Spring 4-5-2021

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Protonation of Methyl Phenyl Porphyrin Isomers Using UV Spectroscopy

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Abstract

The protonation of methyl phenyl porphyrin isomers was studied through UV vis spectroscopy using trifluoroacetic acid (TFA), a strong organic acid. Protonation was achieved by titration of the porphyrin in toluene and toluene/methanol (90:10). A wavelength shift from the free base Soret to the protonated Soret confirms the formation of the dication. The resulting UV spectra was used to calculate an apparent pKa value of each free base porphyrin isomer. Addition of methanol to the porphyrin solution decreased the average pKa values of the Soret and Q-bands for each porphyrin. This could be an indication of a stabilizing monocation, not easily seen in solution.

Introduction

Porphyrins are macromolecules which are crucial to life due to its functions in oxygen transportation, the electron transport chain, and even in photosynthesis. Recently they have been studied extensively in order to use its properties for medical treatments such as photodynamic therapy, fluorescence imaging, and PET imaging.[1] The fundamental structure of porphyrins consists of four pyrrole rings connected by four methene bridges, and they can have different substituents which give them different properties and functions. When a porphyrin is at its neutral state (free base), of the four nitrogens in the core of the molecule, two of the nitrogens each have a hydrogen atom bonded to it while the other two nitrogens do not. When porphyrins are titrated using an acid, the nitrogens which do not have any hydrogens are able to pick up the hydrogens (supplied by the dissociation of the acid) to be able to form either the monocation or the dication.[3,4] A monocation would form if three of the four nitrogens are bonded to hydrogens, while the dication would form if all four of the nitrogens are bonded to hydrogens as seen in **Figure 1.**

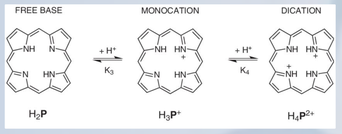

Figure 1: The figure above shows the protonation diagram of free base to dication upon protonation of the nitrogen in the pyrrole ring.

In this study, the basicity of three isomer porphyrins were studied by analyzing the titrations of the porphyrins using trifluoroacetic acid (TFA) and calculating the pKa for each titration. The isomers used were Meso tetra 2-methyl phenyl porphyrin (2M), Meso tetra 3-methyl phenyl porphyrin (3M), and Meso Tetra 4-methyl phenyl porphyrin (4M) which only differ in the location of attachment of the methyl group on the phenyl substituent. The monocation is very difficult to stabilize and this study also compared two different solvents in the attempt to stabilize the monocation. Methanol has been found to help stabilize the monocation through hydrogen bonding with an N−H group in the porphyrin. Thus the first solvent was toluene and the second solvent was a 90% toluene and 10% methanol.

Materials/Methods

Porphyrin solutions for each isomer (2M, 3M, 4M) were prepared so that the molarities were about 5×10^{-6} M. Two different solvents were used which were toluene and a solvent system consisting of 90% toluene and 10% methanol. This yielded a total of 6 solutions (porphyrin isomers in toluene (3) and porphyrin isomers in 90% toluene and 10% methanol (3)). Each of the solutions were titrated using TFA and the changes in the absorbance were recorded using a UV-VIS spectrometer (UV-2600, Shimadzu, Kyoto, Japan) which measured the UV absorbance between 350 and 800 nm, with a 0.5-nm resolution. The pKas were experimentally determined from the UV spectra. For each of the 6 solutions, two spectra were taken and the average of the experimentally determined pKas were taken. To determine the pKa values, two methods were used. In method 1, a plot of *log(A-Af/A0-A)* versus the negative logarithm of the acid gave rise to trendlines for each of the Q-bands and shifted Sorets. The equation of the trendline represented the following equation *log(A-Af/A0-A)=-pKa-log[acid],* which was derived by the definition of the Ka value and [free base]/[protonated porphyrin]. The pKa value is derived by finding the x-intercept of this plot.[5] In method 2, a plot of the negative logarithm of the acid versus the absorbance of the free base and protonated Soret was plotted. Using both trendlines, the y-intercept of the free base was subtracted by the y-intercept of the protonated porphyrin. This value was divided by the slope of the protonated porphyrin subtracted by the free base porphyrin. This produced the pKa value for method 2. Both pKa values were averaged and used in analysis.

Data & Results

meso-Tetra(2-methylphenyl) porphyrin

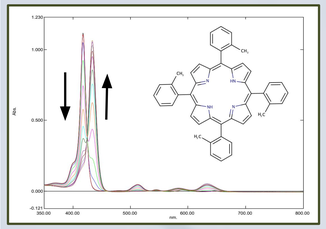

Figure 2: Trial 1 UV spectra of titration of 2-methylphenyl in toluene using 0.13M TFA

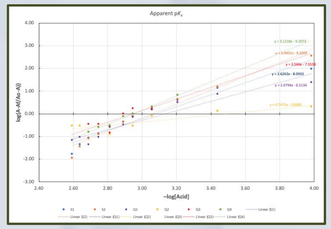

Figure 3: Trial 1 plot of *log(A-Af/A0-A)* vs. *-log[acid]* for the sorets and Q-bands of 2-methylphenyl in toluene solvent

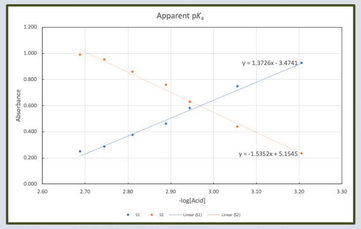

Figure 4: Trial 1 plot of *absorbance* vs. *-log[acid]* represented by the free base soret and the dication soret demonstrates the pKa for 2-methylphenyl in toluene

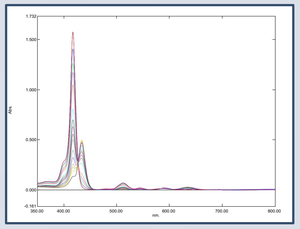

Figure 5: Trial 1 UV spectra of titration of 2-methylphenyl in toluene/methanol (90:10) using 0.13M TFA

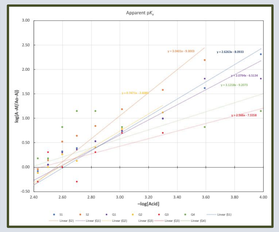

Figure 6: Trial 1 plot of *log(A-Af/A0-A)* vs. *-log[acid]* for the sorets and Q-bands of 2-methylphenyl in toluene/methanol solvent

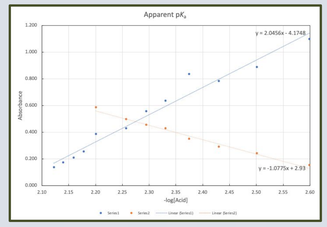

Figure 7: Trial 1 plot of *absorbance* vs. *-log[acid]* represented by the free base soret and the dication soret demonstrates the pKa for 2-methylphenyl in toluene/methanol

meso-Tetra(3-methylphenyl) porphyrin

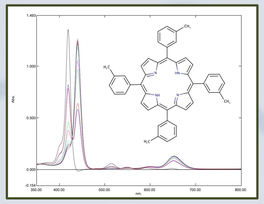

Figure 8: Trial 2 UV spectra of titration of 3-methylphenyl in toluene using 0.13M TFA

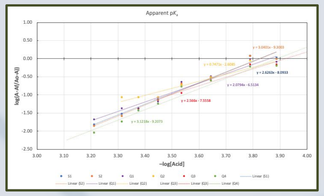

Figure 9: Trial 1 plot of *log(A-Af/A0-A)* vs. *-log[acid]* for the sorets and Q-bands of 3-methylphenyl in toluene solvent

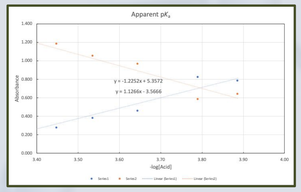

Figure 10: Trial 1 plot of *absorbance* vs. *-log[acid]* represented by the free base soret and the dication soret demonstrates the pKa for 3-methylphenyl in toluene

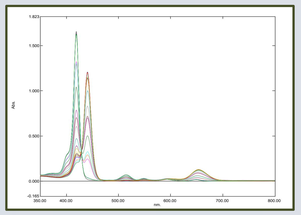

Figure 11: Trial 2 UV spectra of titration of 3-methylphenyl in toluene/methanol (90:10) using 0.13M TFA

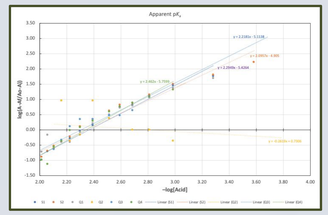

Figure 12: Trial 1 plot of *log(A-Af/A0-A)* vs. *-log[acid]* for the sorets and Q-bands of 3-methylphenyl in toluene/methanol solvent

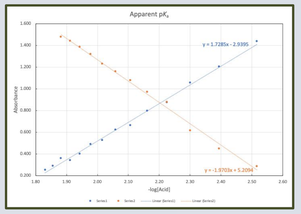

Figure 13: Trial 2 plot of *absorbance* vs. *-log[acid]* represented by the free base soret and the dication soret demonstrates the pKa for 3-methylphenyl in toluene/methanol

meso-Tetra(4-methylphenyl) porphyrin

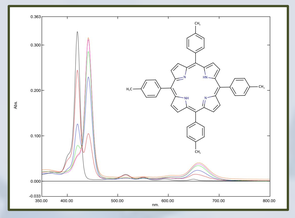

Figure 13: Trial 1 UV spectra of titration of 4-methylphenyl in toluene using 0.13M TFA

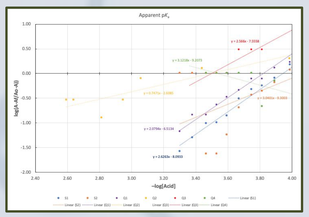

Figure 14: Trial 1 plot of *log(A-Af/A0-A)* vs. *-log[acid]* for the sorets and Q-bands of 4-methylphenyl in toluene solvent

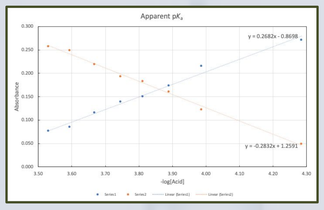

Figure 15: Trial 1 plot of *absorbance* vs. *-log[acid]* represented by the free base soret and the dication soret demonstrates the pKa for 4-methylphenyl in toluene

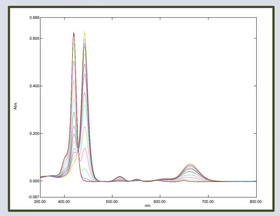

Figure 16: Trial 2 UV spectra of titration of 4-methylphenyl in toluene/methanol (90:10) using 0.13M TFA (above)

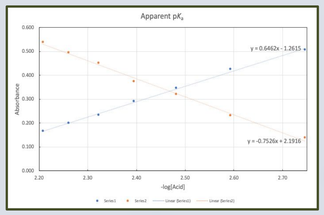

Figure 17: Trial 1 plot of *log(A-Af/A0-A)* vs. *-log[acid]* for the sorets and Q-bands of 4-methylphenyl in toluene/methanol solvent

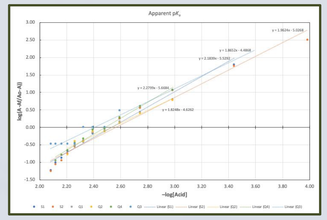

Figure 18: Trial 1 plot of *absorbance* vs. *-log[acid]* represented by the free base soret and the dication soret demonstrates the pKa for 4-methylphenyl in toluene/methanol

Conclusion

The substitution of a methyl group on various positions on the phenyl ring of the porphyrin demonstrated a varying pKa values based on substitution (Thomas et al., 2018). When looking at the 2-Methyl substitution, the associated pKa value was 2.99. The 3-Methyl substituted porphyrin demonstrated a pKa value of 3.87. Additionally, the 4-Methyl porphyrin demonstrated a pKa value of 3.74. Therefore, the substitution of a methyl group in various locations of the porphyrin with the addition of methanol demonstrated a gradual change in pKa values. This is shown as the meta and para substituted porphyrins was more basic as opposed to the ortho substituted porphyrin. (Hambright et al., 2003) The value associated with 2-Methyl porphyrin with methanol was a pKa of 2.41, the value associated with 3-Methyl porphyrin with methanol was a pKa of 2.32, and the value associated with 4-Methyl porphyrin with methanol was a pKa of 2.48. The porphyrin in the methanol solution experienced a different effect as the ortho and para substituted porphyrins demonstrated a minor increase in acidity as opposed to the meta substituted porphyrin. However, the pKa values were very similar, suggesting that the general trend of pKa values and substitution on the phenyl ring is maintained with the addition of methanol to the solvent system. When comparing each substituted porphyrin with its counterpart in a methanol solution, a change in pKa values was shown. It was concluded from the UV spectra data that the pKa values decreased drastically with the addition of methanol to the solvent for each porphyrin (2-Methyl versus 2-Methyl in methanol).

Table 1: pKa Values of Porphyrins

		Trial 1			Trial 2			Both
Phenyl Ring Substituent	Solvent System	Method 1	Method 2	Average	Method 1	Method 2	Average	Averages
2-Methyl	Toluene	3.11	2.97	3.04	2.99	2.88	2.94	2.99
	90% Toluene, 10% Methanol	2.54	2.27	2.41	2.59	2.23	2.41	2.41
3-Methyl	Toluene	3.73	3.88	3.81	3.97	3.89	3.93	3.87
	90% Toluene, 10% Methanol	2.41	2.20	2.31	2.43	2.21	2.32	2.32
4-Methyl	Toluene	3.99	3.25	3.62	3.85	3.86	3.86	3.74
	90% Toluene, 10% Methanol	2.54	2.47	2.51	2.47	2.42	2.45	2.48

References

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