Integrating a Smartphone and Molecular Modeling for Determining the Binding Constant and Stoichiometry Ratio of the Iron(II)−Phenanthroline Complex: An Activity for Analytical and Physical Chemistry Laboratories

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S *Supporting Information*

ABSTRACT: The binding constant and stoichiometry ratio for the formation of iron(II)−(1,10-phenanthroline) or iron(II)−o-phenanthroline complexes has been determined by a combination of a low-cost analytical method using a smartphone and a molecular modeling method as a laboratory experiment designed for analytical and physical chemistry courses. Intensity values were obtained from the digital images by measuring the RGB (red, green, blue) values (on a scale of 0−255 in intensity) of the samples between Fe(II) and o-phenanthroline using a digital camera from a smartphone. The

R channel showed the best linearity for predicting the binding constant. For computational studies, iron(II) complexes using water molecules and 1,10-phenanthroline were used to evaluate the stability of the complex by varying the number of ligands. Complexes have been optimized by reaching a minimum amount of energy. It was possible to observe how stable the complexes are from the optimization calculations, including aspects about the achieved geometries. The approach provides a simple method for performing stability constants over a wide range of complexes, from the undergraduate chemistry laboratories, in the field, and in the research laboratory.

KEYWORDS: *First-Year Undergraduate/General, Analytical Chemistry, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Computational Chemistry, Molecular Modeling, UV−Vis Spectroscopy*
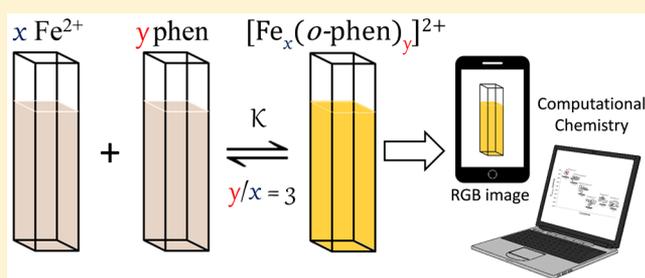
■ INTRODUCTION

The binding constant of metal complexes and the stoichiometry ratio in aqueous solution are important analytical and physical chemistry concepts that should be introduced in first-year undergraduate courses. A simple experiment that allows students to gain hands-on experience in the determination of these parameters using different approaches can be interesting and motivating. Previous experiments published in this Journal have illustrated that the principles of the binding constant are usually determined from spectral or potential measurements such as spectrophotometry,[1] fluorescence spectroscopy,[2] gel chromatography,[3] potenciometry,[4] infrared spectroscopy,[5] cyclic voltammetric,[6] and calorimetry.[7] In order for spectral techniques to be successful in the evaluation of binding constants, some conditions must be reasonably observed: (i) separated absorption maxima; (ii) isosbestic point. The required spectral measurements become difficult when the metal is in a highly reactive oxidation state, with the use of electrochemical methods being necessary. There are several spectrophotometric methods for determining the stoichiometric ratio of ligand coordinated to transition metal ion, including the molar ratio method,[8] Job's method of continuous variation,[9] and the Bjerrum method.[10]

Smartphones are clearly ubiquitous in the hands of students. These devices have many valuable capabilities that have tremendous potential for use in chemical education.[11−14] For example, a smartphone camera can be viewed as a singular spectrometer capable of collecting spectral information and storing it in image files as coordinates in the red−green−blue (RGB) space. These colors are represented by a mixture of red, green, and blue on an 8-bit scale, that is, in a range where the intensities of these colors vary from 0 to 255. Like smartphones, computers are becoming faster and less expensive, and are increasingly found in chemist's laboratories; the growing importance of computational chemistry in modern research has led to a corresponding need to include computational experiences in the undergraduate *curriculum*. Computational chemistry calculations are based primarily on four main methods (*ab initio*, semiempirical, molecular mechanics, and density functional theory) that vary from each other in their form of description of the molecular systems and the associated computational cost. Previous experiments

published in this Journal have illustrated that computational chemistry has become a tool in laboratories.[15−17] These studies introduce students to the main methods and how they can be used in conjunction with experimental observations.

In this laboratory experiment, we describe a smartphone camera that was used as a detector to capture images of the tris(1,10-phenanthroline)iron(II) complex ion to measure the binding constant and stoichiometry ratio (molar ratio method) whose color intensity is directly dependent upon iron concentration. The experiment described herein takes advantage of eliminating the need for expensive analytical equipment by making use of an inexpensive smartphone camera and open source image analysis software. In addition, we investigate the stability of iron(II)−(1,10-phenanthroline)$_n$ complexes using semiempirical method parameters which are fit to experimental results instead of multiple integrals from the approximate solution of Schrödinger's equation.[18,19] The final results corroborate the experimental ones in relation to the stability of these complexes and the correct number of ligands (n) which better stabilize the real complex. We chose to explore the theme of binding constant due to the possibility of synergy between physical chemistry (computational chemistry) and analytical chemistry (instrumental method). The experiment presented here can be used with first-year undergraduate students. On the basis of the class evaluation, the experiment is simple and efficient and can be finished within a 2.5 h period.

■ THEORETICAL BACKGROUND

In knowing the volume of added ligand when the equilibrium is reached, and as a consequence its number of moles, it is possible to determine the stoichiometric ratio and the stability constant for the complexation reaction for a metal ion, Fe^{2+}, with an organic ligand, phen (1,10-phenanthroline) which can be represented as follows:

$$x Fe^{2+} + y phen \rightleftharpoons [Fe_x(o\text{-phen})_y]^{2+} \tag{1}$$
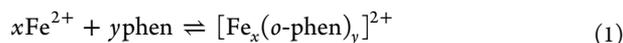
The equilibrium is reached when the maximum absorbance, A_{max}, at the visible range remains constant when ligand is added. As the absorbance remains constant, the color of the solution also remains the same. Therefore, some of the RGB intensities will remain constant too, with their values calculated as the mean of the red, green, and blue color channels, respectively. By knowing this information and using basic stoichiometric calculations, it is possible to calculate the stoichiometric ratio (y/x) through the recorded images by using eq 2:

$$\frac{y}{x} = \frac{n_{phen}}{n_{Fe^{2+}}} \tag{2}$$

where x is the stoichiometric number for Fe^{2+}; y is the stoichiometric number for 1,10-phenanthroline; $n_{Fe^{2+}}$ is the number of moles of Fe^{2+}; and n_{phen} is the number of moles of 1,10-phenanthroline inside the cuvette when the equilibrium is reached, in other words, when the color intensity of the solution turns constant.

The stability constant K using the image data is calculated by eq 3:

$$K = \frac{I/\varepsilon}{(C_{Fe^{2+}} - I/\varepsilon)^x (C_{phen} - 3I/\varepsilon)^y} \tag{3}$$

where I is one of the RGB intensities when the equilibrium is reached; ε is the pseudomolar absorptivity coefficient for the

RGB data; $C_{Fe^{2+}}$ is the initial concentration of Fe^{2+} in the solution; and C_{phen} is the concentration of 1,10-phenanthroline added to the solution when the equilibrium is reached.

The pseudomolar absorptivity coefficient ε can be experimentally determined by eq 4:

$$\varepsilon = \frac{I^{+1}}{C_{Fe^{2+}}} \tag{4}$$

where I^{+1} is one of the next RGB intensities to be observed after the equilibrium point. If the I and ε terms were respectively replaced by the absorbance value at 510 nm (when the equilibrium is reached) and by the molar absorptivity coefficient, eq 3 can be used to calculate K using the UV−visible data.

The formation process of inorganic complexes usually involves transition metals which interact with their ligands by d valence electrons. Some ligands can present aromatic rings, which enables them to interact by noncovalent interactions via π electrons. Functionals such as M06-L or M06-2X should be used to computationally treat such systems because they can provide a good description for transition metals and noncovalent interactions compared to other functionals such as GGA (generalized gradient approximation) or LDA (local density approximation).[20] More robust calculations, as previously employed by our group for transition metal complexes,[21] would demand much more time even in powerful computers, which would make a computational chemistry course or practice unfeasible due to length of the experiment. Consequently, we have used semiempirical methods (low computational cost) for this laboratory experiment which provide comparable results to the experimental ones. A good choice for the single point energy calculation is the PM6-DH2 which was developed from the expansion of Hamiltonian applied to the PM6 method to handle hydrogen bonds and weak interactions.[22]

The PM6-DH2 method provides results similar to those obtained by other methods such as CCSD(T)/CBS.[22] Calcula-Calculations for geometry optimization were performed using PM7.[23] COSMOS technique was employed for the geometry optimization and single point energy to take account of the solvent effect.[24] Despite good agreement to the more robust method, the limitations of the semiempirical methods must be made clear to the course participants, mainly in relation to the PM6-DH2 used in this study, and to provide alternatives for more precise calculations with other approaches. The results should not be quantitatively compared to experimental ones, nor used to obtain equilibrium constants; however, they are very useful in the learning process of undergraduate students providing a molecular overview of many problems in chemistry and physics. Computational experiments provide an opportunity to put the student in touch with new concepts such as implicit solvent, binding energy, and optimization of molecular geometry.

The computational experiment presented in this work is made up of two main parts. In the first part, the common ligand molecules to all complexes (water and o-phen) are built and optimized using PM7 with implicit solvent (water). From the optimized ligand molecules, one starts the modeling phase of the complexes in their octahedral form. Since the aim is to study the formation process of the $[Fe(o\text{-phen})_3]^{2+}$ complex, the calculations were run from iron(II) hexahydrated complex $[Fe(H_2O)_6]^{2+}$, which loses two water molecules at each stage to

the entrance of one bidentate *o*-phen molecule. We force the formation with four and five *o*-phen ligands to prove if the results obtained corroborate the experimental ones. In the second part, all the complexes which are already optimized are submitted to the single point energy calculations with PM6-DH2 using two different structures for each complex. The first one represents the final configuration arising from the optimization performed, and the second one is obtained from the removal of ligands at 8 Å away from iron(II) ion in order to simulate the structure at its starting point where the ligand molecules are approximating the iron(II) ion. An estimation of the stability of the complexes can be derived from the heat of formation between the complex and the configuration before complexation as it will be explained in the next section.

MATERIALS AND METHODS

Reagents and Solutions

The following solutions were prepared in deionized water: (1) Fe(II) 2.57×10^{-3} mol L^{-1}, from $FeCl_2 \cdot 4H_2O$; (2) hydroxylamine hydrochloride 5.0% w/w; (3) sodium acetate 2.0 mol L^{-1}; (4) 100 mL of 1,10-phenanthroline 4.04×10^{-3} mol L^{-1} with 0.25 mL of concentrated HNO_3. All reagents were acquired from Sigma-Aldrich, with a high grade of purity.

Reaction

A set of reactions for the formation of $[Fe(o\text{-}phen)_3]^{2+}$ was performed inside a 4 mL plastic cuvette (optical length of 1 cm). In total, 10 cuvettes were used to carry out 10 reactions varying the volume of ligand (1,10-phenanthroline) from 0 to 250 μL, with the other volumes from the solutions (1−3) being constant and added in the following order: 50 μL of Fe(II) solution (1); 320 μL of hydroxylamine hydrochloride solution (2); 320 μL of sodium acetate solution (3). The volumes of added ligand were respectively equal to 0, 10, 20, 40, 50, 80, 100, 150, 180, and 250 μL. Deionized water was added to fully fill the volume of the cuvette to 4 mL. As the volume of ligand increases, the intensity of the color of the solutions also increases until the equilibrium state is reached.

Image and Spectra Acquisition

The ten cuvettes were placed into an Evolution 60S UV−visible spectrophotometer (Thermo Scientific), and its spectra were recorded in the range from 380 to 700 nm (Figure 1).

Afterward, the same cuvettes were placed onto a white surface with a white background composed by a paper sheet,
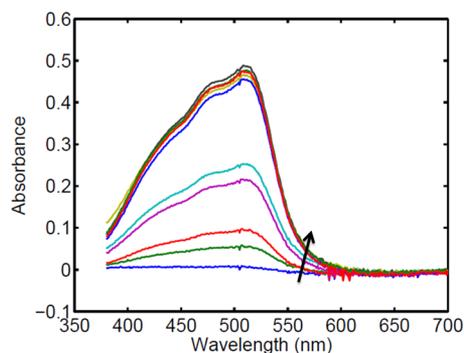

Figure 1. Raw spectra of formation of $[Fe(o\text{-}phen)_3]^{2+}$ complex with ligand volume varying from 0 to 250 μL (bottom to top): 0, 10, 20, 40, 50, 80, 100, 150, 180, and 250 μL; for 50 μL of Fe(II) solution. The arrow indicates the direction in which ligand volume increases.

and its images were recorded by a Smartphone Sony Xperia C2304 with a camera resolution of 8 megapixels. The images were acquired using ambient lighting with the smartphone handled in a static position 30 cm from the cuvette. The images were recorded in .JPEG format with a resolution of 96 × 96 dpi. The region of interest (ROI) of each cuvette for the imaging analysis was cropped as a squared portion of 10 × 10 pixels from the middle region of the bucket image. Thereafter, the red, green, and blue color intensity values were calculated for each ROI. The RGB intensities for the white background in each recorded image must be compared to avoid problems with the lack of control of the white balance in the smartphone images, and to ensure no variability caused by this issue, providing consistency to the measurement.

Computer Software

The image data was cropped using the free GIMP 2.0[25] software and processed using the free R statistics[26] software version 3.2.2; the absorbance values of the UV−visible spectra were extracted using Microsoft Excel 2007, although any spreadsheet freely available can be also utilized.

Molecular Modeling Details

Iron(II) complexes using water molecules and 1,10-phenanthroline or *o*-phenanthroline (*o*-phen) in order to obtain the $[Fe(H_2O)_6]^{2+}$ and $[Fe(o\text{-}phen)_n]^{2+}$ should be built, where *n* is the number of *o*-phen used to evaluate the stability of the complex varying the number of ligands, arbitrarily *n* = 1, 2, 3, 4, and 5. As *o*-phen is a bidentate ligand, each one replaces two water molecules. The ligands (water and *o*-phen) were optimized in isolation using PM7 and implicit solvent (water). Complexes can be optimized following the same procedure used for ligand optimization by reaching the minimum energy. It is possible to observe how stable the complexes are from the optimization calculations, including aspects about the obtained geometries.

As previously mentioned, the PM7 method can be employed for optimizing energy of the complexes in order to obtain the minimum energy which can characterize the stability of the complex. However, other semiempirical methods are often employed to calculate single point energies, such as the PM6-DH2. Calculations are made regarding the formation stages of the complexes. The equation available for this purpose is given by the difference between the formation heat H_f of the complex and the isolated molecules:

$$E_{(PM6\text{-}DH2)}(n) = H_f([Fe(ligand)_n]^{2+}) - nH_f(ligand) - H_f(Fe^{2+}) \quad (5)$$

where $E_{(PM6\text{-}DH2)}(n)$ and n are the energy obtained by PM6-DH2 semiempirical method and the number of ligand molecules, respectively.

From the previous equation, it can be seen that the first term, $H_f([Fe(ligand)_n]^{2+})$, referent to the complex formation, is only obtained by single point calculations. To obtain the other terms, one can use a more didactic process; for instance, using the optimized complex one can break apart the ligands from the central Fe^{2+} for the purpose of considering that all are isolated, with no interaction among them. Then, eq 5 can be rewritten as follows:
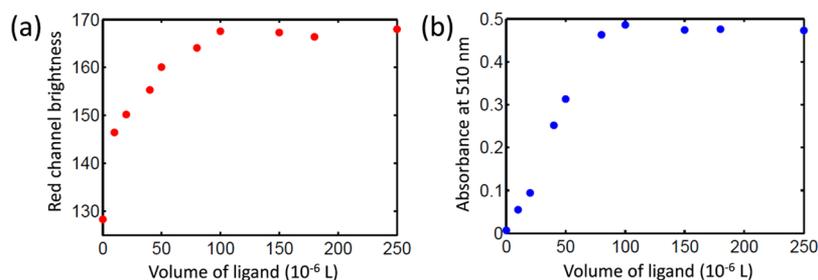
Figure 2. (a) Red channel brightness values $(0-255)$ as a function of volume of added ligand (1,10-phenanthroline). (b) Absorbance values at 510 nm as a function of volume of added ligand (1,10-phenanthroline).

$$E^*_{(\text{PM6-DH2})}(n) = H_f([\text{Fe}(\text{ligand})_n]^{2+})_{\text{complexed}}$$
$$- H_f([\text{Fe}(\text{ligand})_n]^{2+})_{\text{before-complexation}}$$

$$(6)$$

The second term, $H_f([\text{Fe}(\text{ligand})_n]^{2+})_{\text{before-complexation}}$, is obtained after breaking apart the ligands from central ion. This term is computed separating the selected ligand atoms up to an approximate distance of 8 Å. At this distance, the interaction (Fe^{2+}–ligands) can be disregarded. Repeat the procedure for all the complexes. In this way, one calculates the energies related to the $H_f([\text{Fe}(\text{ligand})_n]^{2+})_{\text{before-complexation}}$ term which enables us to calculate $E^*_{(\text{PM6-DH2})}(n)$, a good estimation of the stability of the complexes. Replacement of $E_{(\text{PM6-DH2})}(n)$ by $E^*_{(\text{PM6-DH2})}(n)$ is justified by the change in the definition employed. Because of the geometry dependence of the ligands, the energies calculated by eqs 5 and 6, $E_{(\text{PM6-DH2})}(n)$ and $E^*_{(\text{PM6-DH2})}(n)$, respectively, provide very close results and, hence, will not result in significant changes in the energetic profile of complexes. The students are supplied with a handout that has Supporting Information with detailed descriptions of the procedure.

The experiment (computational chemistry) can be accomplished in a total time of around 2.5 h (modeling and run), and each student runs the calculation on a core i7, 8GB RAM, Windows 7 desktop computer. Molecules were visualized and constructed on Gabedit 2.4.8 software,[27] and the single point energy calculations to generate the heat formation were performed on MOPAC 2012.[28]

■ HAZARDS

With the exception of concentrated HNO_3, there are no significant hazards related to materials and procedures used in this experiment. However, the experiment must be performed with the students appropriately dressed (lab coat, glasses, and gloves), especially for the manipulation of concentrated acid, which needs to be handled into a fume hood, since its steam is harmful.

■ RESULTS AND DISCUSSION

Image and UV−Visible Data

It is possible to obtain the "equilibrium profile" curve by plotting the RGB intensity values from the recorded images as a function of the volume of added ligand to the solution. It was observed that only the red channel presents this profile (see Supporting Information), therefore its intensity was used to determine at which volume of added ligand the equilibrium is reached (Figure 2a). To confirm this trend, the same graph was generated (Figure 2b) using the absorbance at 510 nm

provided by the UV−visible data, which represents the formation of the $[\text{Fe}(o\text{-phen})_3]^{2+}$ complex.[29]

In Figure 2, it is observed that both profiles are very similar to each other, showing the same volume of added ligand (100 μL) when the equilibrium state is reached. Knowing this information and using eq 1, the stoichiometric ratio for reaction 1 was calculated as 3.20 and 3.15 using the image (red intensity) and UV−visible data, respectively. Both values were very similar and can be rounded to 3, showing that the stoichiometric relation between Fe^{2+} and 1,10-phenanthroline is 1:3, as expected for this reaction.

In addition, by knowing the volume of added ligand until the equilibrium is reached, eq 2 and eq 3 were applied to calculate the stability constant for the $[\text{Fe}(o\text{-phen})_3]^{2+}$ complex. The numeric calculation through mathematical software gives a stability constant at the magnitude of 10^{21} using both image and UV−visible techniques, being in agreement with the literature, as shown in Table 1.[30,31] The manual/hand calculation considering less significant figures gives a stability constant at the magnitude of 10^{17} for both techniques.

Table 1. Values of Stability Constant K Calculated Using Image and UV−Visible Methods

Technique	K	$\log K$	$\log K$ Reference[30,31]
Image (red intensity)	9.43×10^{21}	21.9	21.3
UV−visible	7.07×10^{21}	21.8	21.3

Computational Chemistry Analysis

Computational chemistry analysis is based on the stability of complexes before and after their formation. The enthalpy of formation obtained from the calculation using the PM6-DH2 method $(E^*_{(\text{PM6-DH2})}(n))$ can be interpreted as a stability parameter to evaluate the complex formation process varying the ligand's number. Each complex presents a different $E^*_{(\text{PM6-DH2})}(n)$, and then we can define how stable each one is.

Figure 3 presents the $E^*_{(\text{PM6-DH2})}(n)$ in kcal/mol for the $[\text{Fe}(H_2O)_6]^{2+}$, $[\text{Fe}(H_2O)_4 (o\text{-phen})]^{2+}$, $[\text{Fe}(H_2O)_2 (o\text{-phen})_2]^{2+}$, $[\text{Fe}(o\text{-phen})_3]^{2+}$, $[\text{Fe}(o\text{-phen})_4]^{2+}$, and $[\text{Fe}(o\text{-phen})_5]^{2+}$ complexes.

The presented values in Figure 3 can be obtained following the student handout procedures available in the Supporting Information. Some fluctuations in these values are possible since small variations among initial geometry of ligands and complexes can occur due to the different programs and algorithm versions available for use. However, the qualitative result must follow the same trend, in other words, the stoichiometric relation being 1:3 between Fe^{2+} and o-phen must be highly determinant.
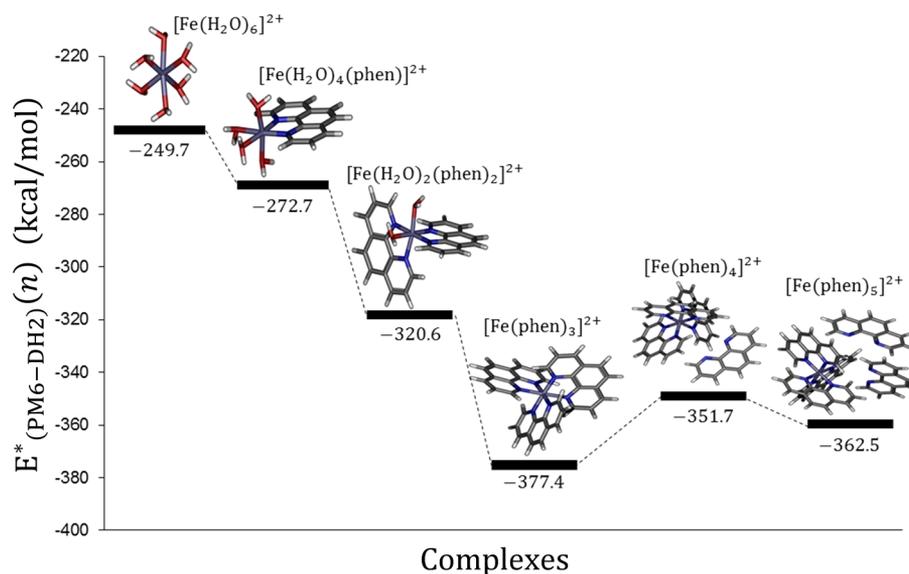
Figure 3. $E^*_{(PM6\text{-}DH2)}(n)$ in kcal/mol for the $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_4 (o\text{-phen})]^{2+}$, $[Fe(H_2O)_2(o\text{-phen})_2]^{2+}$, $[Fe(o\text{-phen})_3]^{2+}$, $[Fe(o\text{-phen})_4]^{2+}$, and $[Fe(o\text{-phen})_5]^{2+}$ complexes.

Employing this simple semiempirical method is enough for the purpose of identifying (more than quantifying) the stability of the complexes coupled to the determination of the correct/experimental number of o-phen ligands in the iron(II) complexation. The iron complex formed only with water was the most unstable among the studied complexes. The complex energies decreased when the water molecules changed from the o-phen molecules until reaching an energy minimum for $[Fe(o\text{-}phen)_3]^{2+}$ complex. The complexes with 4 and 5 o-phen molecules presented a higher energy value compared to $[Fe(o\text{-}phen)_3]^{2+}$ complex, confirming the experimental result with a stoichiometric ratio of 1:3. The chelation process takes place between iron atom and nitrogen atoms of o-phen molecules. Then, when we force the entrance of the fourth and the fifth ligand molecule, the attractive interaction between iron(II) atoms and these ligands is destabilized by the increment of the electron repulsion contribution. Therefore, after the complexation with three ligands (minimum obtained energy), the sequential addition of ligands provokes an increment in the total energy of the complex.

The values of the stability constant previously obtained by experimental techniques cannot be quantitatively compared with values obtained by semiempirical methods. In this case, we should perform frequency calculations for all systems used here by applying a more robust method, such as *ab initio*. However, in this way, the time taken for the calculations would be so long that it would be impossible to finish them in less than a few days in ordinary computers like the ones employed in the present study.

CONCLUSION

This simple, straightforward, inexpensive, and consistent experiment to measure the binding constant and stoichiometry ratio of the complexation of iron(II)−(1,10-phenanthroline) was developed to serve as an undergraduate laboratory project for the analytical chemistry and physical chemistry curriculum.

The time required for the whole experiment (reagents and solutions, reaction, image and spectra acquisition, molecular modeling, and treatment) is approximately 2.5 h, but can be easily expanded to 4 h if necessary. This simple experiment can

be used to explore the fundamental concepts of stoichiometry and stability constant and provides an excellent illustration of the relationship between RGB intensities from digital images and molecular modeling method as a laboratory experiment designed for analytical and physical chemistry courses. Here, the integration of Analytical and Physical Chemistry as a project-driven interdisciplinary approach was used to aid student understanding in an efficacious manner. This method using red color intensity can be used to study iron(II)−(1,10-phenanthroline) formation, and variations of this method using RGB intensities values could be used for characterizing other metal complexes. Students should work in small groups to ensure completion of the project in class, and cooperative learning is encouraged.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00112.

> Detailed student instructions, instructor notes, image acquisition and processing, R code, and program script (PDF, DOC)

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Notes

The authors declare no competing financial interest.

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