Selection of an Analysis Wavelength: An Interesting Example Involving Solvatochromism and the Zwitterionic Dimroth-Reichardt's Betaine ET-30 Dye

Taihe Deng and William E. Acree Jr.*

Department of Chemistry, University of North Texas, Denton, TX 76203-5070; *acree@unt.edu

UV-visible absorption spectroscopy provides a very convenient experimental means for determining percentage compositions and solution concentrations of unknown samples, for measuring reaction rate constants, and for determining the stoichiometry and equilibrium constant of metal-ligand complexes. Over the past few years many experimental spectroscopic methods have appeared in this *Journal* (1-14) and in standard laboratory manuals for use in general chemistry, physical chemistry, or quantitative analysis. Two of the cited experiments (13, 14), involving the simultaneous determination of Cr(III) and Co(II) in mixtures, are performed by students in our Instrumental Analysis course.

One week before starting the analytical determinations, students familiarize themselves with the operation of the different spectrophotometers and fluorescence instruments. With the photodiode array spectrophotometer, students make a few calibration measurements and record several absorption spectra to determine suitable wavelengths for select chemicals. One of the compounds

Figure 1. Molecular structure of the zwitterionic Dimroth-Reichardt's ET-30 dye.

examined is the zwitterionic Dimroth-Reichardt's ET-30 betaine dye (see Fig. 1), which exhibits rather pronounced solvatochromic behavior. Solutions of ET-30 vary markedly in color, depending upon the properties of the solubilizing media. For example, methanolic solutions of the dye appear wine red, ethanolic solutions are violet, and 2-propanolic solutions are blue. Green and yellowish-green solutions are obtained by dissolving the dye in acetone and anisole, respectively.

Experimental Procedure

Students are instructed to find the optimum analysis wavelength for the five aforementioned solutions. Approximately 2 mg of ET-30 (Aldrich Chemical Company, [10081-39-7]) is added to 5 mL of each solvent. This concentration yields solutions having an absorbance of approximately 0.6-0.8 absorbance units. Absorption spectra are recorded in the usual manner from 450 nm to 800 nm using 1-cm² glass cuvettes. The analysis wavelength is taken as the wavelength having the maximum absorbance. Typical student values are as follows: 514 nm for methanol; 550 nm for ethanol; 590 nm for 2-propanol; 676 nm for acetone; and 770 nm for anisole. (NOTE: Our photodiode array instrument is limited to wavelengths less than 800 nm. If the instrument has a higher upper limit, 850 nm, then one could try a more non-

polar solvent such as diethyl ether [$\lambda_{\text{abs}} \approx 828$ nm].) Spectral data for ET-30 dissolved in 362 different solvents are compiled in a recently published review article (15).

To our knowledge, the experiment poses no abnormal health risks. Neither the Aldrich Chemical Catalog nor the label on the bottle lists any safety precautions or health warnings. Students are expected to use regular eye protection and exercise the same care normally given to handling of organic chemicals.

Results and Discussion

What makes the exercise educational is the interesting discussion that follows the measurements. Students are asked to rationalize the different colors and analysis wavelengths. Many students hypothesize the occurrence of acid-base or oxidation-reduction chemical reactions on the basis of their past experience. Some students propose the formation of discrete dye-solvent molecular complexes as the reason for the observed colors. Each explanation can cause color changes, but in this instance, none of the three is correct.

The solvatochromic behavior exhibited by ET-30 provides an excellent opportunity to examine spectral transitions in greater detail. Most analytical textbooks present absorption (or excitation) and emission spectral transitions in the form of a Jablonski diagram, with no discussion of how the polarity of the solubilizing medium affects the transition energy. The correct explanation for the observed solvatochromism begins by noting that intramolecular charge transfer occurs between a donor and an acceptor site within the molecule. An electron is transferred from the negative portion of the molecule to the positive portion. ET-30 is a zwitterionic molecule. Photon absorption causes a substantial change in the chromophore's dipole moment. The dipole moment of the excited state, μ_{ES} , can be either smaller or larger than the ground-state dipole moment, μ_{GS} . Surrounding solvent molecules interact with the solute's dipole moment.

Polar solvent molecules selectively stabilize the electronic state having the larger dipole moment. If $\mu_{\text{ES}} > \mu_{\text{GS}}$, then the more polar solvent molecules will stabilize the electronic excited state more than the ground state, as is depicted in Figure 2a. The transition energy decreases with increasing solvent polarity, and the absorption band maximum shifts to longer wavelengths. If, on the other hand, $\mu_{\text{GS}} > \mu_{\text{ES}}$, then polar solvent molecules selectively stabilize the ground electronic state. This leads to an increase in the transition energy with increasing solvent polarity (see Fig. 2b), and the absorption band shifts to shorter wavelengths (15, 16). The solvatochromism of the ET-30 dye corresponds to Figure 2b.

For many of the chromophoric molecules that analytical students commonly encounter, the shift in absorption wavelength corresponds to only a few nanometers. Such small

Figure 2. Schematic representation of solvent effects on the electronic transition of dipolar solutes. In diagram (a), the excited-state dipole moment is larger than the ground state dipole moment, $\mu_{ES} > \mu_{GS}$. In diagram (b) $\mu_{ES} < \mu_{GS}$.

wavelength shifts go visually undetected. This is no reason, however, for analytical textbooks to completely ignore solvent effects in the pictorial Jablonski diagrams. Several compounds (15), such as ET-30, do exhibit fairly sizeable wavelength shifts. Students need to be aware of the fact that absorption wavelengths are solvent-dependent. Even a seemingly meaningless substitution of 2-propanol for methanol in a published analytical procedure could significantly alter the optimum analysis wavelength, as was the case in the present set of experimental measurements. Students can be reminded of this when they encounter gradient elution liquid chromatography later in the semester. Here, the mobile phase composition is varied systematically as a function of time to achieve the desired chromatographic separation. A similar argument can be made for how fluorescence emission wavelengths are affected by solvent polarity (17).

From an educational standpoint, we have found that the thirty minutes that it takes to prepare the five solutions and record their absorption spectrum is time well spent. Students achieve the stated goal of learning how to operate the photodiode spectrophotometer, while at the same time observing a visual example of solvatochromism. They are fascinated by the fact that a single chromophore gives so many different

colors. If time permits, students are allowed to select a few solvents of their choice. The experimental observations afford an excellent opportunity to discuss in greater detail how solvent polarity affects spectral transitions.

We have used the measurements as a short introductory exercise to familiarize students with the operation of an UV-visible spectrophotometer. The experimental method can easily be modified to serve as a demonstration, or the exercise can provide an additional set of measurements in an existing spectrophotometric laboratory experiment for students enrolled in analytical chemistry or instrumental analysis.

Note

^WA student handout for this experiment is available on *JCE Online* at <http://jchemed.chem.wisc.edu/Journal/issues/1999/Nov/abs1555.html>.

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