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Molecular Recognition of PET Depolymerization Products and Beta-Cyclodextrin

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Executive Summary

Background: Consumption of plastic goods has increased year over year improving the quality of life for consumers due to the low cost, improved physical properties and convenience relative to alternatives. As the production of these products continues to increase methods for recycling these materials are also in need. Polyethylene terephthalate (PET) is among the largest produced polymers in the world. It is commonly used in plastic bottles, textiles, and high strength fibers. When it comes to the classification of PET there is bottle-grade and fiber-grade. A main difference in the two polymers is that bottle-grade PET adds approximately 2 mol% isophthalate which results in a less crystalline structure. A problem in the recycling of bottle-grade PET is when recycled due to the isophthalate and contaminants the recycled material loses physical properties and can only be made into products with the same or lower mechanical strength. The reason for this is that it is very difficult to separate out the terephthalate and isophthalate monomers due to the similarity in reactivity and structure. The research provided in this report is a small part of solving the problem of how to separate the two monomers in an attempt to recycle bottle-grade PET into a higher value material.

Results: One potential method of separating the two monomers found in depolymerized bottle-grade PET is the use of host-guest chemistry or commonly referred to as molecular recognition. In order to assess the viability of the method a first step is to determine the binding constant of the depolymerization products and a host molecule. The first system researched in this report is that of dimethyl terephthalate (DMT) and beta-cyclodextrin (β-CD). This system is based on the terephthalate product from the methanolysis depolymerization of PET. The hypothesis of the experiment was that if the binding constants of the two depolymerization products varied wide enough than the molecular recognition of the system could be used to remove one product from

the other. The experiment used to determine the binding constants of the two systems was a titration experiment using a range of host to guest ratios keeping the guest concentration constant. Due to the fluorescent nature of the molecules being used the range of titration solutions was analyzed a Cary Eclipse Fluorescence Spectrophotometer and a nonlinear regression was used to determine a binding constant, K_a, for each system. For the DMT and β-CD system a range of host to guest concentrations of 0:1 to 125:1, the exact concentrations found in **Table 1**, fluorescence intensity was measured. Using the difference in fluorescence and the initial guest and host concentrations a nonlinear regression was used to determine a K_a value of 863.6 Mol^{-1}. The fit of the observed data in comparison to the calculated data is found in **Figure 4.**

Conclusions: Based on the literature value and the binding constant determined in this experiment, it can be concluded that the fluorescence method is valid for determining K_a for this system and that the K_a value determined in this experiment is within acceptable range of the literature value. A large portion of the time used to determine the binding constant was also used to determine the best method to do such. UV-Vis spectroscopy and NMR shift were two additional methods used to determine the binding constant for the system. It was concluded that the changes seen in absorbance and chemical shift were not large enough to derive an accurate binding constant. An example of this can be seen in **Figure 6.**

Takeaways: This research has had many positive benefits for my knowledge and understanding of polymer chemistry. Although changes in UV-vis absorbance and NMR chemical shift proved to not be viable methods for the researched host-guest systems I was able to gain an understanding of the equipment and procedures for how to analyze the data given. I also have much more experience in polymer chemistry reactions as I was able to partake in some

depolymerization reactions and partial repolymerizations. The knowledge I gained in organic chemistry class four years ago was reinvigorated and used for practical purposes. I gained a sense of confidence and understanding as it pertains to polymer chemistry.

Future Work: The resulting data shows that there is a viable method that can be reproduced with other systems involved in the depolymerization of PET. If there is a series of systems that have a large enough difference in binding constant there is a possibility that chemical recycling of PET can be done economically and used to upcycle the raw materials found in bottle-grade PET products. The future work involved is to use measurements in fluorescence intensity with the other depolymerization products and different cyclodextrin molecules to determine the most viable set of systems to do a larger scale experiment on. Given there is a system of depolymerization products and cyclodextrin, my recommendation is to do a full scale depolymerization of a plastic bottle and then a separation using the host-guest system. For other students working on this project, keep a positive mindset, experiments don't always pan out as expected for the first attempt, and work with the intent to make a positive impact on the world.

Introduction

Plastics have changed the way we live, for the better, as continued research has made producing cheap, effective materials easier and more economic. This increase in production of plastics, specifically plastics used for a short period of time, single-use plastics, has created an environmental problem. The reason plastics are so good at their functions of being strong, and durable is the same reason why they can take hundreds of years to decompose in landfills. Plastic bottles made of polyethylene terephthalate (PET) can take up to 450 years to decompose in landfills according to the US National Park Service[1]. While recycling is the best way to reduce the environmental impact, using raw materials is cheaper and often results in superior products. As we continue to use plastic products determining new ways to reuse the material will be essential to sustainability and reducing the environmental impact.

For this project the research was done on one of the most produced polymers in today's world, PET. PET is produced in different grades for different applications. Bottle grade PET needs to have clear optical properties and have a low intrinsic viscosity for the stretch blow molding process[2]. Accordingly, the material is produced with a small amount, ~ 2 mol%, of isophthalate comonomer. This breaks up crystallinity and gives the material its desired properties at the expense of unnecessary mechanical strength[2]. Fiber grade PET, on the other hand, needs a high degree of mechanical strength[2]. This grade of material is produced without any isophthalate comonomer. A problem in the recycling of bottle-grade PET is when recycled, due to the isophthalate and contaminants the recycled material loses physical properties and can only be made into products with the same or lower physical requirements. In order to utilize recycled bottles in the production of high strength PET fibers a method must be developed for removing

the isophthalate content from them. The research provided in this report is part of a broader effort to do just that.

The majority of plastic recycling takes place by mechanical processes – melting down the material and reprocessing it into new shapes. This is the easiest and often cheapest way of repurposing plastic waste, but it does not allow for an opportunity to remove problematic impurities. Chemical recycling is an alternative strategy wherein polymers are depolymerized down to their monomers and then repolymerized back to high quality material. This process has been heavily reported in the literature. Under the appropriate conditions, treating bottle grade PET with methanol will result in the formation of dimethyl terephthalate (DMT), dimethylisophthalate (DMI) and ethylene glycol. Once broken down into this mixture, an opportunity arises for removing the isophthalate component.

In this research a method of separation using host-guest chemistry was analyzed. The objective of the research contained in this report is to identify binding constants for the depolymerization products of bottle grade polyethylene terephthalate (PET) and cyclodextrin molecules. To separate the two monomers that make up bottle grade PET, terephthalates and isophthalates, given their similar reactivity and structure, the shape of the molecules was researched. The process that was researched is commonly known as molecular recognition which is a host-guest system. A host-guest system is where one molecule in a solution acts as a host to another molecule in the solution and these molecules complex noncovalently using other forces. The system researched in this paper is that of DMT and β-CD. This research has attempted to add to the scientific understanding of host-guest relationships between systems of molecules involved in the depolymerization of bottle grade PET. The problem being addressed is there is not an easy way to separate out the comonomers due to the similarity in physical and reactive

properties. This approach is instead based on the shapes of the molecules. In order to test these systems, it was necessary to determine the binding constants for each system. Much of the research was dedicated to determining a proper method to obtain these binding constants.

Background

Since 1970 cyclodextrin molecules have been used in host-guest complexations due to their slightly apolar cavity which favors organic molecules compared to the water molecules in an aqueous solution[3]. There are three cyclodextrin molecules that pertain to this research and those are α, β, and γ derivatives. Due to the cyclical nature of these molecules, they perform as a great host for organic molecule guests and is why they were chosen as the hosts in this series of experiments[3].

The guest molecules used in these experiments are the different depolymerization products of bottle grade PET. There are three well known methods for the depolymerization of bottle grade PET. These methods are hydrolysis, methanolysis and glycolysis. These depolymerization techniques result in different depolymerization products. Hydrolysis results in terephthalic acid and isophthalic acid, while methanolysis results in dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI), and glycolysis results in Bis(2-Hydroxyethyl) terephthalate (BHET) and the isophthalate isomer (BHEI)[2,4]. The depolymerization techniques were not the main focus of this research and were mentioned in order to show these depolymerization products are common in chemical recycling processes.
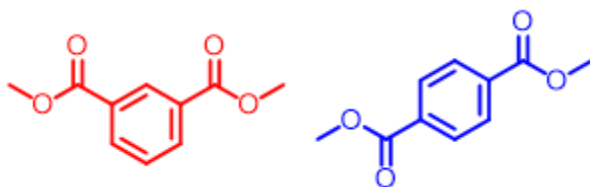
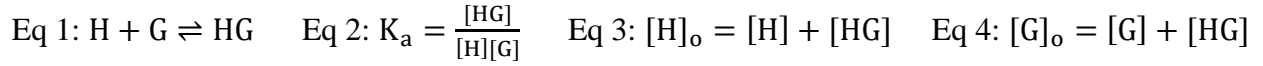**Figure 1**: Chemical structures for DMT and DMI.
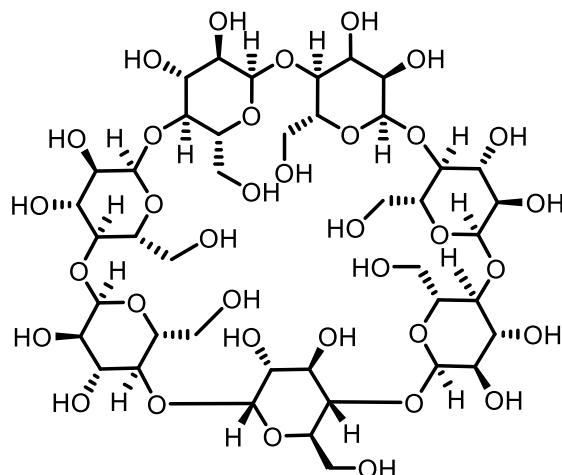
Figure 2: Chemical structure for β-CD.

As host-guest chemistry has become more prevalent methods for determining the binding constants are required. A detailed tutorial on the basics of non-linear regression for host-guest systems responding to a change in physical property was used as a basis for the calculations[5]. The detailed tutorial outlines the mathematical approach to using a nonlinear regression to solve for the binding constant, K_a[5]. Using a series of solutions with varying host to guest concentration ratio an observed change in the physical parameter can be used to regress a K_a for the series of solutions.

Three physical parameters were measured during the course of the research. Ultraviolet-visible spectroscopy (UV-Vis) is used to measure the absorbance of a molecule that is UV active[5]. It is necessary for there to be a significant change in UV-Vis spectra in order to get an accurate binding constant. UV-Vis is also very susceptible to temperature and presence of impurities[5]. NMR shift is used to measure the chemical shift in NMR spectra[5]. This method of titration experiment is the most commonly used method and can give information on the stoichiometry of the host and guest[5]. Fluorescence is used to measure the fluorescence intensity of the molecules that have fluorophores[6].

In Thordarson's previous work, he outlines the mathematics behind the nonlinear regression technique for a 1:1 host to guest system. It begins with the equilibrium equations for a host-guest complex system.

$$\text{Eq 1: } H + G \rightleftharpoons HG \quad \text{Eq 2: } K_a = \frac{[HG]}{[H][G]} \quad \text{Eq 3: } [H]_o = [H] + [HG] \quad \text{Eq 4: } [G]_o = [G] + [HG]$$

K_a is defined as the binding constant. [HG], [H], and [G] are defined as the host-guest concentration, the host concentration and the guest concentration, respectively. $[H]_o$ and $[G]_o$ are the initial concentration of the host and the initial concentration of the guest, respectively[5]. By substitution and rearranging equations 1-4 one can solve for the concentration of the host-guest complex using the initial concentration of the host, the initial concentration of the guest and K_a. The equation for the host-guest complex concentration is as follows[5].

$$\text{Eq 5: } [HG] = \frac{1}{2}\left\{\left([G]_o + [H]_o + \frac{1}{K_a}\right) - \sqrt{\left([G]_o + [H]_o + \frac{1}{K_a}\right)^2 - 4[H]_o[G]_o}\right\}$$

In applying this to a fluorescence experiment it is important to define what fluorescence is. The Beers Law for Fluorescence is $F = I_o\Phi\varepsilon b[x] = k_x[x]$, with F as fluorescence intensity, I_o defined as intensity of excitation light, Φ defined as the quantum yield, ε defined as molar absorptivity, b defined as path length, [x] defined as the concentration of the fluorescent species and $k_x = I_o\Phi\varepsilon b$. Assuming the host species is non-fluorescent, and the concentration of the guest is kept constant the equation for change in fluorescence intensity can be written as:

$$\text{Eq 6: } \Delta F = \Delta k[HG] \quad \text{Where } \Delta k = k_{HG} - k_G$$

$$\text{Eq 7: } \Delta F = \frac{1}{2}\Delta k\left\{\left([G]_o + [H]_o + \frac{1}{K_a}\right) - \sqrt{\left([G]_o + [H]_o + \frac{1}{K_a}\right)^2 - 4[H]_o[G]_o}\right\}$$

The final equation for ΔF is a function of $[H]_o$, $[G]_o$, Δk and K_a and using the observed fluorescence data a fit for Δk and K_a is done in a nonlinear regression[5].

In previous work by Marino and Mendicuti, fluorescence experiments were used to determine the binding constants and other thermodynamic information of the DMT and β-CD system and the DMI and β-CD system[6]. In addition, they did some analyses with dimethyl phthalate (DMP) and the cyclodextrin molecules[6]. In their experiment they held their guest species, DMT, DMI or DMP, concentration constant and increased the host concentration per solution[6]. In their results for the DMT and β-CD system they concluded a K_a of 923 ± 30 M^{-1} at 25 °C[6]. In their results for the DMI and β-CD system they concluded a K_a of 343 ± 36 M^{-1} at 25 °C[6]. Their procedure was used as a reference when running similar experiments.
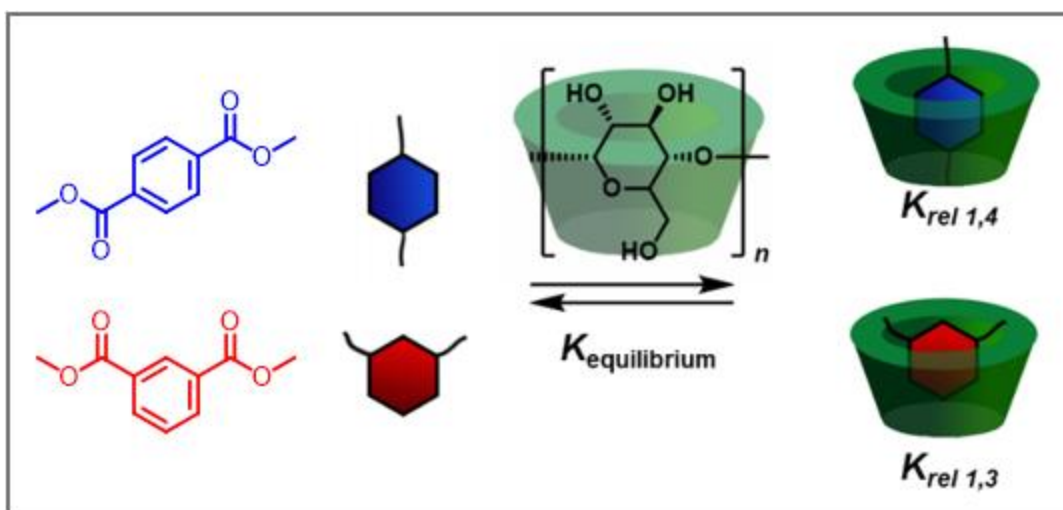
Figure 3: Host-Guest equilibrium reactions for DMT and DMI with a cyclodextrin species.

Experimental Methods

The materials used in these experiments were Acros Organics β-CD, Acros Organics DMT recrystallized in dichloromethane and ultra-pure water. Solutions were made using volumetric flasks. A 1 L stock solution of 0.1 mM DMT was made by measuring out recrystallized DMT filling the volumetric flask three fourths full, adding a stir bar, and used heat and mixing to get to dissolve in the ultra-pure water. Once fully dissolved solution was fully

cooled before filling to the line. β-CD was weighed and measured per the concentration wanted

and added to a 50 mL volumetric flask. The DMT stock solution was used to fill to the line for

each solution.

Using an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer, the

fluorescence intensity was measured for each sample. These values were then used in the

quantitative analysis. The measurements were taken at room temperature, 20 °C.

Two alternative methods were used in the research of the β-CD and DMT system. UV-

Vis measurements were done with the same samples as described above using an Agilent

Technologies Cary 60 UV-Vis. NMR samples were made using deuterium oxide (D_2O) and

measurements were done on a 500 MHz NMR system.

Data and Results

Table 1: The sample concentrations for the DMT and β-CD fluorescence experiment used to determine the binding constant for the system. Guest concentration being that of DMT and host concentration being that of β-CD.

| Sample	[G]o (M)	[H]o (M)	[H]o/[G]o
TDP-1-16-A1	1.00E-04	0.00E+00	0.00
TDP-1-16-A2	1.00E-04	5.08E-04	5.08
TDP-1-16-A3	1.00E-04	1.01E-03	10.10
TDP-1-16-A4	1.00E-04	2.00E-03	20.02
TDP-1-16-A5	1.00E-04	3.50E-03	34.96
TDP-1-16-A6	1.00E-04	4.93E-03	49.25
TDP-1-16-A7	1.00E-04	7.11E-03	71.12
TDP-1-16-A8	1.00E-04	8.10E-03	81.03
TDP-1-16-A9	1.00E-04	1.02E-02	101.91
TDP-1-16-A10	1.00E-04	1.24E-02	124.38
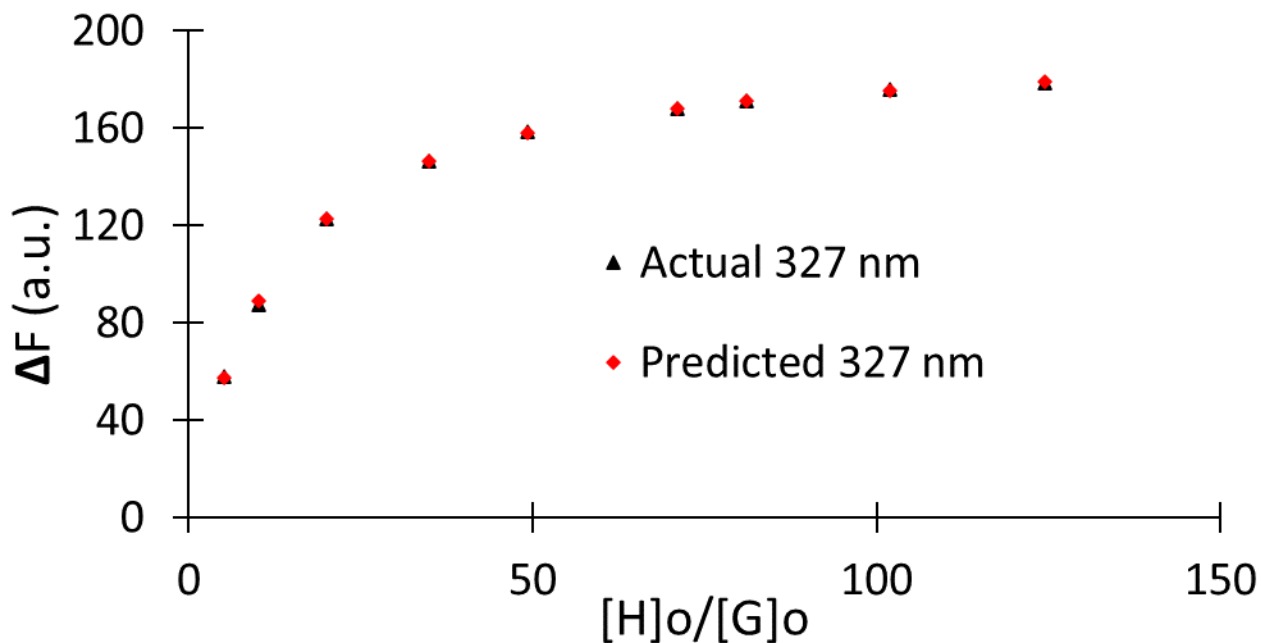
Figure 4: Comparison between the observed and calculated changes in fluorescence intensity for the DMT and β-CD system. Guest concentration being that of DMT and host concentration being that of β-CD.
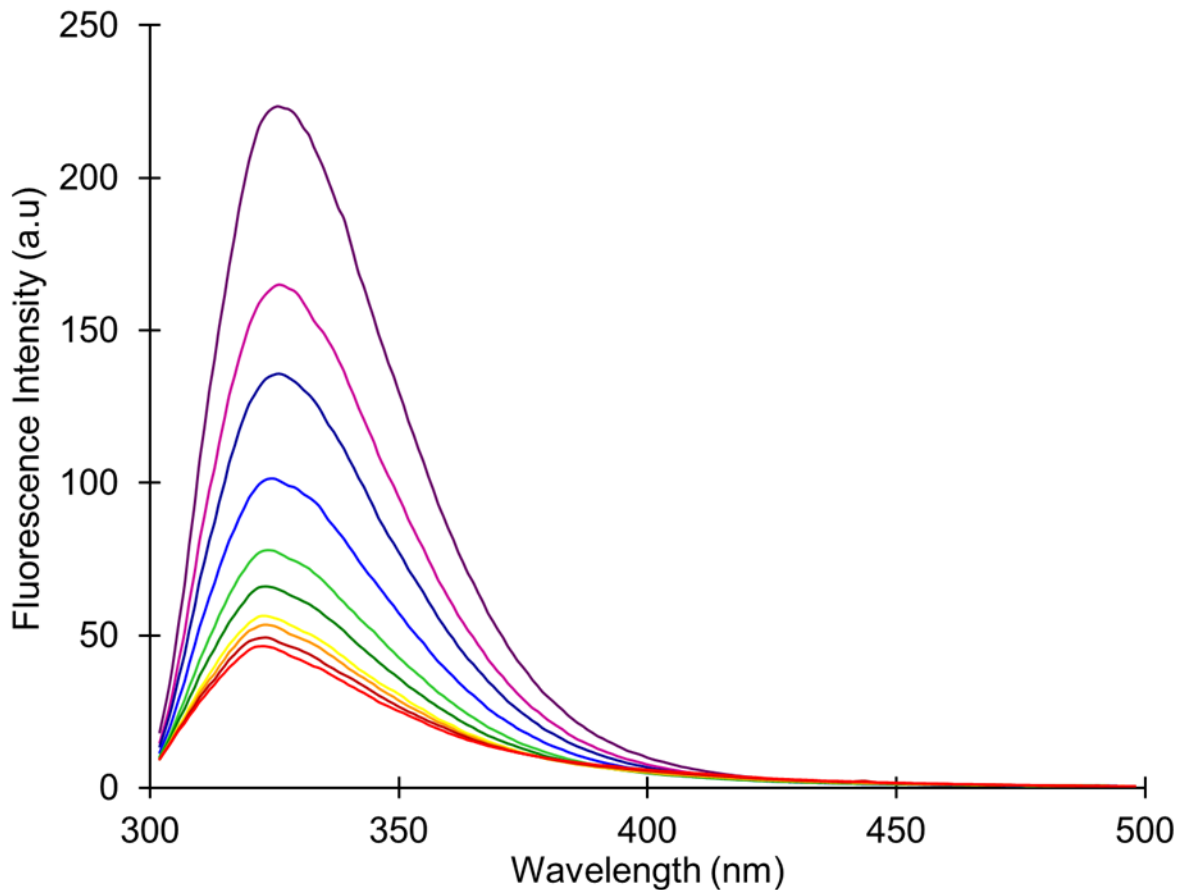
Figure 5: Fluorescence Spectra for the DMT and β-CD system. As the peak reduces in fluorescence Intensity the host-guest ratio increases.

	K_a (M^{-1})		863.6		
	Δk		1958480		
Sample	**F (a.u.) @ 327 nm**	**ΔF actual**	**ΔF predicted**	**SR^2**	**SSR**
TDP-1-16-A1	222.794				4.141878
TDP-1-16-A2	164.658	58.1	57.2	0.790	
TDP-1-16-A3	135.336	87.5	89.0	2.341	
TDP-1-16-A4	99.852	122.9	122.6	0.100	
TDP-1-16-A5	76.046	146.7	146.3	0.179	
TDP-1-16-A6	64.204	158.6	158.1	0.274	
TDP-1-16-A7	54.627	168.2	168.1	0.001	
TDP-1-16-A8	51.686	171.1	171.1	0.000	
TDP-1-16-A9	46.980	175.8	175.7	0.012	
TDP-1-16-A10	44.406	178.4	179.1	0.444	

Table 2: Measurements for the DMT and β-CD system. The samples measured fluorescence intensity, the observed and calculated change, by minimizing the sum of the squared residuals the corresponding binding constant K_a was determined to be 863.6 M^{-1}.
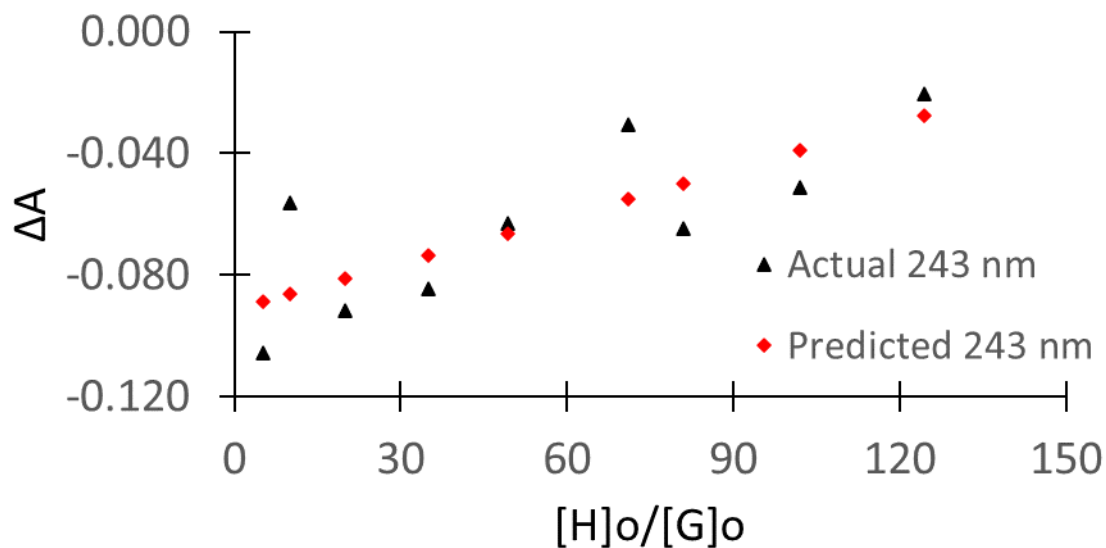
Figure 6: UV-Vis comparison between actual and predicted ΔA at 243 nm for the β-CD and DMT system.

Discussion and Analysis

      To determine the binding constants between cyclodextrin and PET depolymerization products a titration experiment was run where the guest concentration was held constant and increasing amounts of host molecule were added. The specific concentration range per experiment changed over the course of the research but the method behind making the solutions remained the same. A stock solution of the both the host and the guest was made in ultra-pure water. These stock solutions were then used to create the diluted solutions based on the required concentration range. The final solutions were a mixture of a depolymerization product (guest), whose concentration remained constant and a cyclodextrin molecule (host) which increased in concentration. When a group of solutions were made three different quantitative analysis methods were used to determine the binding constant. Given the amount of time available and due to unforeseen complications with two of the experimental methods only one of the various

systems was analyzed. The system analyzed in this research is β-CD as the host species and DMT as the guest species.

The method that was used was fluorescence and the basis for the experiment was found in the literature. A series of solutions were made with a constant guest concentration and a range of host to guest concentrations from 0:1 to 125:1. The exact concentrations and ratios can be found in **Table 1.** Fluorescence Intensity was measured for each sample and the observed spectra are found in **Figure 5.** As seen in **Figure 5** the more host added to a solution decreased the fluorescence intensity. This is as expected as the host species, β-CD, is not fluorescent and as more complexation between the host and guest species occurs the lower the fluorescence intensity. The fluorescence intensity data was taken at 327 nm. Using the fluorescence intensity at 327 nm, ΔF actual was calculated. Using Eq 7, $[H]_o$, $[G]_o$, and a guess value for Δk and K_a, ΔF predicted was calculated. By method of minimizing the sum of the squared residual, a nonlinear regression, a best fit Δk and K_a were determined for the system. A visual comparison of the ΔF actual plotted alongside the ΔF predicted is shown in **Figure 4.** The K_a for the β-CD and DMT system was determined to be 863.6 M^{-1}. **Table 2** shows the samples fluorescence intensity at 327 nm alongside the ΔF actual and the ΔF predicted and the resulting K_a for the system.

The literature value for the β-CD and DMT system is a K_a of 923 ± 30 M^{-1} at 25 °C. The K_a value determined from this experiment is 863.6 M^{-1} at 20 °C. Based on the literature value and the binding constant determined in this experiment, it can be concluded that the fluorescence method is valid for determining K_a for this system and that the K_a value determined in this experiment is within acceptable range.

Two other methods were attempted to determine the K_a value for the β-CD and DMT system. The first alternative method was UV-Vis. This method instead of measuring the fluorescence intensity, measured the absorbance (A). A similar derivation to that described in the background for fluorescence was done for UV-Vis. **Figure 6** shows the best fit for the actual ΔA plotted against the predicted ΔA. As seen in the figure an accurate fit could not be obtained. It was concluded that there was not a large enough change in the absorbance to determine a K_a for this system. The other method used was chemical shift in NMR. This method like UV-Vis was concluded to not have a large enough effect to determine a K_a for this system.

Next steps include determining a K_a for the other systems of inquiry, such as β-CD and DMI, β-CD and BHET, β-CD and BHEI, β-CD and terephthalic acid, β-CD and isophthalic acid, and the above systems with α-CD and γ-CD in place of β-CD. Further work would include determining what group of depolymerization products and what cyclodextrin species results in the greatest difference in K_a values. Using this information continued tests could be done to attempt to separate the terephthalate and isophthalate depolymerization products.

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