The Effects of Solvents on the Spectroscopy of Dyes

Mark F. Vitha, Samuel Nkruma-Agyeefi, Ryan Johnson, Sarah Wildgen, Carly Hurley, Rachel Barkley

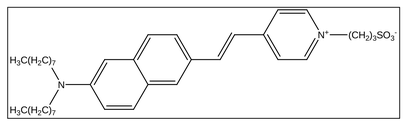
Department of Chemistry, College of Arts and Sciences, Drake University, Des Moines, IA

Abstract:

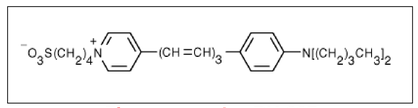
Linear solvation energy relationships (LSER) were used to quantify the intermolecular interactions between solvents and two organic dyes: di-8-ANEPPS and RH-237. LSERs evaluate the sensitivity of a dye 's wavelength of maximum absorbance or emission to solvent acidity (α), basicity (β), polarity/polarizability (π*), and excess polarizability (δ). The quantification of the sensitivity of a dye to these parameters (α, β, π*, and δ) allows for the characterization of the dye's ability to interact through dipole-dipole, dispersion, and hydrogen bonding interactions. To develop these relationships requires the use of UV-visible and fluorescent spectroscopy to measure the wavelength of maximum absorbance and emission of the dyes. The results of di-8-ANEPPS shows that solvent basicity, acidity, and polarity/polarizability affect the spectroscopy of the dye, meaning di-8-ANEPPS is polar and can accept and donate hydrogen bonds in solution. Similar results were found for RH-237. The results, however, are difficult to interpret because nonpolar solvents could not be incorporated in the LSERs due to solubility limitations. Work is currently in progress for Coumarin 30. The long-term goal of the research is to use the dyes to study surfactants to enable the best choice of surfactants to enhance the recovery of oil from reservoirs.

Introduction:

•Di-8-ANEPPS and RH-237 are fluorescent probes used to study micellar environments.
•Absorbance and emission spectra were used to study the dyes' interactions with solvents of varying polarities.



Fluorescent dye di-8-ANEPPS



Fluorescent dye RH-237

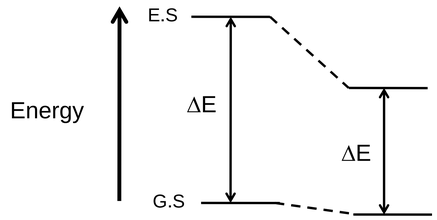
Kamlet and Taft: Linear Solvation Energy Relationships (LSERs):

$\nu_{max} = \nu_o + a\alpha + b\beta + s\pi^* + d\delta$

ν_{max}: the frequency of maximum of absorption or emission of light.
π^* : polarity/polarizability of the solvent.
α : acidity of the solvent.
β : basicity of the solvent.
δ: excess polarizability of the solvent

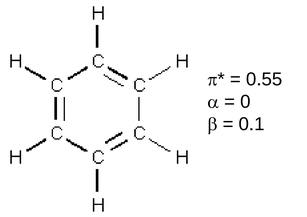
The coefficients s, a, b, and d measure the relative sensitivity of ν_{max} to the indicated solvent properties. Absorption spectroscopy yields ν_{max} values of each dye in solvents of varying polarity. Using linear regression analysis, the ν_{max} values were then related to the coefficients, providing information on the dye's polarity, and its ability to accept and donate hydrogen bonds.

Energy of Transition Diagram:



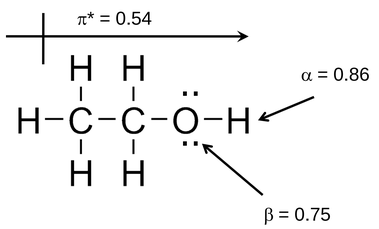
Energy of transition = Energy required to promote an electron from the ground state to the excited state

This energy diagram represents a theoretical interpretation of the excitation of a dye molecule in a nonpolar solvent and a polar solvent. The ground state and excited state energies of a dye are affected by the interactions it has with the surrounding solvent. Electrons in the dye molecule are promoted to higher energy orbitals when excited by light energy, changing the polarity of the dye molecule. In a nonpolar solvent, the dye's change in polarity doesn't affect the interactions with the solvent greatly, and thus does not stabilize the excited state to any great extent. However, in a polar solvent, the dye-solvent interactions increase, stabilizing the excited state. Consequently, dyes absorb higher wavelengths and less energy in more polar solvents.



Benzene

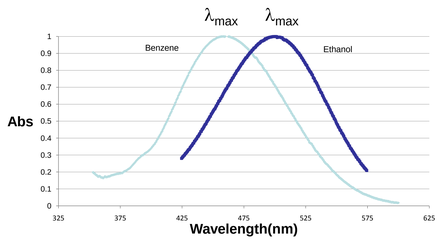
•Non polar aromatic solvent
•Cannot hydrogen bond donate or accept



Ethanol

•Polar solvent
•Able to donate and accept hydrogen bonds

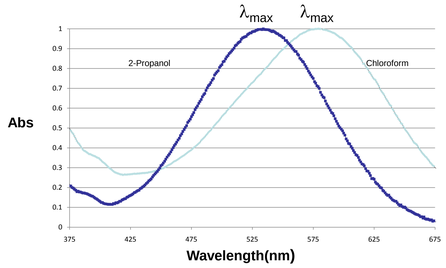
Example of di-8-ANEPPS Spectra



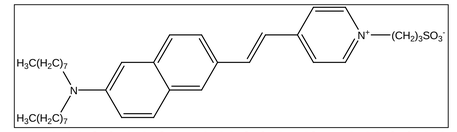
•**Ethanol peak** of maximum absorption appears at a higher wavelength
•ΔE=hc/λ - Wavelength is inversely proportional to energy
•Lower energy of transition means greater excited state interactions between dye and solvent
•**Benzene peak** of maximum absorbance appears at lower wavelength
•Higher energy of transition means little interaction between dye and solvent in the excited state.

Example of RH-237 Spectra

•2-Propanol peak of maximum absorption appears at lower wavelength than polarizable Chloroform.
•This shows that the polarizability plays a large role in the excited state stabilization of RH-237



Results for di-8-ANEPPS:



ν_{max}= -0.33 (+/- 0.31)π* - 0.62 (+/- 0.12)α - 0.09 (+/- 0.25)β

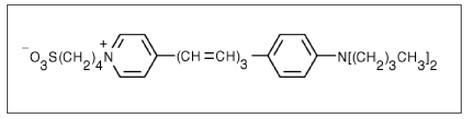
R = 0.80 S.E = 0.24 n = 20

•The polarizability/polarity coefficient's standard deviation prevents a definitive conclusion on the effect of solvent polarizability/polarity on di-8-ANEPPS.
•Di-8-ANEPPS is NOT affected by the hydrogen bond accepting ability of the solvent.
•Di-8-ANEPPS IS sensitive to a solvent's ability to donate hydrogen bonds.
•Non-polar solvents and polarizable solvents were excluded from the data set due to solubility complications or because they were not well fit by the LSER.

Conclusions for di-8-ANEPPS:

•The lone pairs on the nitrogen of di-8-ANEPPS attract partially positive hydrogen atoms allowing for hydrogen bond accepting.
•There are no partially positive hydrogens in the structure of di-8-ANEPPS. This makes it difficult to donate hydrogen bonds to the solvent, which explains its coefficient of zero.
•To accurately determine the polarity/polarizability coefficient, the data set must include more polarizable solvents.

Results for RH-237:



ν_{max}= 0.05 (+/- 0.45)π* - 0.29 (+/- 0.17)α - 0.01 (+/- 0.26)β

R = 0.53 S.E = 0.26 n = 16

•RH-237 is NOT effected by the polarizability/polarity coefficient or hydrogen bond accept ability of the solvent.
•RH-237 IS affected by the solvent's ability to donate hydrogen bonds.
•Nonpolar solvents and polarizable solvents were excluded from the data set due to solubility complications or because they were not fit well by the LSER.

Conclusions for RH-237:

•Standard deviations are high and yield uninterpretable coefficients.
•A more complete data set, including halogenated, less polar, and aromatic solvents would be ideal.

Future Work:

•Creating well-rounded LSER's for both dyes by testing spectroscopy in polarizable solvents.
•A solvent-effect specific study to attribute how the dyes act to similar solvents while varying only a single parameter.
•The Coumarin series of dyes are to be studied. Work on Coumarin 30 has begun.

Acknowledgments:

We acknowledge the Donors of the American Chemical Society Petroleum Research Fund for their support of this project.

Funding was also provided by the American Chemical Society Project SEED Program.

Special thanks to Dr. Vitha for his support and help as our research advisor.