KJM-MENA 4010: Laboratory exercise 3 in UV-visible spectroscopy

The effect of solvents on UV-visible spectra

Spring 2008

Introduction
Chromophores give rise to "characteristic" absorbance bands. Changes in their environment cause changes in their energy levels which then affect the wavelength and intensity of absorbance.

The following experiment shows that external factors, in this case the solvent used, can also influence the chromophore. Because the substance used shows both strong and weak absorbance bands at different wavelengths, two different sample concentrations will be examined.

Theoretical background
The polarisability, $\alpha$, of a molecule is a measure of how easy it is to induce fluctuations in its electron distribution. The dielectric constant – or more correct, the relative permittivity – is the macroscopic analogue and is a measure of the polarity of a bulk medium (e.g. a solvent). The dielectric constant, $\varepsilon_r$, is related to the polarisability and the permanent dipole moment, $\mu_0$, of a molecule:

$$
\varepsilon_r = \frac{1+2(\alpha + \mu_0^2/3k_BT)N/3\varepsilon_0}{1-(\alpha + \mu_0^2/3k_BT)N/3\varepsilon_0}
$$

where $N$ is the number of molecules per unit volume, $k_B$ is the Boltzmann constant, $T$ is the temperature and $\varepsilon_0$ is the vacuum permittivity.

Experimental work
Use a 1.0 cm quartz cuvette in all the following experiments:
1. Prepare 5 solutions of 10.0 mg benzophenone in 10.0 mL of each of the following solvents: metanol, cyclohexane, n-hexane, acetonitrile and dichloromethane. These solutions represent the high concentration, $c_{\text{high}}$.
2. Repeat the following for each of these solutions:
   a. Dilute the concentration $c_{\text{high}}$ by taking 2 drops of the solution and add 10 mL solvent. This is then the concentration $c_{\text{low}}$.
   b. Record a reference spectrum of the solvent.
   c. Record an absorbance spectrum of the “$c_{\text{high}}$-solution”.
   d. Record an absorbance spectrum of the “$c_{\text{low}}$-solution”.

1
Evaluation of experimental results

The report should include an experimental section including all relevant details and the obtained spectra. Include the following in the report:

1. The electronic transitions associated with the observed absorption bands.
2. Prepare a table of $\lambda_{\text{maks}}$ of the absorption bands of benzophenone in the different solvents. The table should also include the value of the dielectric constant of the solvents (a list of dielectric constants can be found at http://www.asiinstr.com/dc1.html#SECTION-C).
3. Discuss the solvent effects on the two absorption bands and suggest an explanation.
4. Discuss any observed changes in the structure of the absorption bands in the wavelength region 300–400 nm as a function of the solvent polarity.