Experimental

Make a $1*10^{-2}$ M solution of pyrene ($C_{16}H_{10}$, molecular weight M = 202.25 g/mol) in methylcyclohexane. From this solution, make three dilutions with c = $5*10^{-3}$, $2.5*10^{-3}$ and $1*10^{-3}$ M. 20 ml of each solution is a sufficient amount for the measurements.

Measure the emission spectra for these four solutions at room temperature with the Varian Cary Eclipse spectrofluorometer. Use an excitation wavelength of 370 nm and measure the emission spectrum at the 375-500 nm range. Use the following settings: Excitation slit "5 nm", Emission slit "2,5 nm", Scan control "medium", Excitation filter "Auto", Emission filter "open". Set the PMT Detector voltage at first to the "medium" value, but if necessary, change the voltage setting to "manual" and a smaller value, so that the fluorescence of the most concentrated sample stays withing the measurement scale. Also, set the intensity values visible in the spectra (label peaks "Y labels", threshold "30.0").

Do the temperature-dependent measurements for the $5*10^{-3}$ M solution. In fluorescence measurements the oxygen dissolved in the solution will cause problems by quenching the fluorescence. The amount of dissolved oxygen is also temperature dependent, so in temperature-dependent measurements it may cause a significant error. This is why the oxygen should be removed from the solution by bubbling nitrogen through the solution. Use the pasteur-pipette attached to the nitrogen hose in the fume cupboard. Detach the cuvette holder from the spectrometer and set the cuvette in it. Fill the cuvette with the $5*10^{-3}$ M pyrene solution and put the tip of the pipette on the bottom of the cuvette. Adjust the nitrogen flow rate with the needle valve. Bubble nitrogen through the solution for 5-7 minutes and then close the cuvette with a stopper with a small hole for the thermometer probe.

Put the thermometer probe into the solution through the hole in the stopper and put the cuvette into the spectrometer. Warm the solution to about 30 °C and let the temperature stabilize for about 5 minutes. Measure the emission spectrum as before. Write down the temperature during the measurement and save the spectrum. Repeat the measurement for temperatures of 40, 50, 60, 65, 70, 75, 80, 85, 90 and 95 °C. **Note**: The sample in cuvette does not warm up exactly to the value shown in the temperature controller, so

use as the set value for example 31, 41, 52, 62, 68, 73, 79, 84, 90, 95 and 99, and make your calculations using the real values shown by the thermometer. After measurements, set the temperature controller value back to about room temperature so that it won't start heating immediately when the next measurer turns it on.

For the report

Compare the fluorescence spectra of the solutions with different concentrations. Concentrate especially on the relative changes in the excimer and monomer contribution to the spectra. Describe how and why the concentration affects the excimer formation.

Plot the fluorescence spectra in different temperatures in the same graph. Observe how the spectra change as a function of temperature and explain the changes. Tabulate the monomer and excimer emission intensities ($R_M°$ and $R_D°$) at the maximum intensity wavelenghts in different temperatures. The wavelengths of the maximum intensity may change a little as a function of temperature, but use the same wavelength for all measurements. Plot a graph of $R_M°$ vs. $R_D°$ at temperatures between 60 and 85 °C. From the slope of this plot determine the constant –a/b to get the constant b/a for equation (18).

Determine the enthalpy and entropy of formation, $\Delta H°$ and $\Delta S°$ from equation (18) using an appropriate linear fit. In the equation, use the pyrene concentration and the constant b/a determined earlier, and the measurements at temperatures between 60 and 85 °C. Then determine the excimer binding energy B and the ground state repulsion energy R.

Estimate the errors for $\Delta H°$, $\Delta S°$, B and R and compare your results to the literature values:

$\Delta H° = -7.8$ kcal mol^{-1} (in cyclohexane)

$\Delta S° = -18.5$ cal mol^{-1} K^{-1} (in ethanol)

$R = 7.9$ kcal/mol (in ethanol)

Questions for discussion

1. In excimer lasers, the lasing is based on the emission of an excimer formed of a rare gas atom and a halogen atom. Why is it easy to make a laser this way? Hint: Think about the population of the lasing states.

2. Does the following statement make sense: The ground state of an excimer is an excited state.

3. The probability that the ends of a linear polymer molecule come into close proximity can be probed by attaching pyrene probes to the ends of the molecule. How does such a technique work?

4. For some excimers, the fluorescence emission can be observed also at low temperatures. However, the excimer emission nearly vanishes when the solvent becomes glassy or crystalline, why?

References:

The English instructions: Halpern A.M., *Experimental Physical Chemistry 2nd Edition*, 1997, Prentice-Hall, Inc

Literature values: Stevens and Ban, *Trans. Faraday. Soc.* 60:1515 (1964)