**Experiment #2, Absorption Spectrum of Conjugated Dyes**

*Reference: Experiments in Physical Chemistry, C. Garland, J. Nibler, and D. Shoemaker*

**Objectives:**

1. Relate the wavelength of the maximum absorbance in the visible region of the electromagnetic spectrum to the “length” of the carbon chain in a series of conjugated dyes.
2. Investigate how well the one-dimensional “particle-in-a-box quantum mechanical model predicts the length of the carbon chain in a series of conjugated dyes.

**Background:**

In this lab you will use UV-vis absorption spectroscopy to evaluate the length of several symmetric polymethine dyes using the simple particle in a box quantum mechanical model.

The visible bands for polymethine dyes arise from electronic transitions involving the *π* electrons along the polymethine chain. The wavelength of these bands depends on the gap between the highest occupied level to the lowest unoccupied level. Consider a dilute solution of 1,1’-diethyl-2,2’-carbocyanine iodide





The cation can “resonate” between the two limiting structures above, which really means that the wavefunction for the ion has equal contributions from both states. Thus all the bonds along this chain can be considered equivalent, with bond order 1.5 (similar to the C-C bonds in benzene). Each carbon atom in the chain and each nitrogen at the end is involved in bonding with three atoms by three localized bonds (the so-called *σ* bonds). The extra valence electrons on the carbon atoms in the chain and the three remaining electrons on the two nitrogens form a mobile cloud of *π* electrons along the chain (above and below the plain of the chain). We shall assume that the potential energy is constant along the chain and that it rises sharply to infinity at the ends; i.e., we can use an electron in a 1-D box model of length, *L*. The quantum mechanical solution for the energy levels of this model is

 (1)

where *h* is the Planck constant and *m* is the mass of an electron.

Since the Pauli exclusion principle limits the number of electrons in any give energy level to two (these two have opposite spins: +1/2, -1/2), the ground state of a molecule with *N* number of *π* electrons will have the *N*/2 lowest levels occupied (or filled, if *N* is even) and all higher energy levels empty. When the molecule (or ion in this case) absorbs light, this is associated with a one-electron jump from the highest occupied level (*n*1 = *N*/2) to the lowest unoccupied level (*n*2 = *N*/2+ 1). The energy change for this transition is

 (2)

Since Δ*E* = *hν* = *hc*/*λ*, where *c* is the speed of light and *λ* is the wavelength,

 (3)

Let us denote the number of carbon atoms in a polymethine chain by *p*; then *N* = *p* + 3. Kuhn1 assumed that *L* was the length of the chain between nitrogen atoms plus one bond distance on each side; thus *L* = (*p* +3)*l*, where *l* is the bond length between atoms along the chain. Therefore

 (4)

Putting *l* = 1.39 Å = 0.139 nm (the bond length in benzene, a molecule with similar bonding) and expressing *λ* in nanometers, we find

 (5)

If there are easily polarizable groups at the ends of the chain (such as benzene rings), the potential energy of the *π* electrons in the chain does not rise so sharply at the ends. In effect this lengthens the path *L*, and we can write

 (6)

where *α* should be a constant for a series of dyes of a given type. If such a series is studied experimentally, this empirical parameter *α* may be adjusted to achieve the best fit to the data; in any event, *α* should lie between 0 and 1.

**Procedure:**

1. Choose any one of the available dyes, and prepare 10 mL of a solution using methyl alcohol as the solvent. The concentration should be approximately 10-3 *M*.
2. Obtain the UV-vis spectrum of this initial solution. Taking absorbance readings at widely spaced intervals throughout the spectrophotometer range until the absorption peak is located.
3. Then take readings at much closer intervals throughout the peak.
4. Dilute the initial solution and re-determine the spectrum.
5. Repeat procedure until a spectrum is obtained with an absorbance reading of about 1 at the peak (transmittance ~0.1). The peak shape may change at high concentrations, since may dyes dimerize. At the final concentration used in this experiment, no dimer contribution is expected.
6. Prepare solutions of the other dyes at approximately the same molar concentration that gave the best results previously.
7. Obtain their spectra in the same way.

**Report:**

1. Plot Abs versus wavelength for the three dyes, making sure to label everything clearly. Determine *λ*max for each dye.
2. Using equation (3), calculate *L* for each dye.
3. Using equation (6), calculate *λ* for each compound and determine the best fit of parameter, *α*.
4. Report all experimental and theoretical data in a table summarizing the results.
5. The written report should include structures of the dyes used.