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Study of Metal-Complexes Composition by Metal-Indicatory Method

Leila Japaridze*, Tsiala Gabelia*, Eter Salukvadze*, Omar Lomtadze*, Giorgi Kozmanashvili*

**Petre Melikishvili Institute of Physical and Organic Chemistry, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia*

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ABSTRACT. The ratio between the complexing metal and ligand in the complexes Fe (III), Zn (II), Mn (II), Cu (II), Co (II) and D-fructose was determined by the metal-indicatory method. In the study methods of isomolar series and shift of equilibriums are used. On the basis of Bent-Branch method logarithmic relations between metal ion concentration and optic density of solutions were calculated. Optical densities of complex solutions were measured on spectrophotometer UV-VIS. In the process of study of optical properties of Fe (III)-D-fructose, the colorimetric reagent of Fe ions – pyrocatechol-violet (pcv) was used as the indicator, while nitrate Fe(III) was taken as the standard solution. Optical densities of the investigated complexes – Fe (III)-D-fructose were measured at 520 nanometer wave length. The dependence of the optical density of the metal-indicator system on the D-fructose concentration were measured, after adding D-fructose to solutions of $Fe(NO_3)_3$ and pcv in various quantities (at PH=6). Concentration of metal in the complex that is bound to metal-indicator was determined by means of preliminary constructed calibration curves. The relationship between the values of –lg[Fe-Fru]·[Pki]/[Fe-Pki] and - lg [Fru] was determined by immediate calculations. Tangent of angle inclination of the line, which reflects the dependence of these value, corresponds to the number of fructose ions participating in equilibrium ($tg\alpha = n$). By researches of the optical properties of the complexes of metals Fe (III), Zn (II), Mn (II), Cu (II) and Co (II) with D-fructose, respectively, at wavelength of 520, 530, 540, 590 and 630 nm, it was established , that the relation of the constituent components (metal : ligand) in all the cases is 1:1. *© 2018 Bull. Georg. Natl. Acad. Sci.*

Key words: spectrophotometer, fructose, indicator, complex, optical, density

Spectrophotometric – metal-indicatory method enables us to determine qualitative or quantitative composition of the investigated compounds according to the absorption intensity. Quantitative investigations performed by the above method are based on Bouguer-Lambert-Beer law, according to which the main decisive factor at measuring of the wave length is optic density and concentration of the investigated colored solutions [1].

The goal of the research was the determination of the ratio of complex-forming metals and ligand in complex compounds containing Fe (III), Zn (II), Mn (II), Cu (II), Co (II) and D-fructose by the metal-indicatory method.

Methods

A method of isomolar series was used. Computations were based on Bent-Branch law which establishes logarithmic relations between metal ion concentration and optic density in solutions [1-5]. Optic densities of complex solutions were measured by the Packard system spectrophotometer UV-VIS. In the process of studying the optical properties of Fe (III) -fructose solutions, the colorimetric reagent of Fe-ions - pyrocatechol violet (pcv) was used as an indicator. The standard compound used was iron nitrate.

Results and Discussion

Absorption spectra of the standard compound - Fe $(NO_3)_3$, (pcv) and their complexes were obtained to establish optimal condition for research optical densities of complex solutions (ratio 1:1 and pH= 6). The Fe-fructose complex was studied in a wavelength region, where its absorption degree differs significantly from the absorption of the complex of Fe-indicator and the net indicator (λ = 520 nm, pH = 6.0). In this case, the overlapping of the absorption bands of these compounds is excluded. In addition to the above, optimal concentrations of solutions for the preparation of isomolar series are determined.

For spectral studies, the solutions were prepared in the following order: 5 ml (2.10-4 mol/l) of Fe(NO3)3 and 5 ml (2.10-4 mol/l) of (pcv) were placed in the volumetric flasks (25 ml), then in flasks various amounts solutions of D-Fructose (Fru) were added. Volume of mixtures was filled with water to the mark.Optical densities were measured only when the equilibrium of the obtained mixtures was achieved (after 48 hours). The dependence of the optical density of the metal-indicator system on the concentration of added fructose is graphically shown in Fig. 1.

Composition of Fe - Fructose complex was computed by the method shift of equilibrium [2, 3]. Equilibrium in the Fe (III)-pcv – Fructose system is expressed by the equation:

$$Fe\text{-}pcv + n\ Fru <-> Fe\text{-}(Fru)\ n + pcv;$$

The constant of the equation

$$K = [Fe\text{-}(Fru)n] \cdot [pcv] / Fe\text{-}pcv \cdot [Fru]n$$

is obtained, when its logarithm is found and common transformations are performed:

$$lg[Fe\text{-}(Fru)n] \cdot [pcv]/[Fe\text{-}pcv] - n\ lg[Fru] + Const = 0.$$

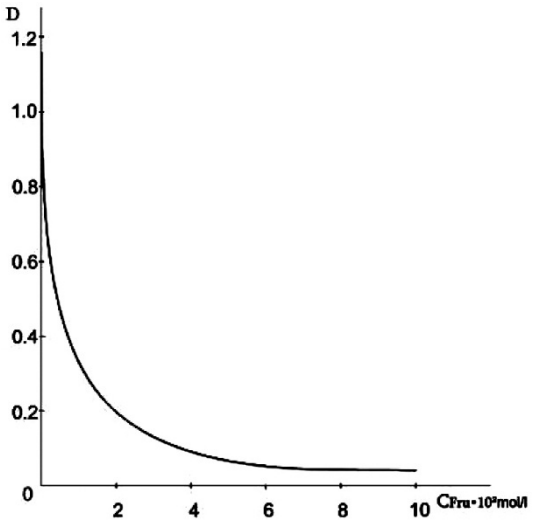

Fig. 1. Optical absorption curve of Fe.pcv-Fructose system PH=6.0; λ=520 nm.

Concentration of metal that is bound to metal-indicator in the complex was determined by means of preliminarily construed calibration plot [1], which establishes the relations between metal-indicator system's optical density and dilution. Thus we get:

$$[Fe\text{-}(Fru)\ n] = [Fe]\ general - [Fe\text{-}pcv].$$

$$[Fe]free \cdot [pcv]free = [pcv]general - [Fe \cdot pcv]$$

The graphical relationship between:

$$-lg[Fe\text{-}(Fru)_n] \cdot [pcv]/ [Fe\text{-}pcv] \text{ and } - lg\ [Fru].$$

When equal scales of these values were determined the angle tangent of the incline line ($tg\alpha = n$) , which conforms to the number of the participating fructose ions. Terms of the experiment and intermediate computations are offered in Table 1.

According to Fig. 2 for the fructose solution $\alpha \approx 45$, while $tg\alpha = 1$.

To prepare the standard series for solutions Cu - Fru- complex copper sulfate was used. Measurements of optical densities of blue solutions

Table. Fe-pcv + Fructose system investigation according to equilibrium shift method

D	[Fe-pcv]· 10^5 mol/l	[pcv] · 10^5 mol/l	[Fe-$(Fru)_n$]· 10^5 mol/l	[Fe-$(Fru)_n$]·[pcv] -lg ---------- [Fe·pcv]	[Fru]· 10^5 mol/l	-lg[Fru]
0.30	1.55	2.25	2.30	4.40	13890.30	0.80
0.40	2.00	1.75	1.70	4.80	7475.20	1.10
0.50	2.50	1.25	1.25	5.00	4170.55	1.35
0.60	3.10	0.65	0.65	5.70	1588.15	1.70
0.70	3.65	0.20	0.20	6.79	145.60	2.80

were carried out after addition of ammonia to the solutions studied at a wavelength of 590 nm.

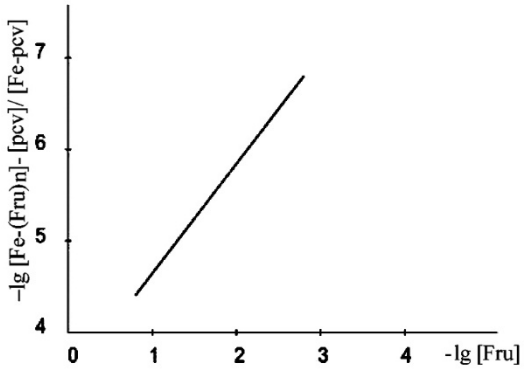

Fig.2. Graphical relationship between –lg [Fe-Fru]. [pcv]/ [Fe-pcv] and – lg [Fru]. (PH=6).

Dithizon that was dissolved in carbon tetrachloride was used as colorimetric reagent for Zn- Fru- complex solutions. Measurements were performed in alkali medium at 530 nanometer wave length.

Optical densities of Co – Fru- complex solutions were measured in alkali medium at 630 nm wave length (colorimetric substance – nitroso R – salt, 0.1% solution).

Optical densities of Mn- Fru complexes were measured in acidic medium, at 540 nm.

It was established that maximum difference in absorption of Fe-indicator complex and that of the pure indicators (pH= 6) was fixed in 520 nm zone.

Analogous results were obtained by the application of the metal indicator method as a result of study of solutions of Co, Zn, Cu, and Mn – fructose complexes, in the case of copper in the 590 nm zone,in the case of zinc in the 530 nm zone,in the case of cobalt in the 630 nm zone and in the case of manganese in the 540 nm zone,

The conditions for the formation of complex between fructose and various transition metals are different. The formation of complex of fructose with Fe^{3+} occurs at pH 6 with Zn^{2+} and Co^{2+} ions in the alkaline medium with Cu^{2+} and Mn^{2+} ions in a weakly acid medium. The ratio of constituent components in all cases is 1: 1.

Conclusion

Thus, the stoichiometric characteristics of complex formations of transitional metals Fe, Co, Zn, Cu and Mn with D-Fructose in solutions were investigated by the use of optical methods. It was proved that the above listed metals form complexes with fructose in the case of the ratio of components metal : ligand = 1: 1

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ფიზიკური და ორგანული ქიმია

ლითონკომპლექსების შედგენილობის კვლევა ლითონინდიკატორული მეთოდის მიხედვით

ლ. ჯაფარიძე*, ც. გაბელია*, ე. სალუქვაძე*, ო. ლომთაძე*, გ. კოზმანიშვილი*

* *ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პ. მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო*

(წარმოდგენილია აკადემიის წევრის ნ. მითაგვარიას მიერ)

ლითონინდიკატორული მეთოდის გამოყენებით განსაზღვრულია კომპლექსწარმომქმნელი ლითონის და ლიგანდის თანაფარდობა **Fe(III)** - ფრუქტოზის, აგრეთვე **Zn(II), Mn(II), Cu(II), Co(II)**- ფრუქტოზის კომპლექსებში. კვლევის პროცესში გამოყენებულია იზომოლარული სერიების და წონასწორობის ძვრის მეთოდები. ბენტ- ბრენჩის მეთოდზე დაყრდნობით გამოთვლილია ლოგარითმული დამოკიდებულება ხსნარებში ლითონების იონების კონცენტრაციასა და ოპტიკურ სიმკვრივეს შორის. კომპლექსების ხსნარების ოპტიკური სიმკვრივეები გაზომილია **Pacard**-ის სისტემის სპექტროფოტომეტრზე **UV-VIS. Fe(III)**-ფრუქტოზის (**Fru**) კომპლექსის ოპტიკური თვისებების კვლევის პროცესში ინდიკატორად გამოყენებულია პიროკატეხინ იისფერი (პკი) რკინის იონების კოლორიმეტრული რეაქტივი, ხოლო სტანდარტულ ნაერთად სამვალენტიანი რკინის ნიტრატი.

საკვლევი რკინა- ფრუქტოზის კომპლექსის ხსნარის ოპტიკური სიმკვრივე გაზომილია 520 ნმ ტალღის სიგრძეზე. $Fe(NO_3)_3$-ის და პკი-ის ხსნარებზე დამატებულია სხვადასხვა რაოდენობის D-ფრუქტოზის ხსნარები. წონასწორობის დამყარების შემდეგ (**PH=6,0**) გაზომილია ლითონინდიკატორული სისტემის ოპტიკური სიმკვრივის დამოკიდებულება დამატებული ფრუქტოზის კონცენტრაციაზე. **Fe(III)**- კომპლექსის შედგენილობა გამოთვლილია წონასწორობის ძვრის მეთოდის საშუალებით. ლითონინდიკატორთან შეკავშირებული ლითონის კონცენტრაცია განსაზღვრულია წინასწარ აგებული საკალიბრო მრუდის საშუალებით.

შუალედური გამოთვლების საშუალებით დამყარებულია დამოკიდებულება **-lg[Fe-Fru] x [პკი] / [Fe- პკი]** და **- lg[Fru]** სიდიდეებს შორის. შედეგად, აგებულ მრუდზე განსაზღვრულია წრფის დახრის კუთხის ტანგენსი (**tgα=n**), რაც წონასწორობაში მონაწილე ფრუქტოზის იონების რიცხვს შეესაბამება. ფრუქტოზის ხსნარებისათვის **α= 45**, ხოლო **tgα=1**. ამრიგად, მოცემულ პირობებში (**PH=6,0**) **Fe(III)**- ფრუქტოზის კომპლექსში კომპონენტთა თანაფარდობა **Fe:Fru** შეადგენს **1:1**.

ლითონების **Fe(III), Co(II), Zn(II), Mn(II), Cu(II) D**-ფრუქტოზასთან კომპლექსების შედგენილობის კვლევის შედეგად შესაბამისად **520, 530, 540, 590** და **630** ნმ ტალღის სიგრძეზე დადგინდა, რომ ყველა შემთხვევაში ლითონისა და ლიგანდის თანაფარდობა შეადგენს **1:1**.

REFERENCES

1. Shemikin F.M., Karpov A.N., Brusilov N.K (1960) Analiticheskaia khimia, pp. 389, M. (in Russian).
2. Babko A.K., Pyatnitsky I.V. (1968) Kachestvennii analiz, pp. 494, M. (in Russian).
3. Bulayov N.M., Kalinkin I.P. (1986) Prakticheskoe rukovodstvo po fotometricheskim metodam analiza, pp. 123- 151, Leningrad (in Russian).
4. Panhwar O. K. (2010) Synthesis, characterization, spectroscopic and anti-oxidation studies of Cu (II)–Morin Complex. *Journal of Molecular Structure*. 967: 47 – 53.
5. Malesav D. (2001) Investigation of metal–flavonoid chelates and determination of flavonoids via metal-flavonoid complexing reactions (reviews). *Serb. Chem. Soc*. **72**, 10: 931 – 939.

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