Investigation of rate constant of Fenton-like reactions in the presence of Glutamic and Glutaric acid at pH 5 determined by UV/VIS spectroscopy

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Introduction

- Fenton reactions are crucial in producing °OH in the atmospheric aqueous particle phase.
- Reported second-order rate constants for **Fenton** (**Fe^{2+} + H_2O_2**) at 68 L mol^{-1} s^{-1}. This rate can be modified with the Fe speciation (**Fenton-like**).[1]
- **Glutamic acid**, as a multifunctional amino acid which is abundant in nature, undergoes different protonation states depending on the pH of the solution[2]
- Iron can form a complex with **amino acids**, such as glutamic acid, which may significantly modify the reaction kinetics.

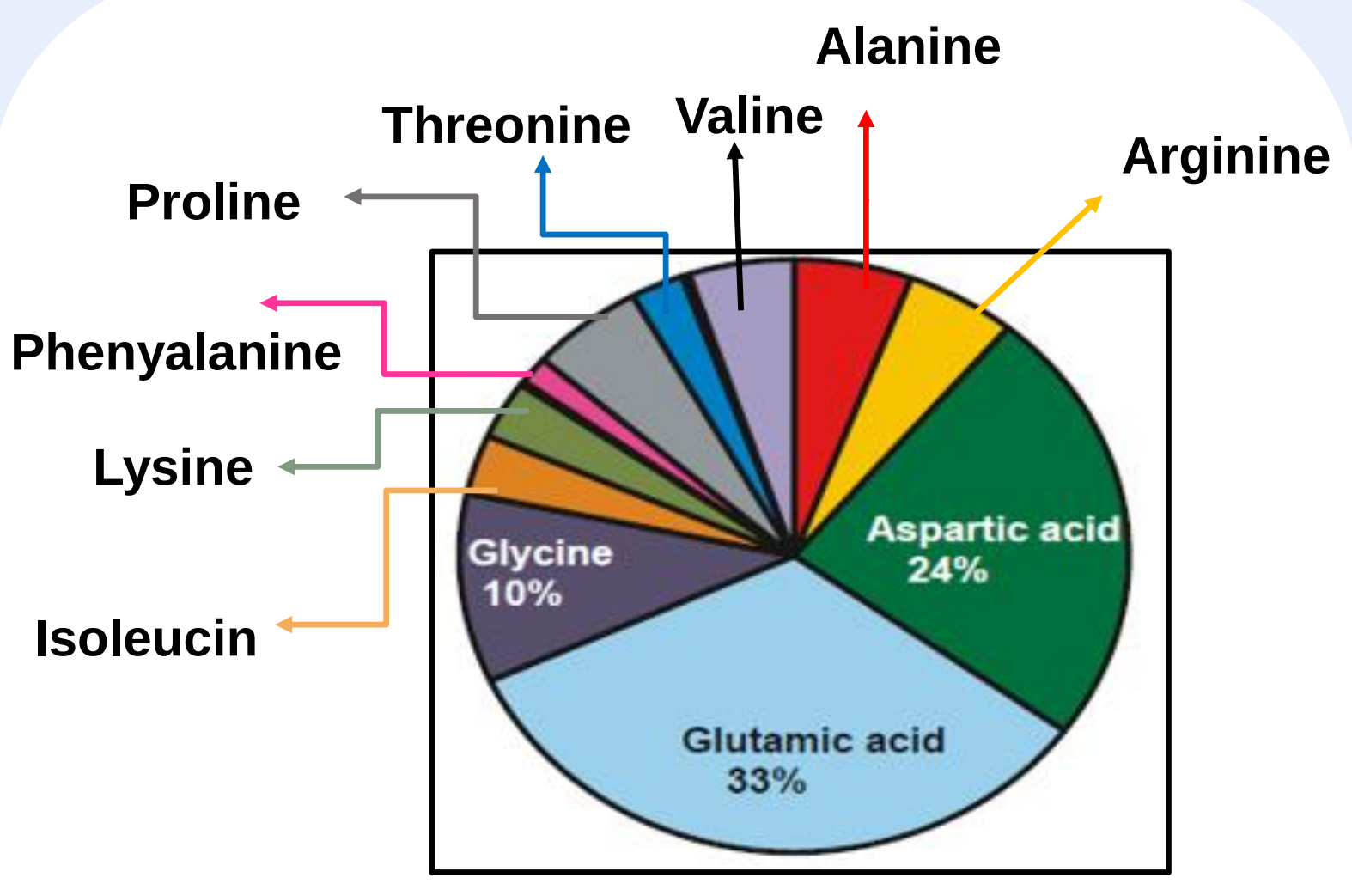

Fig.1: Proportional distribution of amino acids in the coarse-mode particles as combined amino acids. [1]

$$Fe^{2+}(C_5H_9NO_4) + H_2O_2 \rightarrow [Fe(C_5H_9NO_4)\,]^{2+} + HO^{\bullet} + HO^{-}$$

Experimental

Iron conversion

- APHA 3500 Fe test (APHA, 1997).[3]
- Fe(II) and ortho-phenanthroline complex.
- DMSO used as a scavenger of HO•

Rate constants determination

- First and second-order rate constant.
- Employing UV-Vis spectroscopy.

Redox Potential

- Explore the redox behavior of the Fe^{2+} / Fe^{3+} in the presence of glutamic acid
- DMSO used as a scavenger of HO•

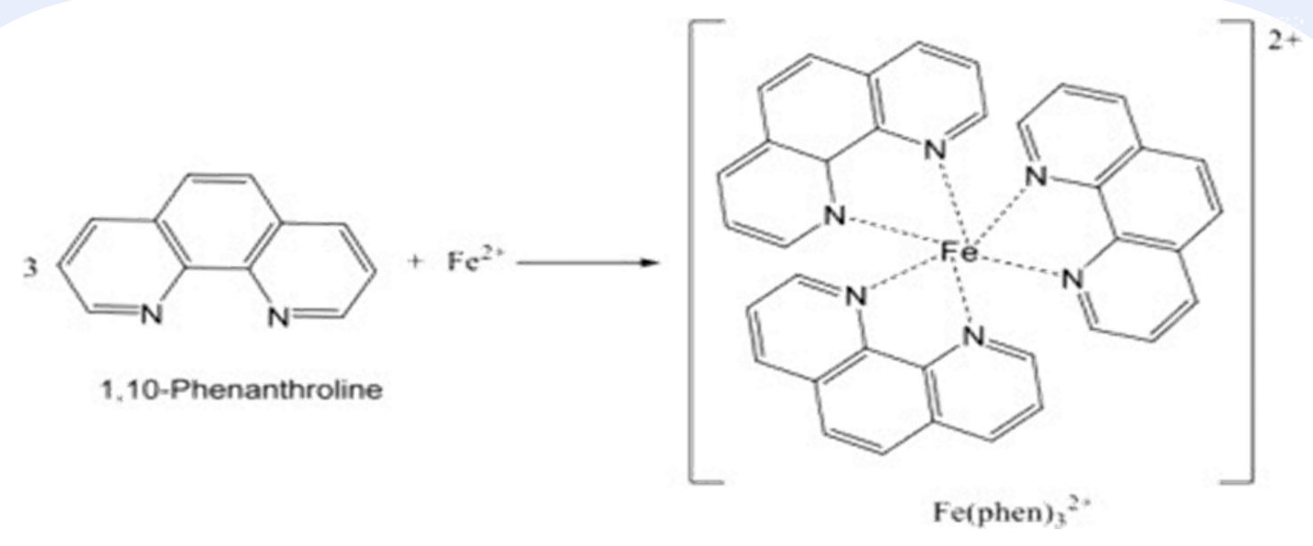

Fig. 2: Formation of complex between Fe(II) and 1,10-Phenanthroline

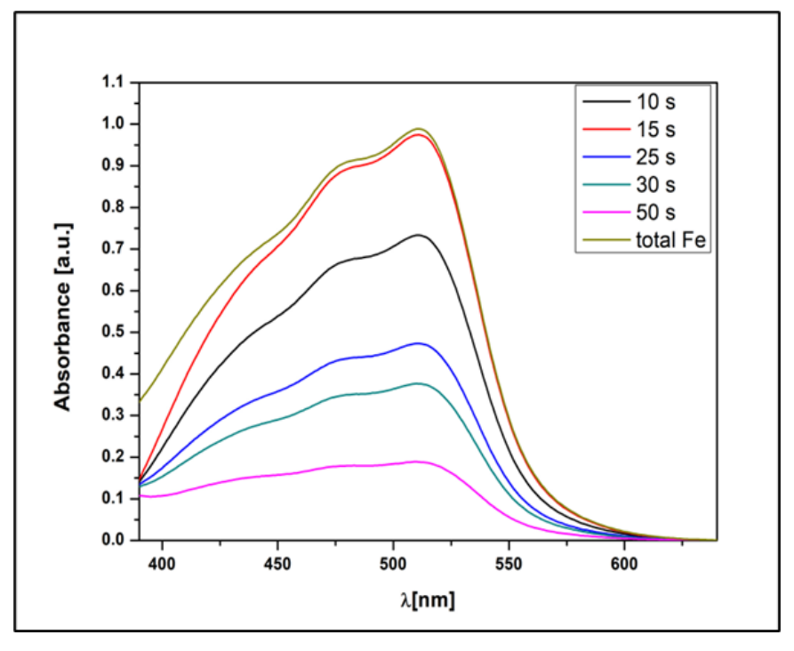

Fig. 3: Absorption spectra of the complex at 4.5 ×10^{-5} mol L^{-1} Fe and 4 ×10^{-4} mol L^{-1} H_2O_2 throughout the Fenton reaction

Results

Kinetics of Fenton-like reaction

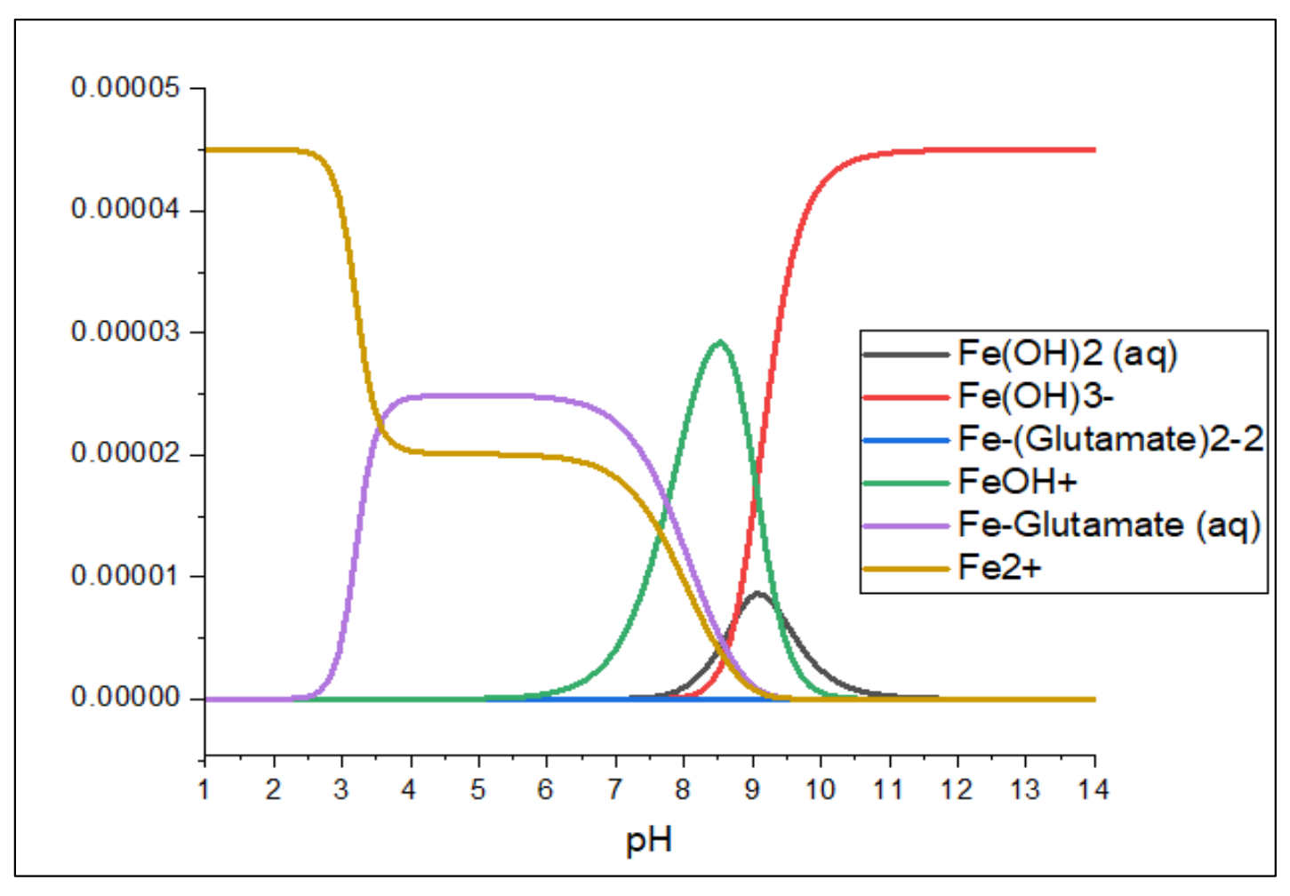

Fig. 4: Speciation of Fe(II) in the presence of Glutamic acid at different pH. Conc. Fe(II) 4 × 10^{-3} mol L^{-1} and Glutamic acid 4 × 10^{-4} mol L^{-1}. (Visual MINTEQ 3.1)

- Low pH favors the formation of certain Fe–glutamate complexes.
- As pH increases, the speciation of these complexes shifts, influenced by changes in ligand protonation and metal–ligand binding affinities (availability of free Fe^{2+} ions decrease) leading to the formation of insoluble $Fe(OH)_2$ or the oxidation to Fe^{3+} ions, which form $Fe(OH)_3$ precipitates[4]

First-order and second-order rate constant

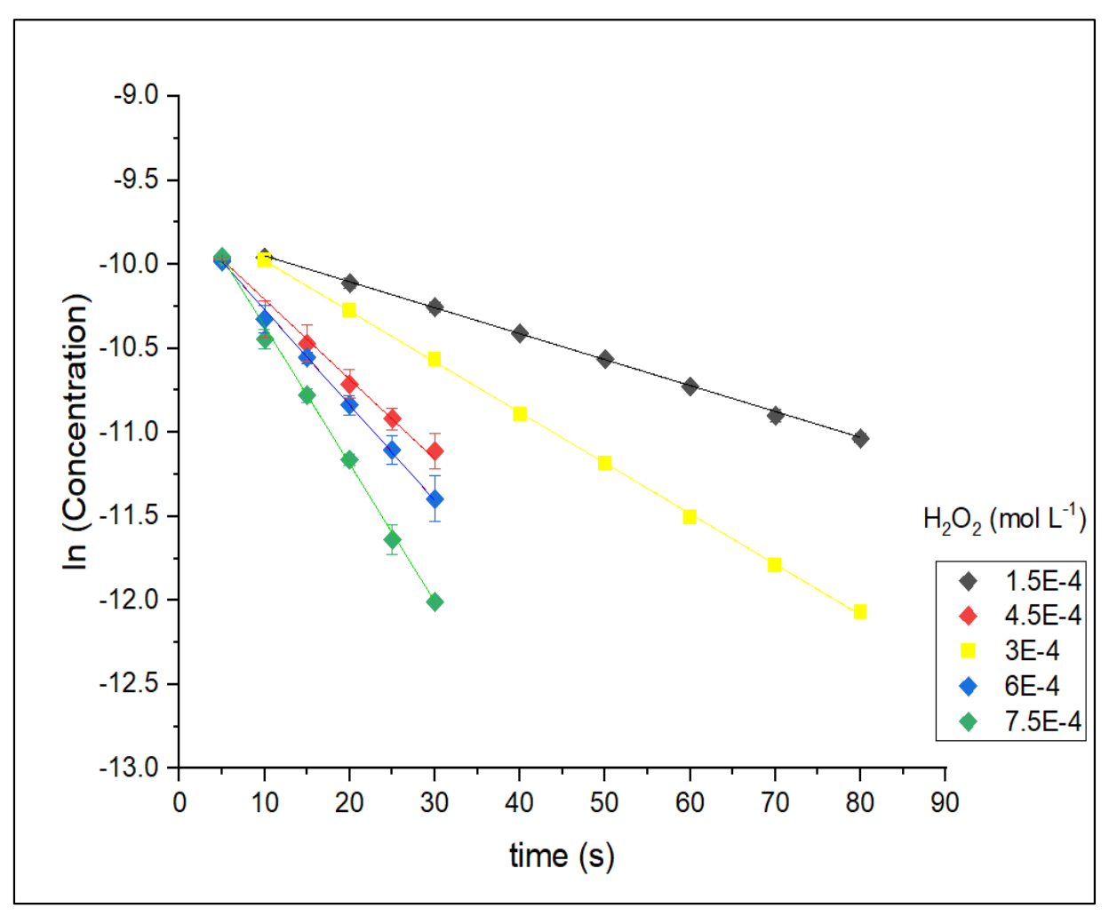

Fig.5 : Plot of ln of Fe (II) concentration as a function of time at different concentrations of hydrogen peroxide for glutamic acid

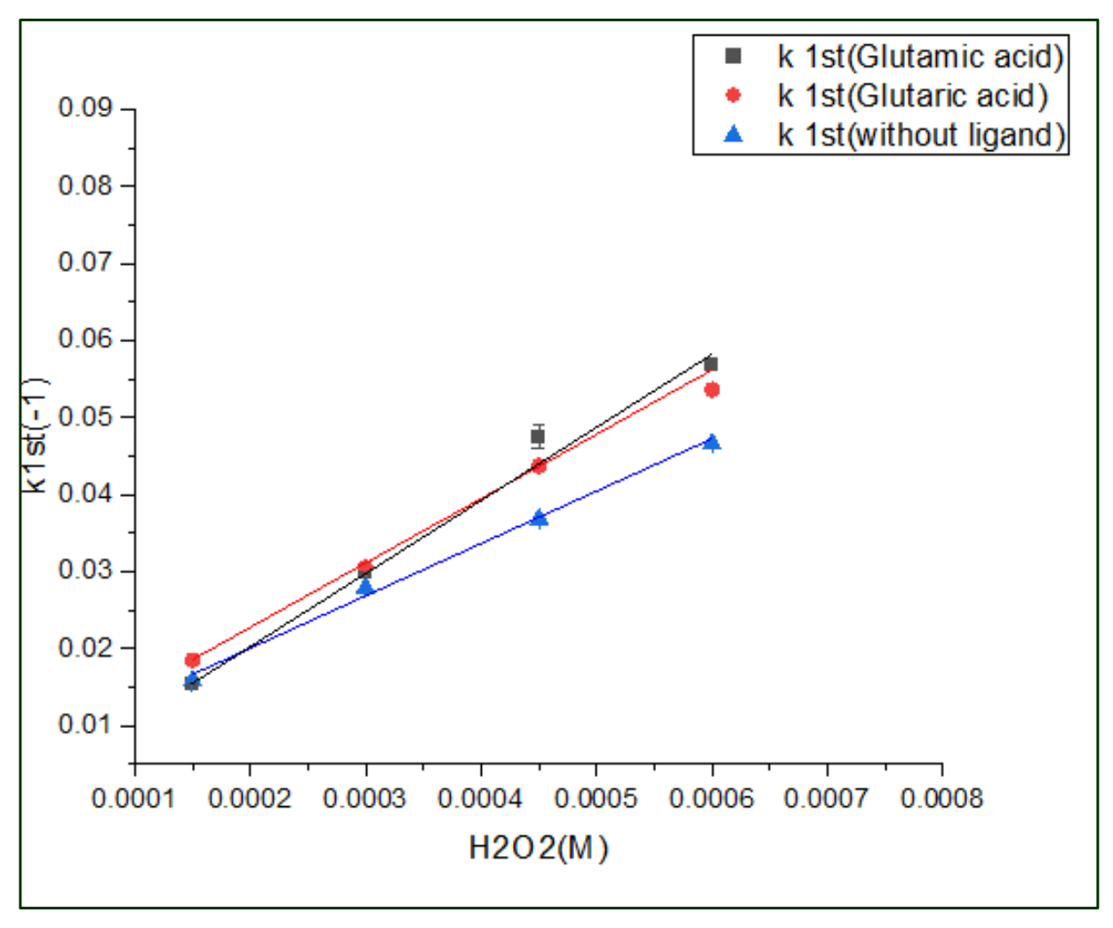

Fig.6 : Plot of the first-order rate constants against the different hydrogen peroxide for glutamic acid ,glutaric acid and without ligand.

- The first-order rate constant was calculated by analyzing the reaction progress at different H_2O_2 concentrations. The reaction rate was proportional to the concentration of **H_2O_2** which ranged from **1.5×10^{-4} to 6×10^{-4} mol L^{-1}.**
- The presence of the ligand significantly increased the slope of the plots, leading to accelerated the reaction rates.
- The slope with glutamic acid was higher than without any ligand, indicating a noticeable effect of complexation of glutamic acid with iron on the kinetics of the reaction.

Slope corresponds to the **second-order rate constant** for the **Fenton-like** reaction

Table 1. Second-order rate constants obtained with different ligands at pH 5

Reactions at pH 5	k_2 / L mol^{-1}s^{-1}
without ligand	68 ± 2
with glutamic acid	102 ± 5
with glutaric acid	82 ± 2
with glutamic acid (observed)	130

Conclusions

- The Fenton-like reaction at pH 5 was initially measured with a second-order rate constant of 68 ± 2 L mol^{-1}s^{-1} in the absence of any ligand, serving as the reference.
- By introducing glutamic acid, the rate constant increased to 102 ± 5 L mol^{-1}s^{-1}, indicating a significant enhancement in reaction kinetics due to ligand coordination.
- Glutaric acid increased the second-order rate constant (82 ± 2 Lmol^{-1}s^{-1}) compared to the reaction without a ligand, which was less significant compared to glutamic acid.
- The Fe-glutamic acid complex, with a redox potential of 0.514V, exhibits favorable thermodynamic properties, highlighting the stability and reactivity of iron-glutamic acid complexes in redox processes.

Improving Complex Formation with UV-vis Spectrum Analysis

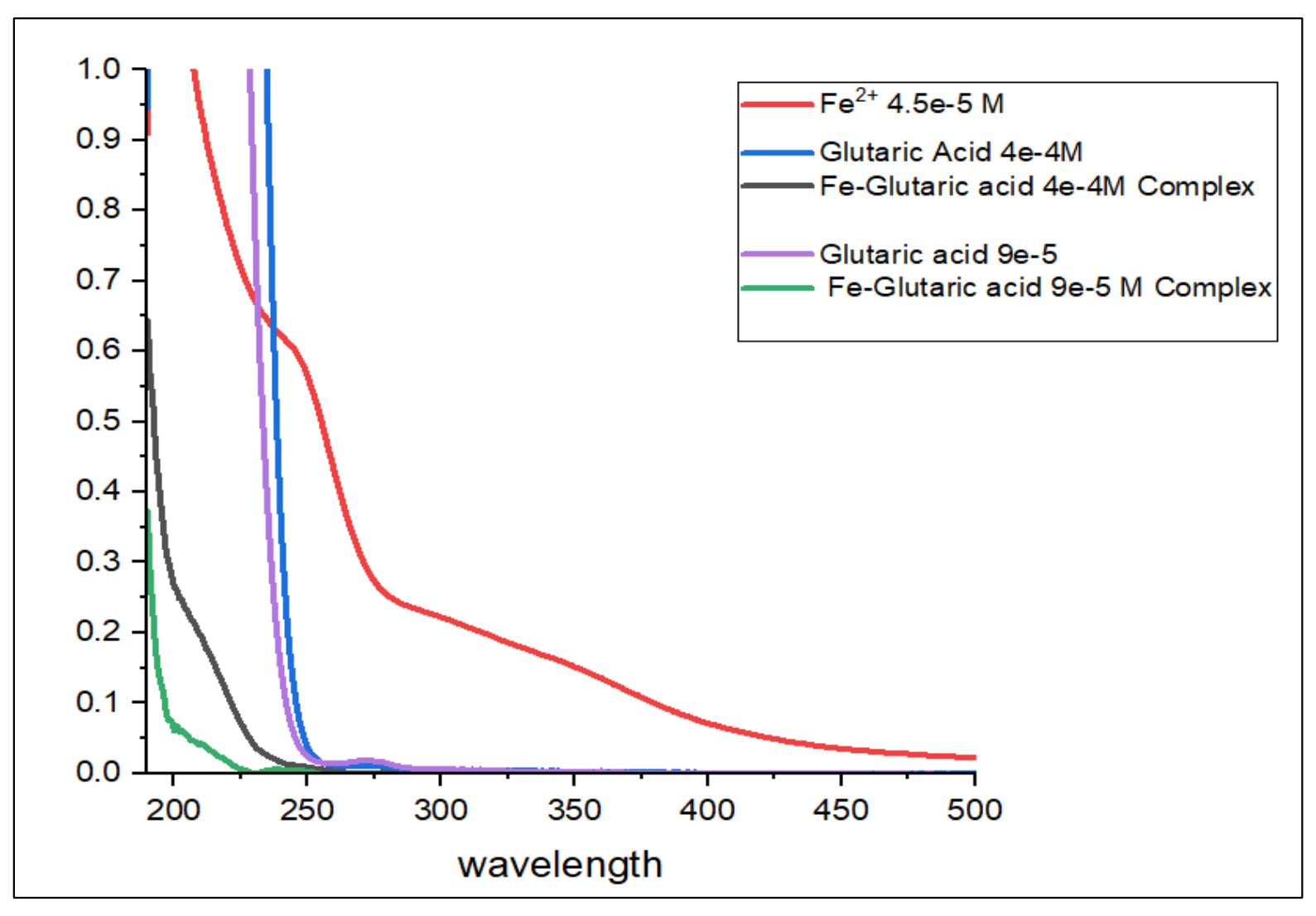

Fig. 7: UV-Vis Spectrum for Forming complexes with two different concentrations of glutaric acid at pH 5

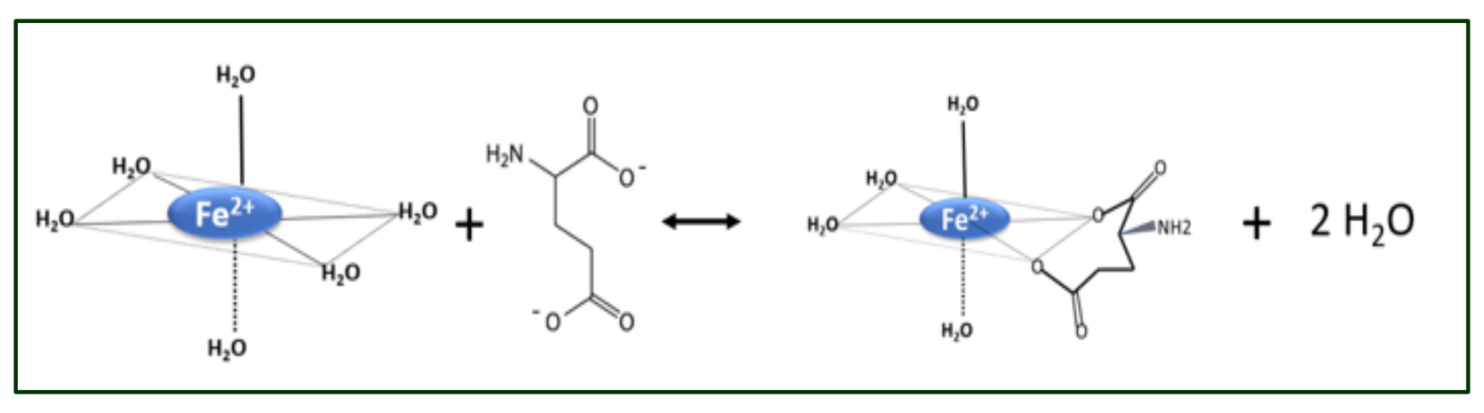

Fig. 8: Formation of the complex using structural formulas

- The UV-vis spectrum shows iron (Fe^{2+}) forms a stable complex with glutaric acid. This shift to lower wavelength indicates coordination between Fe^{2+} and glutaric acid, similar to glutamic acid complexes.
- While the stability constant for the Fe^{2+}-glutamic acid complex is known, the value for the Fe^{2+}-glutaric acid complex is unspecified. Based on the similarity between the two complexes, a comparative spectral investigation was conducted to explore their complexation behavior.

Redox Potential

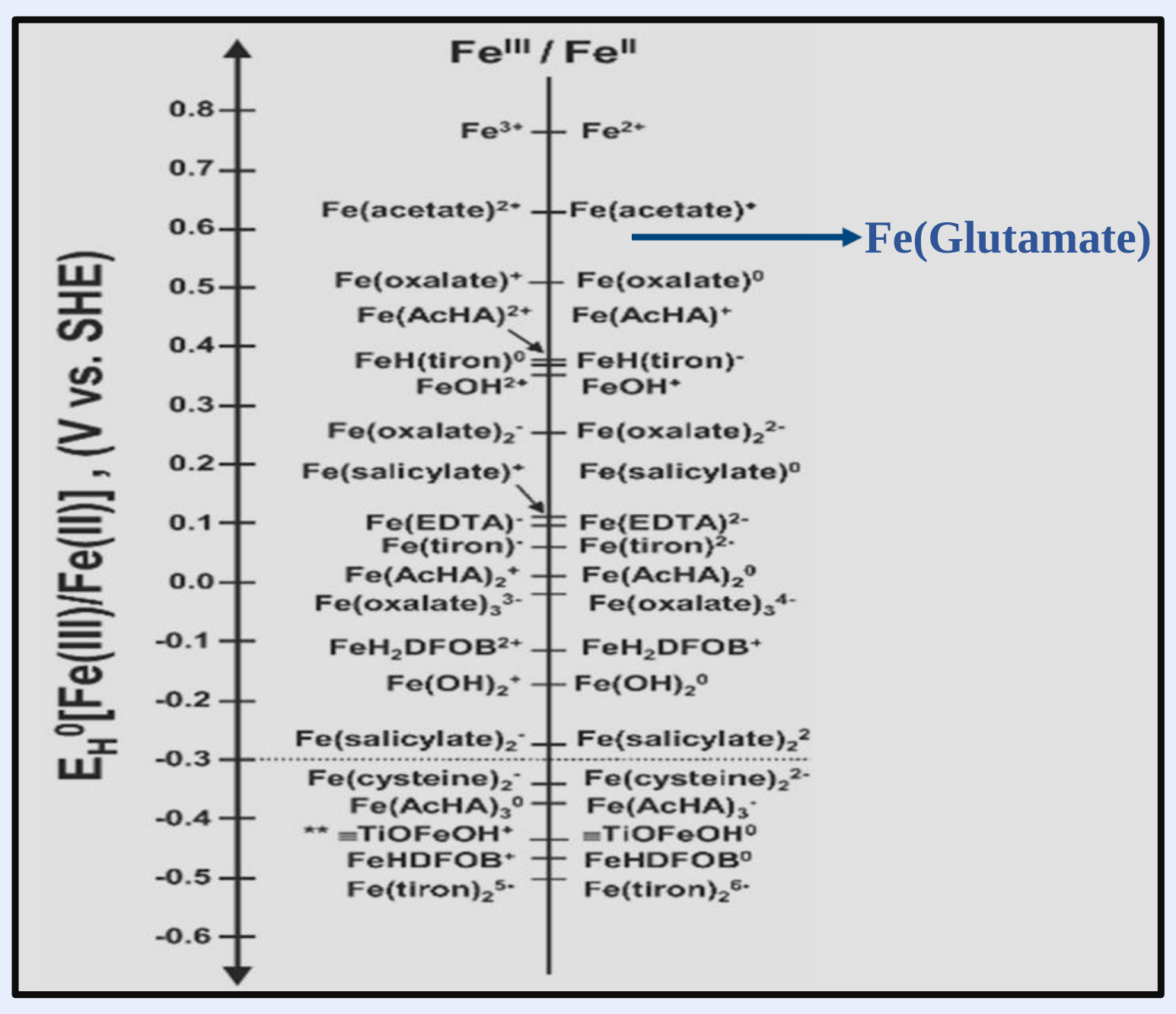

Fig. 9: Redox reactivity of organically complexed iron(II) species [6]

- Glutamic acid influences the redox behavior of Fe ions by altering their oxidation potentials.
- Stable complexes are formed with Fe^{2+} and Fe^{3+}, affecting their electrochemical properties, and the redox potential of the Fe^{2+}/Fe^{3+} gained from Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} lnQ \quad [5]$$

- The redox potential of 0.514 V demonstrates the important role of ligands like glutamic acid in modifying iron's electrochemical properties.

Atmospheric aqueous phase implications

- In the atmospheric aqueous phase, organic acids such as glutamic acid can complex with metal ions like Fe^{2+}, modifying their reactivity and influencing atmospheric chemistry. This metal-ligand complexation is critical as it regulates the formation of reactive oxygen species (ROS), particularly hydroxyl radicals (HO•), which are key to the oxidation of pollutants and aerosols.[7]
- These complexes are particularly important in aerosols and cloud droplets, where they facilitate redox reactions that drive atmospheric oxidation cycles under acidic conditions (pH 1-5). [8]

References

[1] Koppenol, Dalton Trans., **2022**, 51, 17496-17502. [2] Tanaka, Y. & Nakamura, K., **2023**, Env. Sci. Technol. 57 (10), 1234-1245. [3] APHA (**1997**) Standard Methods for the examination of water and wastewater Visual MINTEQ 3.1 .[4] Visual MINTEQ (3.1) [5] Feiner A.S. & McEvoy A.J.,**1994**, J. Chem. Educ., 71(6), 493. [6] Strathmann T. J., **2011**, Redox reactivity of organically complexed iron(II) species with aquatic contaminants. [7] Tilgner et al., Atmos. Chem. Phys., **2021**, 21,p.13483-13536. [8] Song et al., RSC Adv., **2024**, 14, 33489-33511.