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Studies of binary complexes of transition metal ions with Gallic Acid by Potentiometry

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Abstract: Phenolic acids are a complex group of substances that have gained enormous attention in the last years , because of their biological properties , especially from their importance as a secondary plant metabolites , their ecological role and natural antioxidant capacity , physiological effects , use as markers in taxonomic studies , and their properties related to food quality. The dissociation constants of polyphenolic acids are biologically important physicochemical parameters.They constitute important data for the thorough understanding of certain chemical phenomena such as activity and rates ,biological uptake and receptor binding of substances at the molecular level.Traditionally, water has been considered the solvent which best represents the biological conditions .The binary complexes of metal ions Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Fe^{3+} with gallic acid as a ligand are studied at 27°C at ionic strength 1N NaNO_3 .Stability constants calculated by half integral method and pointwise method are compared and found to follow Irving and Williams order .

I. Introduction

Aromatic hydroxy carboxylic acids are of considerable importance due to their complex formation ability with different metal ions[6].Although several studies have been made in the use of hydroxy benzoic acid in complex formation , complexes containing gallic acid (3,4,5 trihydroxy benzoic acid) as a ligand are still scarce .No systematic studies have been reported on the complexation reaction of gallic acid with metal ions .Thus , it seems to be of interest to investigate the stability of the complexes of metal ions with Gallic acid.

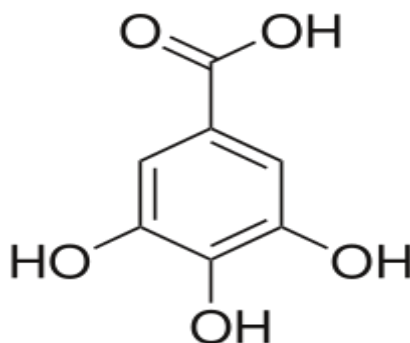
Gallic acid or 3,4,5-trihydroxybenzoic is a trihydroxyl derivative of benzoic acid that is found in plants and fruits, such as gallnuts, grapes, tea, hops and oak bark or by hydrolysis of tannic acid with sulfuric acid. Gallic acid consists of two functional groups, hydroxyl group and carboxylic acid group and exists in two forms, as free molecular gallic acid and as part of tannin acid. As a pure component, gallic acid is a colorless crystalline powder[8].

Gallic acid and its esters are also used in many diverse range of industry, such as antioxidant in cosmetics, pharmaceutical and food industry. As an antioxidant in food industry, Gallic acid and its esters have a problem related to their toxicity at high level in the human body. To overcome this toxicity problem, microcrystalline cellulose has been used to make an ester with Gallic acid by the indirect esterification method. Gallic acid microcrystalline cellulose ester has higher ability to remove free radicals which cause oxidation as compared to Gallic acid and propyl. It also has good stability for room temperature storage, high temperature sterilization process, ultraviolet sterilization and it is stable in pH 3.0 – 9.0 [8].

Furthermore, Gallic acid is well known as a source material for paints, inks and colors developer. Gallic acid has anti-fungal and anti-viral properties. Usually it is used in the pharmaceutical industry to prevent oxidative damage, cancer cells, as a remoter astringent in cases of internal hemorrhage, to treat albuminuria, diabetes, psoriasis and external hemorrhoids [8].

Green tea is honored drink, is used medicinally and as a refreshment after meals. A study suggests a correlation between the natural anti-oxidants found in green tea and overall good health. The two largest components of green tea are carbohydrates, includes cellulosic fiber and protein both of which are water insoluble. The next largest group comprises the polyphenols which are water soluble and may constitute up to 40% of the dry weight of green tea. Polyphenols are useful in the fight against numerous diseases. Tea inhibits the activity of several enzymes related to tumor promotion and cell proliferation including anything, protein kinase c, cyclooxygenaselipoxgenase. It can also inhibit the Formation of long cancer in mice arising from NNK, a common tobacco carcinogen. Gallic acid is one of the polyphenols which are water soluble of green tea. Gallic acid (GAL) (3,4,5 –trihydroxybenzoic acid), which contains O-diphenolic groups, has been described as a product of Lignin and humic acid [1].

The literature survey reveals that very few workers [1,2,4,6,8] have studied the complexation of Gallic acid.The present work is an attempt to explore it's stability with metal ions.



Molecular Structure of Gallic Acid

II. Materials and methods

For the present investigation, Gallic acid acid used as ligand was of AR Grade SD fine. Sodium hydroxide, Sodium Nitrate, Metal nitrates, Nitric acid used of AR Grade SD fine and prepared in double distilled water. Buffer solution of pH=4 and pH=7 are used for calibration. The relative stabilities of the complexes formed are investigated potentiometrically adopting Irving and Rossotti [13] pH –titration technique. PH metric measurements carried out using ELICO digital pH meter model L-120 with a combined glass electrode. The ionic strength was maintained using 1N NaNO₃. Proton ligand (PK) and metal –ligand Stability constants (log K) are determined using the SCOGS computer program.

Procedure

The following solutions are prepared (total volume 50ml) and titrated potentiometrically against standard NaOH (0.2N) solution.

- a) HNO₃ (2ml) + NaNO₃ (2ml)
- b) HNO₃ (2ml) +ligand (2ml) + NaNO₃ (2ml)
- c) HNO₃ (2ml) +ligand (2ml) +Metal solution (2ml) + NaNO₃ (2ml)

III. Results and Discussion

The metal-ligand stability constants of binary complexes are evaluated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydrogen bearing complexes are absent. An examination of titration curves indicates that complex formation has taken place in the solution on the following grounds.

- 1) The metal titration curves showed displacement with respect to the ligand titration curves along the volume axis. This indicated the affinity of the ligand with metal ions which released protons and produced volume difference ($V_2 - V_1$).
- 2) The colour change of the ligand in the presence of metal ions appeared showing the formation of new species.
- 3) The hydrolysis of the metal ions are suppressed due to complex formation and precipitation did not appear during the titration

The result obtained are analyzed by the computer program and the stability constant values are calculated. Graph of n_A^- vs.pH for the proton ligand system is plotted and found to extend between 0-2. The ligand titration curve has a lower pH value than an acid titration curve. Displacement of ligand titration curve along the volume axis with respect to acid titration curve is an indication of proton dissociation. Value of n_A^- obtained was 1.2-1.8 and 0.2- 0.8 indicating formation of 1:2 and 1:1 complexes. Deviation of A+L curves from A+L+M curves indicates formation of complexes. pK_1 corresponds to dissociation of -COOH group and pK_2 corresponds to dissociation of -OH group.

- 1) The maximum value of n is 2 indicating the formation of 1:1 and 1:2 complexes only.
- 2) The metal ion solution used in the study is very diluted, hence there is no possibility of formation of polynuclear complexes.

- 3) The hydrolysis of the metal ions are suppressed due to complex formation and precipitation did not appear during the titration.
- 4) The metal titration curves are displaced to the right hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand .
- 5) The large decrease in pH for the metal titration curves relative to the ligand titration curves points to the formation metal complexes.
- 6) In most cases, the color of the solution after complex formation observed to be different from the color of the ligand at the same .

Proton Ligand Constant and Metal Stability Constants

In the Gallic acid system , the carboxyl acidity constant $pK_1 (\text{COOH}) = 5.30$ is obtained. The value of most acidic $-\text{OH}$ group , $pK_2 (\text{OH}) = 9.294998$ is obtained which are in agreement with reported values.

Proton ligand constant	Half integer method	Pointwise method
pK_1	5.30022	5.272329
pK_2	9.294998	9.291562

Sr.no	Metal ion	$\text{Log} k_1$	$\text{Log} k_2$	$\text{Log } \beta$
1	Fe^{3+}	11.6545	10.825	22.48
2	Cu^{2+}	7.9150	7.0946	15.01
3	Zn^{2+}	6.2561	6.0034	12.259
4	Ni^{2+}	5.6428	5.2030	10.845
5	Co^{2+}	5.8957	5.3244	11.22
6	Cd^{2+}	6.2115	4.7593	10.970

IV. Conclusion

The order of stability of transition metal ions with Gallic acid ligand is found to be in the order $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$. The order is in agreement with the Irving Williams order [10] and reported by many workers [12,13]. The stability constant value varies with the ionic size of metal ion .The smaller the ionic radius of the central atom, more stable is the complex formed. It also depends upon experimental conditions used.

V. References

- [1] Mahmoud Hassan Moustafa, Studies on the binary and ternary complexes of mercury (II) with Gallic acid and adrenaline, *Ass. Univ. Bull. Environ. Res. Vol. 13 No. 2, October 2010-77-90*
- [2] Beverly Sandmann, May H. Chien, Robert A. Sandmann, Stability Constants of Calcium, Magnesium and Zinc Gallate using a divalent ion-selective Electrode, *ANALYTICAL LETTERS*, 18(A2), 149-15
- [3] Chuen-Ying Liu, Yu-Wan Ho, Yi-Fen Pai, Preparation and evaluation of an imidazole-coated capillary column for the electrophoretic separation of aromatic acids, *Journal of Chromatography A*, 897 (2000) 383–392
- [4] Nasreen Fatima, Zahida T. Maqsood, study of formation constants of Vanadium (III)-Catecholate Complexes, *J. Saudi. Chem. Soc.* 9(3), 519-525, 2005
- [5] Iran Fattahpour sedeh, Lars-Olof Ohman and Staffan Sjöberg, *Acta Chemica Scandinavica* 46(1992) 933-940.

- [6] Abu Bakr M.S., H.M. Rageh, E.Y. Hashem and Moustafa N.H., studies of mixed ligand complexes of Copper(II) with Gallic acid and their benzologues, *Montashefte fur Chemie*, 1994, 125, 1197-1205
- [7] J.L. Beltrán, N. Sanli, G. Fonrodona, D. Barrón, G. Özka, J. Barbosa, Spectrophotometric, potentiometric and chromatographic peak of polyphenolic acids in water and acetonitrile–water media, , *Analytica Chimica Acta* 484 (2003)
- [8] Erzalina Hernowo, E-thesis, *National Taiwan University of Science and Technology, Taiwan, 2011.*
- [9] M.F. El-Sherbiny, *Chem.Pap.* 59(5)332-335 (2005)
- [10] H. Irving and R.J.P. Williams, *J. Chem. Soc.* 1953, 3192.
- [11] Ahmed Eid Fazary, Mohamed Taha, and Yi-Hsu Ju*, *J. Chem. Eng. Data* 2009, 54, 35–42
- [12] Shailendrasingh V. Thakur, R.L. Ware, Mazahar Farooqui and S.D. Naikwade, *Asian J. Research Chem.* 5(12): Dec., 2012
- [13] Sayyed Hussain, Abdul Rahim, Mazahar Farroqui, studies of binary complexes of divalent metal ions with Nicotinic acid by potentiometry, *Journal of Advanced Scientific Research*, 2012, 3 (4), 68-69.
- [14] H. Irving and H. S. Rossoti, *J. Chem. Soc.*, 2904, 1954