Absorption Spectrum of Conjugated Cyanine Dyes

Theoretical background: P.W. Atkins: *Physical Chemistry*, ch. 8,13 (10th edition)
Type of practice: individual.
Purpose of the experiment: Collection and interpretation of UV-vis spectra for different conjugated dyes based on the *particle in a one dimensional box quantum mechanical model*.

1 Introduction

The colour of many organic compounds is rooted in an electron-transfer process, that – at first approximation – is related to a small part of the molecule. Such molecular parts are called chromophores. The structure of the cyanine dyes investigated during the laboratory experiment is shown in the next figure (where x = 1, 2, 3):

In these dyes the conjugation of the electrons is between the nitrogen atoms. The benzene rings are not efficiently contributing the conjugation, as the non-bonding electrons of the heteroatoms in between are not in the same plane as the conjugated part of the molecule. Here the chomophore is the amidinium ion, that can be visualized with the following two resonance structures, showing the delocalization of the π-electrons:

The energy levels of the π electrons can be approximated with the 1 dimensional particle in a box quantum mechanical model. The model predicts the following energy levels for a 1 dimensional box with a length of L:

$$E = \frac{n^2 h^2}{8 m L^2}, \quad n = 1, 2, 3, \ldots, \tag{1}$$

Where n is the quantum number of the energy level, h is the Planck constant, m is the mass of the electron. According to the Pauli exclusion principle, any energy level can be only occupied by two electrons. For N electrons, this means that only the lowest $N/2$ energy levels are occupied in ground state. The lowest energy transition is therefore related to the process, when an electron is excited from the highest energy occupied level ($n_1 = N/2$) to the lowest energy empty level ($n_1 = N/2$). The energy required for the transition:

$$\Delta E = \frac{\left(n_2^2 - n_1^2\right) h^2}{8 m L^2} = \frac{(N+1) h^2}{8 m L^2}. \tag{2}$$

Based on equation (2), the length of the box can be calculated from ΔE. In case of the cyanine dyes, the structure (geometry) of the molecules is the same in the ground- and excited states. Therefore, the energy of the transition can be given with the wavelength at which the dyes shows maximum absorbance, as $\Delta E = h\nu = \frac{hc}{\lambda}$, where c is the speed of light in vacuum:

$$\lambda = \frac{(8mc/h) L^2}{(N+1)}. \tag{3}$$

Based on this equation, L can be calculated from a measured λ, or λ can be calculated from a known L.

2 Experimental

2.1 Preparations

If they are not available, prepare solutions of $4 \cdot 10^{-6}$ M from the diethyl-tia-cyanine dyes (including the unknown dye) by diluting the provided stock solutions. Use absolute ethanol as solvent. Special care should be taken for the followings:

- Cyanine dyes precipitate when low amount (a few tenths of a percentage) water is present. The water content should therefore be minimized by using completely dry equipment and water-free solvent.
- *The absolute ethanol and the cyanine dyes are expensive chemicals, therefore the use of these should be minimized!* The volumetric flasks should only be rinsed 2-3 times with $1-2$ cm^3 absolute ethanol! Use an automatic pipette (with a dry tip) for transferring the dye stock solution in the volumetric flask.
- To avoid cross-contamination, separate pipette tips must be used for the different dye solutions!

2.2 Experimental steps

Record the visible absorption spectra of the three diethyl-tia-cyanine dyes and the unknown dye in the 340 – 870 nm wavelength range, using a cuvette of 1 cm long light path. Pay attention to the followings during the measurements:

- The cuvettes should be rinsed 3 times with the solution to be measured, using $1-1$ cm^3 aliquots. The cuvettes should be filled up to their 2/3 height for the measurements, and a lid should be placed on them (to avoid the concentration change caused by the evaporation of the ethanol solvent).
- The spectrophotometer is equipped with a UV and a visible light source of which only the latter will be used during the experiments. This should be turned on at least 15 minutes before the first measurement.
- The absorbance spectra should be recorded with 2 nm resolution in the wavelength range of 340 – 390 nm, and with with 10 nm resolution between 390 – 870 nm. The measurements should be repeated with 2 nm resolution in the ± 10 nm vicinity o the absorbance maximums .
- The absorbance of regular cuvettes can differ notably in the 340 – 500 nm wavelength range. In case of using multiple cuvettes during the experiment, the difference between these should be measured, "cuvette correction" should be applied in the wavelength range of the experiments:

  1. Fill all of the used cuvettes with absolute ethanol. Using one of these as reference (absorbance background), measure the absorbance spectrum of all the other cuvettes with respect of this.
  2. Subtract the measured absorbance spectra from those recorded for the dyes in the respective cuvette.

  Attention! The reference cuvette must be the same for every measurements! If multiple cuvettes are used during the experiments, the cuvette correction should be performed prior to recording the absorbance spectra of the dye solutions.

3 Evaluation of the measured data

- Plot the absorbance spectra (after cuvetter correction, if necessary) of all four dyes in one graph!
- Determine the wavelength of the absorbance maximums, and calculate the molar absorption coefficients (ε_{max}) from the Beer – Lambert law.

Table 1: Summary of the results.

x	λ_{max}(nm)	$\varepsilon_{max}(M^{-1}cm^{-1})$	N	L (nm)

- Determine the number of delocalized electrons (N) for the three known diethyl-tia-cyanine dyes from their molecular structure, and calculate L from equation (3). Summarize the results according to table 1.
- Plot the L – x function and estimate the C – C bond length from the slope of the fitted linear.
- Estimate the expected λ_{max} value for the unknown dye and compare it to the measured value. Calculate all other parameters and include these in table 1. The structure of the unknown dye is either one of the followings, or very similar to them:

- Calculate the wavelength of the second absorption peak for the diethyl-tia-tricarbocyanine (x = 3) dye, related to the excitation from the ground state to the 2nd lowest energy unoccupied energy level! Is there any visible sign of this transition on the recorded spectrum?
- Explain the origin of the "shoulders", visible on the high energy side of the absorption peaks!

Control questions

1. What is a chromophore?
2. Draw the structure of the chromophore of the dyes investigated during the experiment!
3. Give formula for the energy levels of the 1 dimensional particle in a box model!
4. Give the energy of the electron transition from the highest energy occupied level to the lowest energy unoccupied level (HOMO $\rightarrow$ LUMO) for a chromophore containing N conjugated π-electrons!
5. Give the energy of the electron transition from the highest energy occupied level to the **second** lowest energy unoccupied level (HOMO $\rightarrow$ LUMO) for a chromophore containing N conjugated π-electrons!
6. Give the formula for calculating the wavelength at the maximum absorbance for a chromophore containing N conjugated π-electrons!
7. What is the Beer – Lambert law?
8. How could you estimate the carbon – carbon bond length from the data measured during the experiment?
9. Why do we consider the conjugation of the π electrons continuous only between the nitrogen atoms in the studied cyanine dyes?