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Role of Ligands and Stability Constants in Formation of Coordination Compounds of Iron

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ABSTRACT: In the formation of metal complexes in an aqueous medium, equilibrium constant or stability constant is used to determine the strength of interaction between reagents that make the final product after the formation of bonds. In general stability means that a complex may be stored for a long time under suitable conditions or this compound may be existing under suitable conditions. Regarding how much is the concentration of complexes in solution, stability constant provides this information via calculations. These calculations are very much important in many areas of science like chemistry, biology, and medicine. During the complex formation in aqueous medium, two types of stabilities are considered: one is the thermodynamic stability, and the other is kinetic stability. Stability of metal complexes may be affected by various factors like nature of central metal ion and ligand, chelating effect, etc., and some parameters like distribution coefficients, conductance, refractive index, etc. are useful for the determination of stability constants. Various modern techniques are used to determine the stability constant of simple as well as mixed ligand compounds.

KEYWORDS : metal, complexes, reagents, ligand, coordination, stability

I. INTRODUCTION

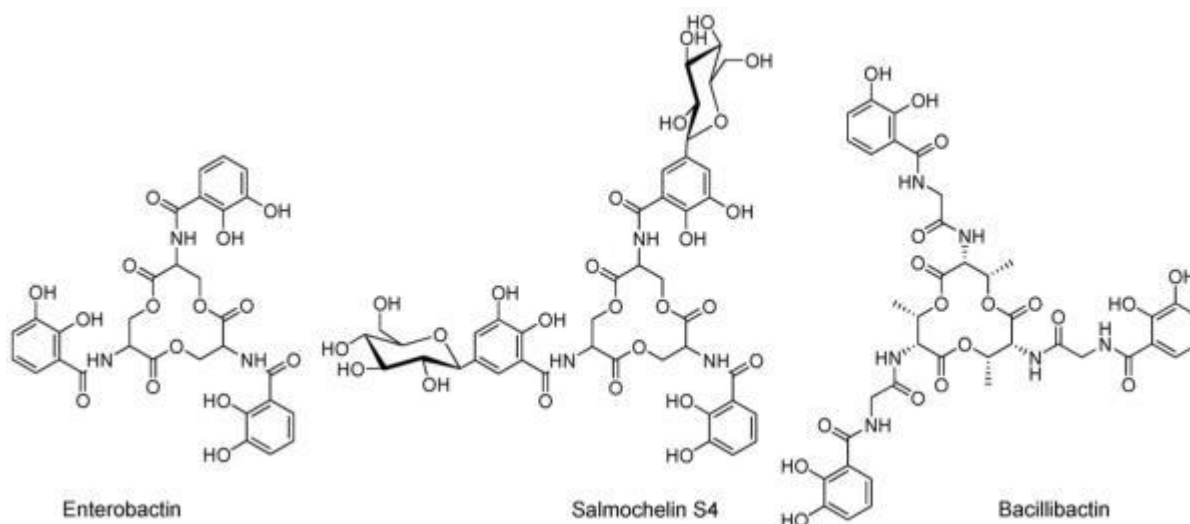
Two remarkable features of many siderophores produced by oceanic bacteria are the prevalence of an α -hydroxy-carboxylic acid functionality either in the form of the amino acid β -hydroxy aspartic acid or in the form of citric acid, as well as the predominance of amphiphilic siderophores. This review will provide an overview of the photoreactivity that takes place when siderophores containing β -hydroxy aspartic acid and citric acid are coordinated to iron(III). This photoreactivity raises questions about the role of this photochemistry in microbial iron acquisition as well as upper-ocean iron cycling. The self-assembly of amphiphilic siderophores and the coordination-induced phase-change of the micelle-to-vesicle transformation will also be reviewed. The distinctive photosensitive and self-assembly properties of marine siderophores hint at possibly new microbial iron acquisition mechanisms.[1]

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Enterobactin, bacillibactin and salmochelin are all tris-catechoyl siderophores framed on a cyclic tri-ester scaffold. Enterobactin, isolated from many different enteric and pathogenic bacteria including *Escherichia coli*, is a cyclic trimer of 2,3-dihydroxybenzoyl-L-serine. Salmochelin, isolated from *Salmonella enterica*, and uropathogenic *E. coli*, resembles enterobactin except that up to two of the catechols groups are glucosylated. The glucosylation in salmochelin is proposed to increase bacteria virulence. Bacillibactin, which is isolated from *Bacillus subtilis* and other *Bacilli* species, incorporates a scaffold of threonine trilactone and glycine spacers, which elongate the three chelating arms as compared with enterobactin. [2]

II. OBSERVATIONS

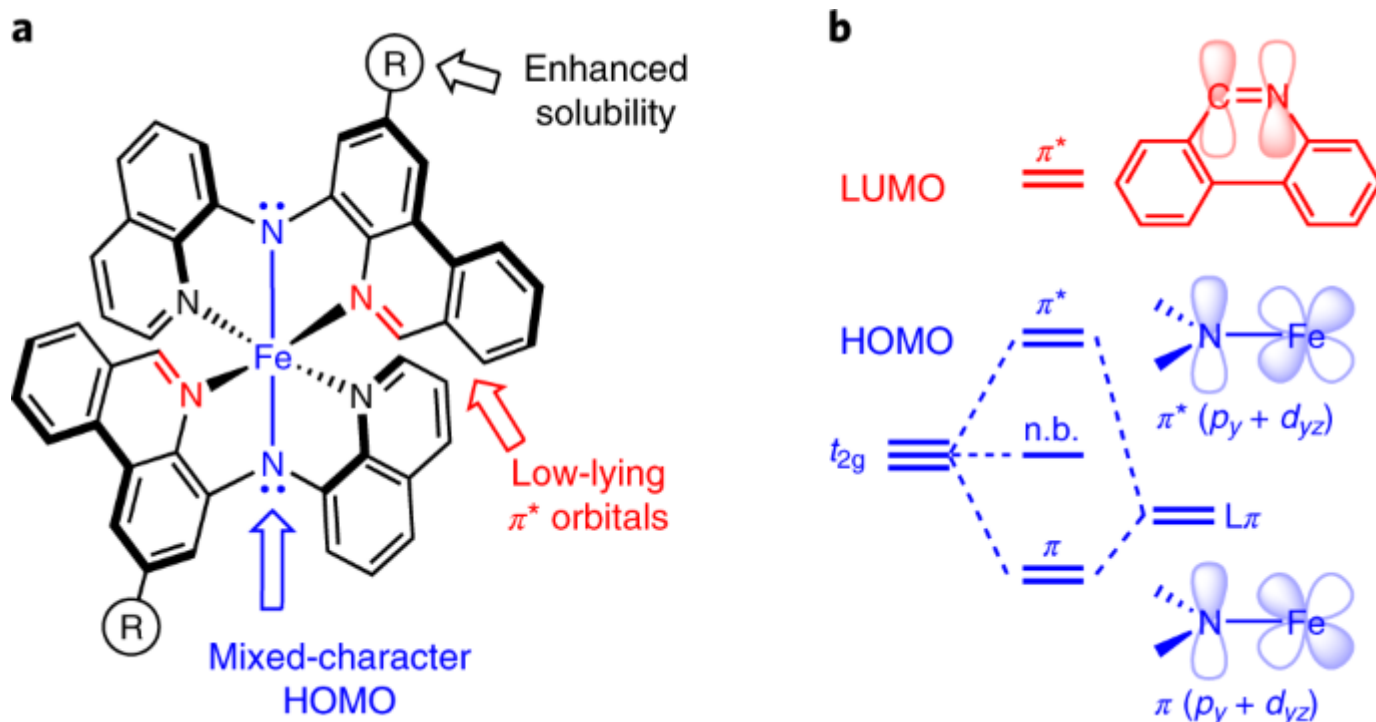
Metals in atmospheric aerosols play potentially an important role in human health and ocean primary productivity. However, the lack of knowledge about solubility and speciation of metal ions in the particles or after solubilisation in aqueous media (sea or surface waters, cloud or rain droplets, biological fluids) limits our understanding of the underlying physico-chemical processes. In this work, a wide range of metals, their soluble fractions, and inorganic/organic compounds contained in urban particulate matter (PM) from Padua (Italy) were determined. Metal solubility tests have been performed by dissolving the PM in water and in solutions simulating rain droplet composition. The water-soluble fractions of the metal ions and of the organic compounds having ligand properties have been subjected to a multivariate statistical procedure, in order to elucidate associations among the aqueous concentrations of these PM components in simulated rain droplets. In parallel, a multi-dimensional speciation calculation has been performed to identify the stoichiometry and the amount of metal-ligand complexes theoretically expected in aqueous solutions. [3] Both approaches showed that the solubility and the aqueous speciation of metal ions were differently affected by the presence of inorganic and organic ligands in the PM.

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IRON COORDINATION COMPLEXES

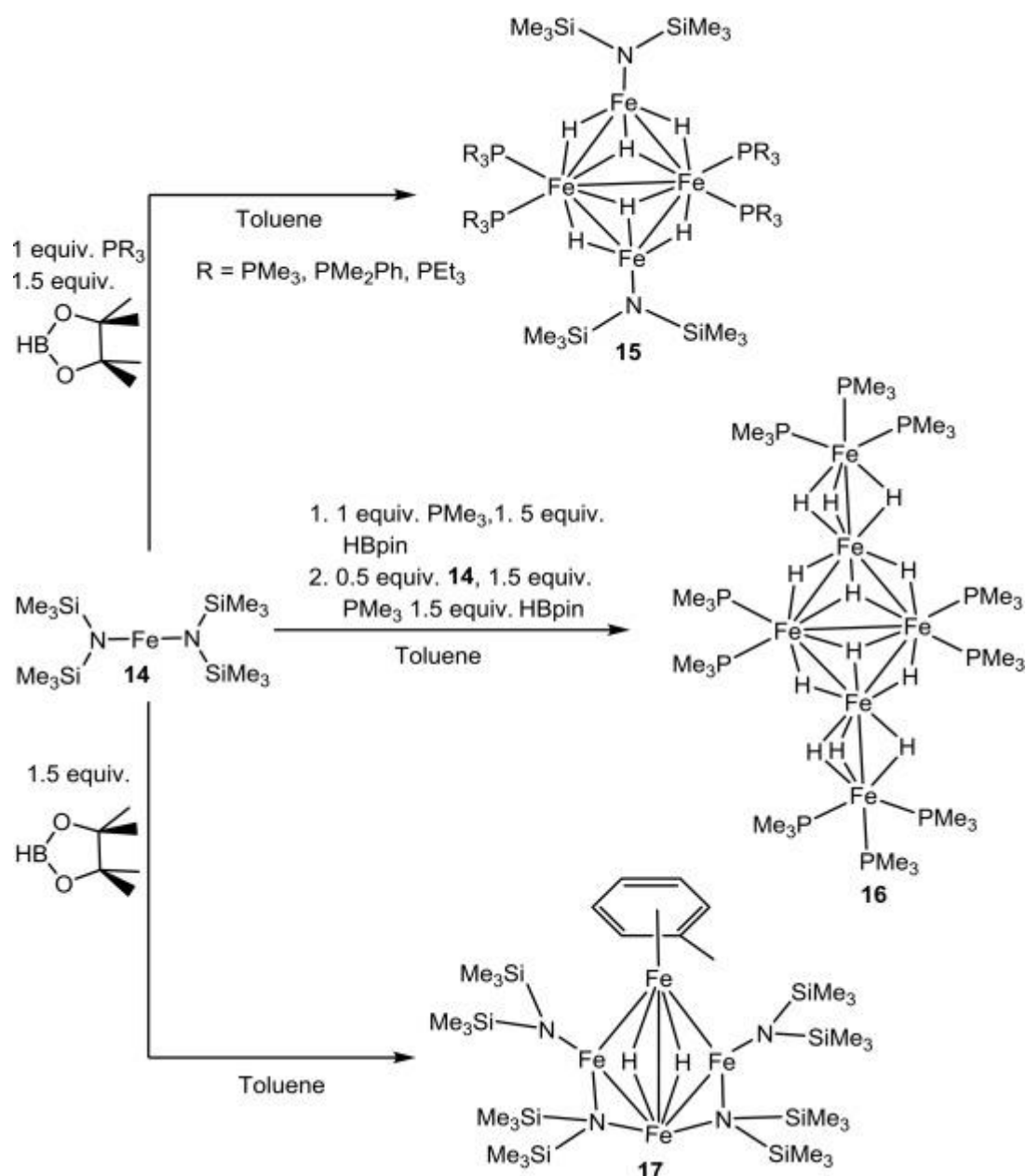
The solubility of Al, Cr, and Fe was strongly correlated to the concentrations of oxalic acid, as their oxalate complexes represented the expected dominant species in aqueous solutions. Oxalates of Al represented ~98% of soluble Al, while oxalates of Cu represented 34–75% of the soluble Cu, and oxalates of Fe represented 76% of soluble Fe. The oxidation state of Fe can strongly impact the speciation picture.

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If Fe is present as Fe(II) rather than Fe(III), the amount of Cr and Cu complexed with diacids can increase from 75% to 94%, and from 32% to 53%, respectively. For other metals, the solubility depended on the formation of soluble aquo-complexes, hence with a scarce effect of the organic ligands. An iron-oxalate complex was also directly detected in aerosol sample extracts.[4]

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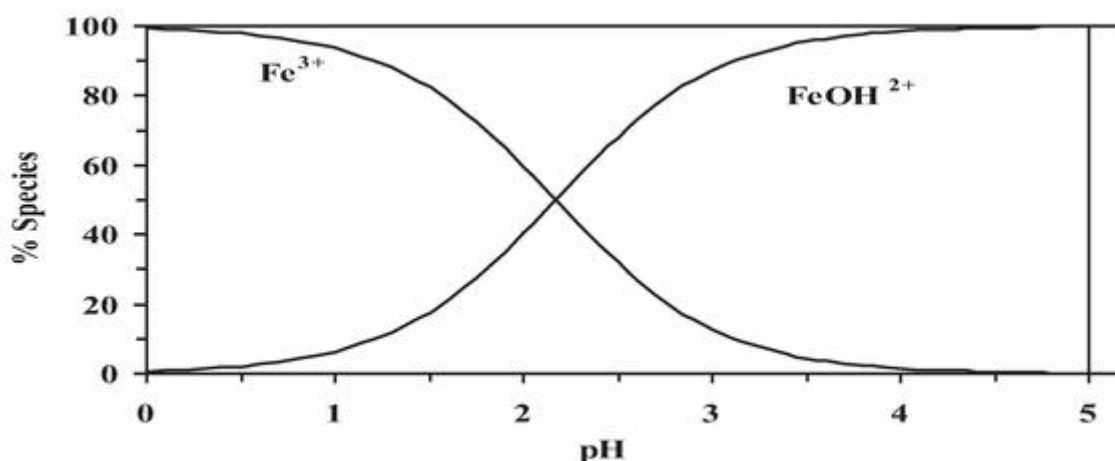
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III. DISCUSSION

Iron(III) chelate systems are used as catalysts for the removal of H₂S from various gas streams including natural gas and for the oxidation of H₂S to S, by air. The reaction is usually carried out in two steps. In the absorber, H₂S is absorbed from the gas by a neutral or mildly alkaline solution of the catalyst and is oxidized by the ferric chelate to sulfur, S, which is eventually removed by filtration or other means, while the catalyst is converted to the ferrous form of the complex. The reduced catalyst is then oxidized by air in a separate part of the apparatus, called the oxidizer. In most cases the catalyst used commercially is an iron(III)/iron(II) chelate, and the chelating agent is an aminopolycarboxylic acid, such as NTA (nitrilotriacetic acid), EDTA (ethylenediaminetetraacetic acid), [16] or HEDTA (N-hydroxyethylethylenediamine-N,N,N"-triacetic acid), but such information is for the most part proprietary.



FORMATION OF IRON TERNARY COMPLEXES

The use of iron chelates of aminopolycarboxylic acids as catalysts in this process is covered by a number of patents, only a few of which are cited here (1-3). Significant operating costs are incurred in the process due to the oxidation and eventual loss of the chelating ligand, which then has to be continuously replenished. The oxidation is probably a radical reaction, and two papers describing this problem in detail have been published (4, 5). This paper describes the chelating agents that form iron(III)/iron(II) chelate systems that promise to be effective catalysts for hydrogen sulfide oxidation. The choice of chelating agent is controlled by the conditions required for carrying out an efficient industrial process. The questions involved in the possible oxidative degradation of the chelating agent are not addressed. Such studies would require a separate, in-depth, study of the oxidation of the iron chelates involved.[5, 15]

IV. RESULTS

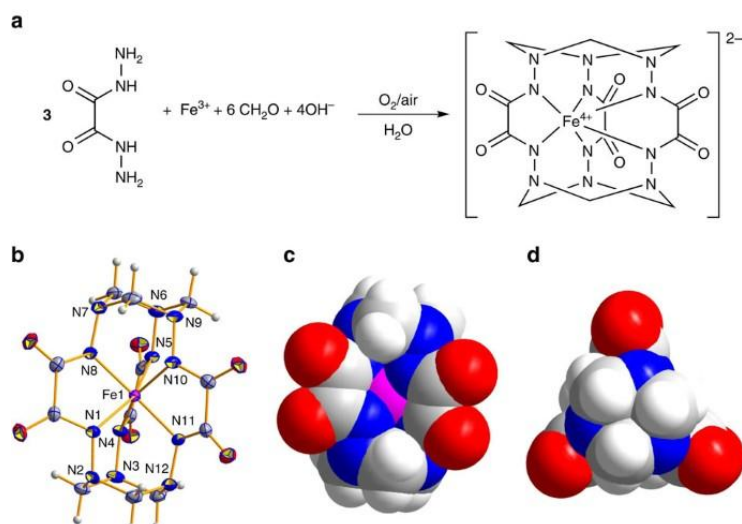
In nature, iron, the fourth most abundant element of the Earth's crust, occurs in its stable forms either as the native metal or in its compounds in the +2 or +3 (low-valent) oxidation states.[14] High-valent iron (+4, +5, +6) compounds are not formed spontaneously at ambient conditions, and the ones obtained synthetically appear to be unstable in polar organic solvents, especially aqueous solutions, and this is what limits their studies and use. Here we describe unprecedented iron(IV) hexahydrazide clathrochelate complexes that are assembled in alkaline aqueous media[6] from iron(III) salts, oxalodihydrazide and formaldehyde in the course of a metal-templated reaction accompanied by air oxidation. [13] The complexes can exist indefinitely at ambient conditions without any sign of decomposition in water, nonaqueous solutions and in the solid state. We anticipate that our findings may open a way to aqueous solution and polynuclear high-valent iron chemistry that remains underexplored and presents an important challenge.[7]

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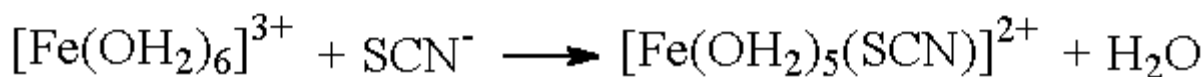
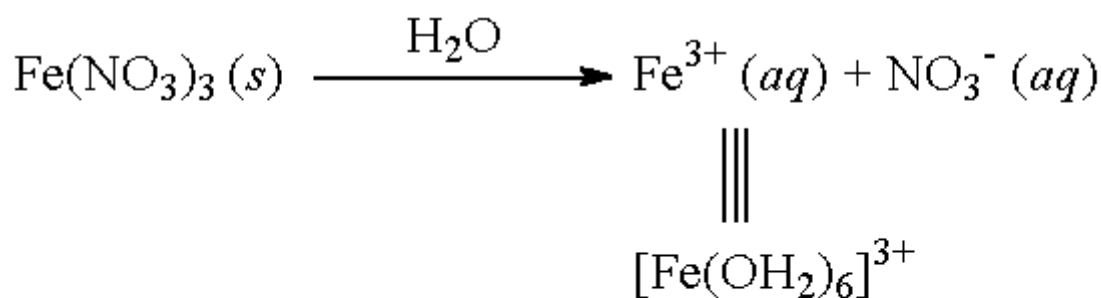
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Synthesis and X-ray crystal structure of hexahydrazide cage iron(IV) complexes

V. CONCLUSION

Method oksidimetriya is a highly sensitive, low-cost, easy-to of the experiment and was used extensively in the study of complex transition metal anions of monobasic organic acids in the acid pH range.[12] In the presence of polybasic acids or multi-ligand, when the probability of formation of heterovalent coordination compounds, complexes with protonated complex composition, mixed ligands require new approaches and methods of thermodynamic calculations. Proposed oxidative function and the principle of equilibrium modeling,[11] which allows to study the processes of formation of complexes of any complexity in the whole pH range, as well as using computer programs to accelerate the calculations and improve their accuracy.



The possibility of using oxidative function and principle of modeling for the study of complex systems with multi-ligand: Fe (II)-Fe (III)-hydroxybenzoic (salicylic) acid-water. Drawn up on the basis of the experimental data model is the model parameters: structure, stability, the existence, degree of accumulation (mole fractions) formed salicylate

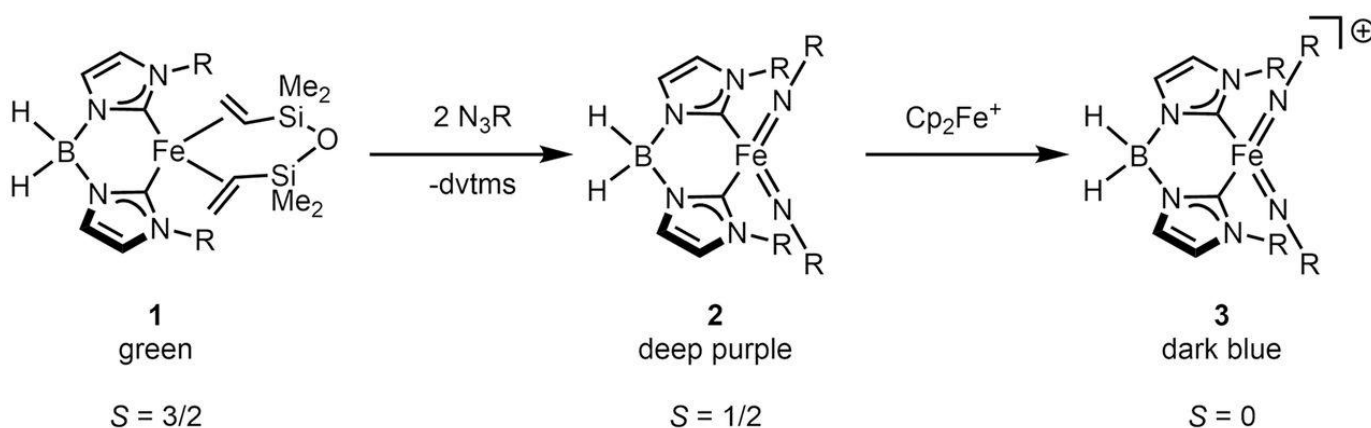
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coordination compounds of iron. Shown that the most stable are binuclear coordination compounds and heterovalent complex - $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{L}_2\text{OH}^0$. Model parameters allowed a clear distinction between the domain of existence, domination and isolation of a stable solution with a high degree of accumulation of biologically active complexes of practical interest. So they can be ready.[8]



VI. FUTURE SCOPE

Method of oxidation potential using the proposed c oxidative function and the principle of equilibrium modeling systems define the composition, stability, the existence, degree of accumulation of salicylate coordination compounds of iron: $[\text{FeHL}]^{2+}$, $[\text{FeHL}(\text{OH})]^+$, $[\text{Fe}_2(\text{HL})_2]^{4+}$, $[\text{Fe}_2\text{L}_2(\text{OH})_2]^0$, $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{L}_2\text{OH}]^0$, $[\text{Fe}_2\text{L}_2(\text{OH})_4]^{2-}$, $[\text{FeHL}]^+$, $[\text{FeL}(\text{OH})]^-$, $[\text{Fe}_2\text{L}_2]^0$. [9] The possibility of using the principle of oxidative function modeling in redox systems hydroxybenzoic acid, which speeds up the calculation and increase their accuracy. The estimated model parameters complexes allowed a clear distinction between the domain of existence and stable, highly complex accumulation of fluid. Therefore, the model parameters can be ready reference tool for the directed synthesis and implementation of the various thermodynamic calculations. [10]

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