

# Aggregation in Dyes: A Spectrophotometric Study

Frank Walmsley

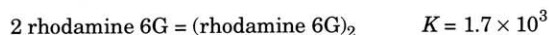
Trinity University, San Antonio, TX 78212

Dyes find applications in two important areas: coloration of materials such as fibers and in photochemical processes such as photography and dye lasers. In both of these areas, knowledge of aggregation equilibria is important. In dyes, the aggregation principally forms dimers except at high concentrations in solvents with a high dielectric constant. For coloration of materials, it is the monomer that is adsorbed onto the surface. There may be subsequent build up of dye units through aggregation but the initial layer must be composed of monomers. In dye lasers, the dimer constitutes an absorptive loss of pump power because the fluorescence of the dimer aggregates is quenched.

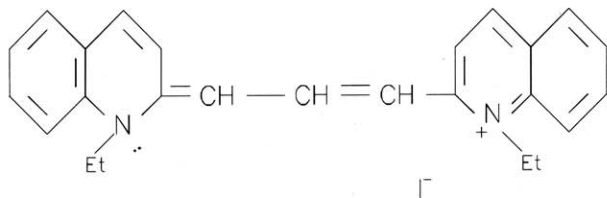
Self-aggregation is not a topic limited to dyes. Hydrogen bonding causes aggregation in carboxylic acids (1), lactams (2), and phosphinic acids (3) all of which form cyclic dimers. Hydrogen bonding and hydrophobic effects cause aggregation in biochemical materials such as dianionic guanosine 5'-monophosphate (4, 5). Both porphyrins and metalloporphyrins form dimers (6).

Aggregation has been studied by a variety of techniques including IR, UV-vis, and NMR spectroscopy and dielectric polarization. This experiment illustrates an important phenomenon in chemistry and biochemistry and how visible spectroscopy can be used in its study.

The monomer dye units are held together by dispersion forces to make a dimer with the planes of the molecules parallel. Coulombic forces counteract this attraction if the dye is charged but a solvent with a high dielectric constant, such as H<sub>2</sub>O, will lower this repulsion. It is thought that the dye units stack one on top of the other (7). In water, the monomer-dimer equilibrium lies well to the side of the dimer. For example, the equilibrium constant for rhodamine 6G in water at 22 °C is large (8).



To illustrate the study of self-aggregation, the dye pinacyanol iodide (1,1'-diethyl-2-2'-carbocyanine iodide) can be studied in water using visible spectroscopy.



The monomer absorbs at 600 nm and the dimer at 547 nm. The monomer band has a slight shoulder on the low wavelength side that is partially under the dimer band. This means the absorbance of the band at 547 nm is not an accurate measure of the dimer concentration although the error is smaller here than in most other dyes studied. In this case the absorbance of the band at 600 nm is a reasonable measure of the monomer concentration and a molar absorption coefficient at 600 nm has been reported as  $1.60 \times 10^5$  (9, 10). Larger aggregates reportedly exhibit a band at about 500 nm (11) at concentrations higher than those

used here. This dye is available in 97% purity from Aldrich Chemical Co. It is an irritant and is light sensitive. Due to its light sensitivity, it has been proposed for use in increasing photographic sensitivity (12) and as a saturable absorbing species in an azine dye tunable laser (13).

## Procedure

Prepare a stock solution by dissolving about 20 mg (weighed to 0.1 mg) in H<sub>2</sub>O using a 100-mL volumetric flask. Using a 10-mL pipet and a 25-mL volumetric flask, prepare five sequential dilutions so that, in the final solution, the strongest band will have an absorbance of about 0.1 in a 1 cm cell. Measure the visible absorption spectrum of each solution in a 1 cm cell from 750 to 350 nm, adjusting the absorbance scale on the print-out as necessary. To clean the glassware, rinse thoroughly with methanol to remove the dye which is adsorbed on the surface.

## Calculations

Calculate monomer concentration in each solution using Beer's law, absorbance at 600 nm and the molar absorption coefficient given above:

$$c_{\text{monomer}} = A_{\text{monomer}} / \epsilon_{\text{monomer}}$$

Calculate dimer concentration in each solution from the total and monomer concentrations:

$$c_{\text{dimer}} = (c_{\text{total}} - c_{\text{monomer}}) / 2$$

The equilibrium constant is calculated for each solution,

$$K = c_{\text{dimer}} / (c_{\text{monomer}})^2$$

and the values averaged. A typical value of  $K$  is  $2.0 \times 10^6$ .

Pinacyanol iodide is one of the dyes used in a physical chemistry experiment relating spectral band position with chain length in conjugated systems (14). This experiment could be done in conjunction with that or as part of another inorganic or instrumental analysis course, as appropriate. Extensions to this experiment could involve the study of temperature and of salt concentration effects (7).

## Litature Cited

1. Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974; pp 287-8.
2. Walmsley, J. A. *J. Phys. Chem.* **1978**, *82*, 2031.
3. Walmsley, J. A. *J. Phys. Chem.* **1984**, *88*, 1226.
4. Walmsley, J. A.; Barr, R. G.; Bouhoutsos-Brown, E.; Pinnavaia, T. J. *J. Phys. Chem.* **1984**, *88*, 2599.
5. Sagan, B. L.; Walmsley, J. A. *Biochem. Biophys. Res. Commun.* **1985**, *128*, 980.
6. White, W. I. In *The Porphyrins: Physical Chemistry Part C*; Dolphin, D. Ed.; Academic Press: New York, 1978; p 303.
7. Pal, M. K.; Pal, P. K. *J. Chem. Phys.* **1990**, *94*, 2557.
8. Selwyn, J. E.; Steinfeld, J. I. *J. Phys. Chem.* **1972**, *76*, 762.
9. Sheppard, S. E.; Geddes, A. L. *J. Am. Chem. Soc.* **1944**, *66*, 2003.
10. Thege, I. K.; Pungor, E. *Acta Chim. Acad. Sci. Hung.* **1961**, *27*, 417.
11. West, W.; Pearce, S. *J. Phys. Chem.* **1965**, *69*, 1894.
12. Tani, Tadaake. *J. Imaging Sci.* **1986**, *30*, 41.
13. Taylor, J. R. *Opt. Commun.* **1986**, *57*, 117.
14. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 5th ed.; McGraw Hill: New York, 1989; pp 440-5.