, which is not applicable for the preparation FFS. The most effective solvent for preparing film-forming solutions is ethanol (94–96 wt. %) [5–7, 13]. Unfortunately, currently there is no data in the literature about complexation between the metal salt and organic ligand in ethanol solution. These data are of great interest because

knowledge of structure of salicylate complexes in the film-forming solution allows to explaining the processes leading to receiving of thin-film oxide materials and gives the chance to regulate these processes.

The purpose of this work was to determine composition, structure of iron (III) salicylate of complexes in ethanol solution, and also a ligand dentate in the received complex and to show a possibility of use of it in quality film-forming solution for receiving films of oxide of iron (III) with structure of hematite.

EXPERIMENTAL PART

The solutions based on the iron(III) complex with salicylic acid were prepared from iron(III) chloride crystal hydrate of analytically pure grade and salicylic acid of analytically pure grade at a 1 : 1 metal : ligand ratio $(C(Fe^{3+}) = C(C_6H_4OHCOOH) = 0,3$ mol/L$)$ using 96 wt. % ethanol as a solvent. The chemicals and reagents (Russian grade) were used brands are chemically pure without further purification. Deep purple colored solution was obtained after dissolving $FeCl_3 \cdot 6H_2O$ in ethanol solution of $C_6H_4OHCOOH$. Changing the color is testified indirectly about the formation of the complex compound between iron(III) salt and salicylic acid.

Composition, structure of iron (III) salicylate complex particles in ethanol solution was determined by applying a set of spectral research methods. The interaction between iron(III) chloride crystal hydrate and salicylic acid in ethanol was studied by spectrophotometrically and by NMR measurements. The optical density of the solution was examined on a PE5400UV scanning spectrophotometer in the range from 220 to 400 nm. The ^{1}H NMR spectra were acquired at 25 °C on a TESLA-BS-497 (made in Czech) spectrometer, operating at 100 MHz. All chemical shift values were reported in δ (ppm). The electronic absorption spectra in the UV region and NMR spectra of free ligand and iron(III) chloride ethanol solutions and $FeCl_3$–$C_6H_4OHCOOH$ solution applied to the surface of the quartz substrate and dried in a drying oven for 1 h at 60°C were recorded in the same conditions. All spectra were measured relative to solution solvent – ethanol. The spectra were analyzed in accordance with literature data [14–15].

The isomolar series method was used to establish the major solute species (the predominant ratio metal : ligand in iron(III) salicylate complex) in $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution. Concentration of solutions $FeCl_3$ and $C_6H_4OHCOOH$ made $1 \cdot 10^{-5}$ mol/l. Absorbance spectra in the visible region of ethanol solutions $FeCl_3$, $C_6H_4OHCOOH$ and $FeCl_3$–$C_6H_4OHCOOH$ in different volume ratio of iron chloride (III) and salicylic acid, were measured to determine the composition of the complex. The analysis was carried out on PE5400UV scanning spectrophotometer (made in Russia) (λ_{eff} = 750 nm). The predominant composition of the complex was determined from the variation of the optical density of the complex particles from the molar proportion of complexing agent.

The composition of iron(III) salicylate complex in the solid state was determined according to calculations based on the results of thermal analysis of dried at 60 °C $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution. The thermal analysis of dried solution was carried out on the STA 449 C Jupiter (made in Germany) instrument in a temperature range of 40–900 °C in oxygen atmosphere. The X-ray diffraction analysis of the product of thermal destruction of dried $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution was performed on a RigakuMiniFlex 600 diffractometer (made in Japan) using JCPDS PDF data.

The Fe_2O_3 films were applied from solutions based on $FeCl_3$–$C_6H_4OHCOOH$ onto substrates made of singleecrystal silicon via centrifugation at a rotation speed of 3000 rpm. In order to remove the sollvent, ensure gel formation, and increase the adhesion to substrates, the films were dried in a drying oven at 60°C for 1 h. Subsequent heat treatment was carried out in a muffle furnace at 600°C for 1 h.

RESULTS AND DISCUSSION

Physicochemical studies of salicylates [1–7] have shown that there exist a large number of ways in which a salicylic acid is coordinated around the central atom. The salicylic acid contains two types of functional groups – a phenolic and carboxyl:
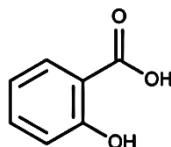
That is why in the complexation with metals it functions as either mono- or bidentate ligand.

The electronic absorption spectra of $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution and those of ethanolic solutions of salicylic acid and iron(III) chloride in the wavelength range of 400–220 nm were analyzed (Fig. 1). The electronic absorption spectrum of salicylic acid in ethanol (Fig. 1, curve 2) shows two intense peaks. These spectral peaks in the UV region are assignable to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions in salicylate-ion [1, 15, 16]. As can be seen from Fig. 1 (curve 2), the two absorption maxima of salicylic acid solution are observed at 297 and 230 nm, respectively. In the considered wavelength range (220–400 nm) the optical density of the $FeCl_3$ solution monotonically increases with decreasing wavelength (Fig. 1, curve 1). The introduction of $FeCl_3$ into an ethanol solution of salicylic acid leads to slightly shift the absorption maximum of the electronic $\pi \rightarrow \pi^*$ and $n\rightarrow\pi^*$ transitions peaks of organic ligand toward longer wavelengths (Fig. 1, curve 3). Besides, as can be seen from Fig. 1, curves 3, the intensity of peaks decreases. The alteration of the absorption spectrum indicates that iron(III) chloride interacts with salicylic acid via oxygen atoms of the phenolic and carboxyl groups.
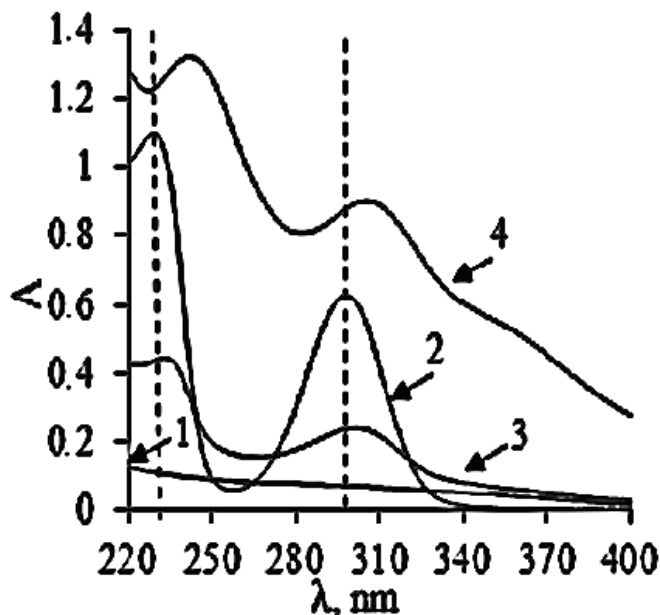

FIGURE 1. Electronic absorption spectra of the ethanol solution: 1 – $FeCl_3$; 2 – $C_6H_4OHCOOH$; 3 – $FeCl_3$–$C_6H_4OHCOOH$; 4 – $FeCl_3$–$C_6H_4OHCOOH$, applied to the surface of the quartz substrate and dried at 60°C

The complexation in $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution was also confirmed by ^{1}H NMR spectroscopy. This technique allows to detect the interaction between salicylic acid and iron(III) chloride by observing changes in the chemical shift of the hydrogen nuclei of ligand. Table lists chemical shifts of the hydrogen nuclei of salicylic acid in 96% ethanol and of ethanol solution based on $C_6H_4OHCOOH$ with $FeCl_3$.

TABLE 1. Comparison of the chemical shifts of the protons in $C_6H_4OHCOOH$ and $FeCl_3$–$C_6H_4OHCOOH$ ethanol solutions

Groups	δ ($C_6H_4OHCOOH$), ppm	δ ($FeCl_3$–$C_6H_4OHCOOH$), ppm
–CH– (1, 2)	6.83–7.48	6.51–7.55
–OH (3)	7.80–7.88	–
–COOH	8.20–8.30	–

In the ^{1}H NMR spectra of ethanol salicylic acid solution there are four lines that show the number of chemically non-equivalent protons. The chemical shifts of 6.83–7.48 ppm correspond to the chemical shifts of hydrogen atoms in the benzene ring and in the –CH group adjacent to a hydroxyl group. The chemical shifts of 7.80–7.88 and 8.20–8.30 ppm characterize the chemical shifts of protons in the phenolic and carboxyl groups, respectively (table). The introduction of iron(III) chloride to the ethanol salicylic acid solution leads to the disappearance chemical shifts of the -OH and -COOH functional groups in the ^{1}H NMR spectra (table 1). Thus, the ^{1}H NMR results clearly showed

that $C_6H_4OHCOOH$ forms complex compound with $FeCl_3$ in ethanol solution with coordination to the oxygen atoms of both functional groups of organic ligand.

The dependence of the optical density of the complex from molar ratios of the ligand, obtained by the method isomolar series is presented in Fig. 2.
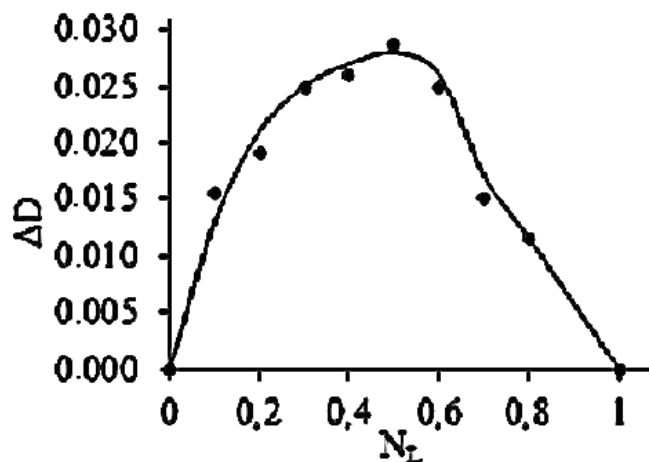

FIGURE 2. Isomolar series for $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution

As can be seen from Fig. 2, the location of the extremum on the composition axis (y = 0.5) corresponds to the formation of a predominance iron(III)–salicylate 1 : 1 complex in the $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution.

Hence, relying on the data of UV spectrophotoscopy and NMR measurements we can state that the bond between a metal ion and ligand in the complex is formed due to the oxygen atoms of the phenolic and carboxyl groups of salicylic acid:
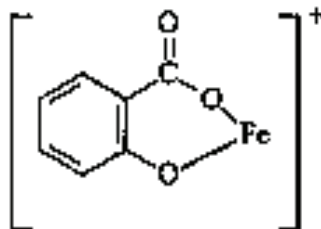
We used ethanol solution based on the iron(III) complex with salicylic acid to fabricate complex compound in the solid thin film state on quartz substrates. The films were applied to quartz substrates by dip-coating from $FeCl_3$–$C_6H_4OHCOOH$ ethanol solutions at a speed of 2 mm/s at room temperature. After that they were dried in a drying oven at 60°C for 1 h. Since at this temperature only solvent molecules (ethanol) are removed from solution, it can be assumed that composition and structure of iron(III) complex with salicylic acid in ethanol solution before and after drying are similar. This fact is attested by identical patterns of the electronic absorption spectra of $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution (Fig. 1, curve 3) and $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution, applied to the surface of the quartz substrate and dried at 60°C (Fig. 1, curve 4).

The results of thermal analysis of the dried $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution (Fig.3) allowed us to calculate the molar mass of the compound in it. The calculated molar mass of compound is 240.7 g/mol and corresponds to the complex with composition $[FeC_6H_4OCOO]Cl·H_2O$ ($M_{teor.}$ = 245.4 g/mol). The presence of chloride-ion has been proven by qualitative reaction with the Ag^+– ions. The thermogravimetric data for dried $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution confirm the composition established for the complex in solution by other methods.
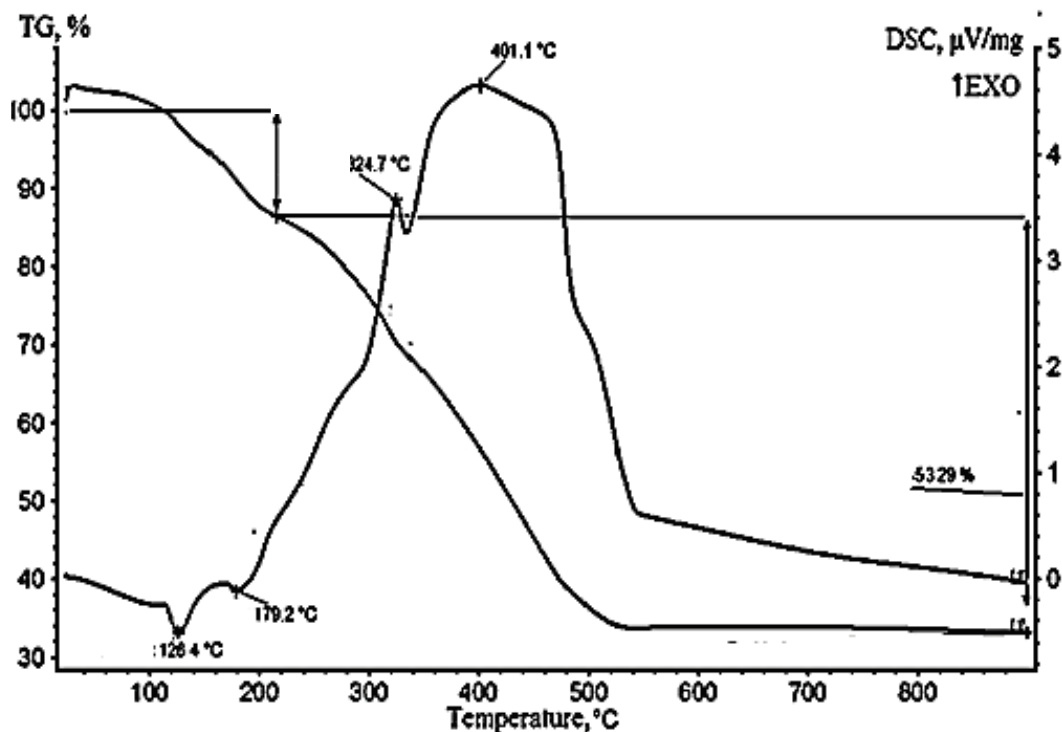
FIGURE 3. Thermal analysis data for FeCl$_3$–C$_6$H$_4$OHCOOH ethanol solution, dried at 60°C

As can be seen from Fig. 3, the thermogravimetry (TG) curve of the sample has two weight change regions. The first decomposition step of the dried FeCl$_3$–C$_6$H$_4$OHCOOH ethanol solution, in the temperature range from 60 to 210 °C, is associated with the removal of the chloride–ion in the form of HCl. The differential scanning calorimetry (DSC) curve at the Fig. 3 demonstrates that this process is accompanied by two endothermic peaks at 126 and 179 °C. In the high-temperature region from 210 to 600 °C, we observe the decomposition of the iron(III) salicylate complex. This region is accompanied by two exotherms at 325 and 401 °C (Fig. 3), that are characteristic for oxidation of the salicylate–ion. The observed pattern of decomposition [FeC$_6$H$_4$OCOO]Cl·H$_2$O corresponds to the decomposition of complex compounds of metals with salicylic acid [6]. The decomposition process of dried FeCl$_3$–C$_6$H$_4$OHCOOH ethanol solution reaches completion at a temperature of 600°C (Fig. 3). According to the X-ray diffraction data (Fig. 4) the final product is iron(III) oxide with hematite structure.
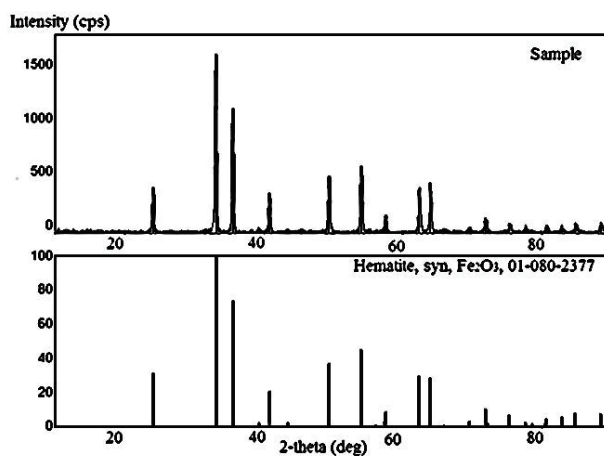

FIGURE 4. X-ray diffraction data for product of thermal destruction of dried at 60 °C FeCl$_3$–C$_6$H$_4$OHCOOH ethanol solution

CONCLUSION

The results presented here demonstrate for the first time that addition of iron(III) chloride at ethanol solution of salicylic acid leads to the formation of $[FeC_6H_4OCOO]^+$ complex, where salicylate ligand behaves as bidentate with coordination to the oxygen atoms: O-phenolate and O-carboxylat. The drying of $FeCl_3$–$C_6H_4OHCOOH$ ethanol solution at 60 °C leads to formation hydrated iron(III) chloride salicylate crystal hydrate complex of 1:1 stoichiometry in dispersed and solid film state. The complex on the solid phase $[FeC_6H_4OCOO]Cl\cdot H_2O$. This complex is resistant to temperature 100 °C. The thermal decomposition of iron(III) salicylate in air proceeds in several stages, accompanied by the complete oxidation of salicylate–ion with two exotherms in the temperature region of 210–600°C. Hematite structure of iron oxide, is formed from a complex compound at a temperature 600°C. It is found that the ethanol solution has a film-forming ability. The films Fe_2O_3 on singleecrystal silicon substrates obtained from the film-forming solution are characterized by thickness 50 nm and refractive index 2.58.

ACKNOWLEDGMENTS

REFERENCES

1. I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, E. Oliveros, Journal of photochemistry and photobiology A: Chemistry **307–308**, 9–15 (2015).
2. V.M. Nurchi, T. Pivetta, J.I. Lachowicz, G. Crisponi, Journal of inorganic biochemistry **103**, 227–236 (2009).
3. V.M. Nurchi, M. Crespo-Alonso, L. Toso, J.I. Lachowicz, G. Crisponi, G. Alberti, R. Biesur, A. Dominguez-Martin, J. Niclos-Gutierrez, J.M. Gonzalez-Perez, M.A. Zoroddu, Journal of inorganic biochemistry **128**, 174–182 (2013).
4. A. Garai, I. Pant, P. Kondaiah, A.R. Chakravarty, Polyhedron **102**, 668–676 (2015).
5. O.S. Khalipova, S.A. Kuznetsova, V.V. Kozik, Russian journal of inorganic chemistry **59**, 9, 913–917 (2014).
6. O.S. Khalipova, S.A. Kuznetsova, Russian journal of inorganic chemistry **58**, 8, 892–897 (2013).
7. V.V. Kozik, O.S. Khalipova, S.A. Kuznetsova, V.K. Ivanov, Yu.D. Tret'yakov, Doklady Chemistry **444**, 1, 120–123 (2012).
8. R.A. Lunt, A.J. Jackson, A. Walsh, Chemical physics letters **586**, 67–69 (2013).
9. L. Dghoughi, B. Elidrissi, C. Berne'de, M. Addou, M. AlaouiLamrani, M. Regragui, H. Erguig, Applied Surface Science **253,** 1823–1829 (2006).
10. M.F. Al-Kuhaili, M. Saleem, S.M.A. Durrani, Journal of alloys and compounds **521**, 178–182 (2012).
11. S.S. Kulkarni, C.D. Lokhande, Materials chemistry and physics **82**, 151–156 (2003).
12. M.M. Rakhimova, N.Z. Yusupov, T.M. Nurmatov, J.A. Davlatshoeva, L. Kvyatkovskaya, A.R. Bakhtibekova, M. Bobonazarov, American Journal of Chemistry **3**, 23–29 (2013).
13. S.A. Kuznetsova, I.A. Senokosova, Russian journal of applied chemistry **83**, 11, 1935–1939 (2010).
14. D.Brown, Floyd A., M.Sainsbury, *Organic spectroscopy* (J. Wiley, New York, 1988).
15. L.A. Kazitsyna, N.B. Kupletskaya, *Application of UV, IR and NMR - spectroscopy in organic chemistry* (Higher School, Moscow (in Russian), 1971), pp. 1–264.
16. A.L. Sobolewski, W. Domcke, Chem. Phys. **232**, 257–265 (1998).