Organic Cume
University of Missouri-Columbia
June 1995
## Dr. Rainer Glaser

Solvent Polarity Indicators

Suggested Reading: Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319-2358.

	Max.	Yours
Question 1	24	
Question 2	34	
Question 3	12	
Question 4	12	
Question 5	18	
Total	100	

Question 1. Reaction Series and Absorption Series. (24 points)

(a) Linear free energy (LFE) relationships involve empirical relationships between rates or equilibria of chemical reactions, which show some similarity within a "reaction series". Considering the reaction

$$(S)_M + (R)_M <==> [S\bullet\bullet\bullet R]^\ddagger --> (P)_M$$
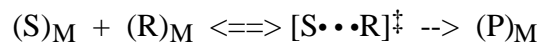
there are *three possibilities* of introducing small changes in order to establish a reaction series. One of these possibilities is provided as an example. Name the other two possibilities, state briefly what kind of LFE relations are obtained and provide a simple example (no detail necessary). (12 points, 6 points each)

First: Change the *substrate and leave everthing else the same.*

    The substarte might be changed by introduction of substituents in the m- and p-positions.
    This kind of change leads to the well-known Hammett equation and similar LFEs.

Second: Change the

Third: Change the

(b) A simple modification of the previous equation leads to the basic equation for the development of the so-called absorption series. To establish absorption series, there are two possibilities to alter the parameters of this equation. Provide the equation and provide brief descriptions of the two options addressing the same issues as in the case of the reaction series. (12 points, 4 points each)

The basic equation for absorption series (clearly state the meaning of all symbols used):

First: Change the

Second: Change the

Question 2. Solvatochromism. (points)

(a) Provide definitions for the following terms (6 points, 2 points each)

| |
|---|
| Solvatochromism |
| Hypsochromic Shift |
| Negative Solvatochromism |

(b) Since the time required for a molecule to get electronically excited (about _____ sec) is much _____ (shorter/longer) than that required to execute vibrations or rotations (about _____ to _____ sec), the nuclei of the absorbing entity do not appreciably alter their positions during an electronic transition. This is called the _____ principle, or FC principle for short. On this background, explain the difference between an "FC excited state" and an "equilibrium excited state". (10 points; 5 points for the blanks, 5 for explanation)

"FC excited state" versus "equilibrium excited state"

(c) Let's look at the solvatochromism of a dye with a large permanent dipole. Let's further assume that the dipole increases during the electronic transition. Thus, one would expect _____ (positive or negative) solvatochromism . In the Figure, the energy levels are shown for the unsolvated ground state and for the unsolvated excited state of this dye molecule. Clearly indicate how these levels (and the gap) are affected by increasingly polar solvation in the case of *absorption*. (10 points).

Gas Phase   Polar Solvent   Very Polar Solvent
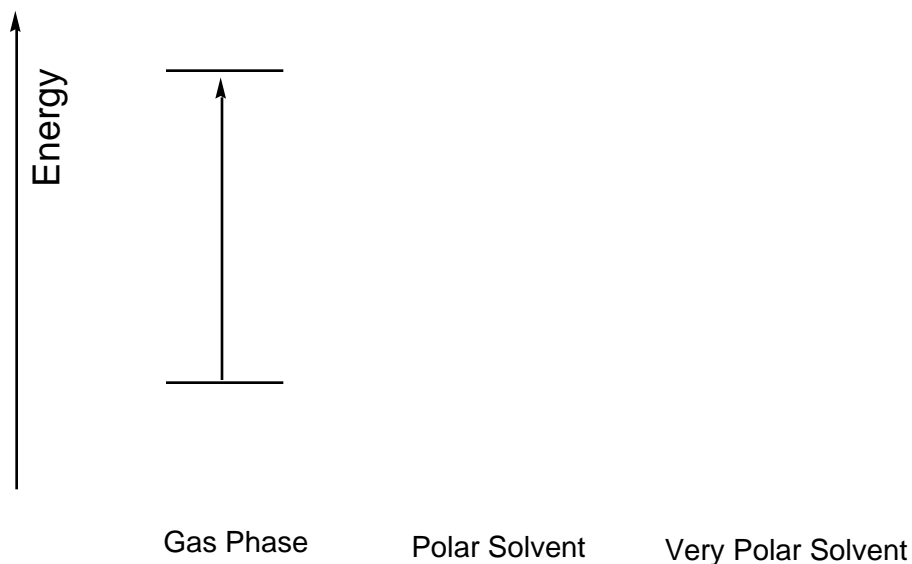
(d) Now let's compare the solvent effects on absorption and fluorescence. The energy levels are shown for the unsolvated ground and excited states of this dye molecule. Clearly indicate how these levels (and the gap) are affected by polar solvation in the case of *absorption* and *fluorescence*. Label the FC ground and excited states and label the equlibrium ground and excited states. (8 points)

Absorption   Fluorescence

Gas Phase   Polar Solvent   Polar Solvent
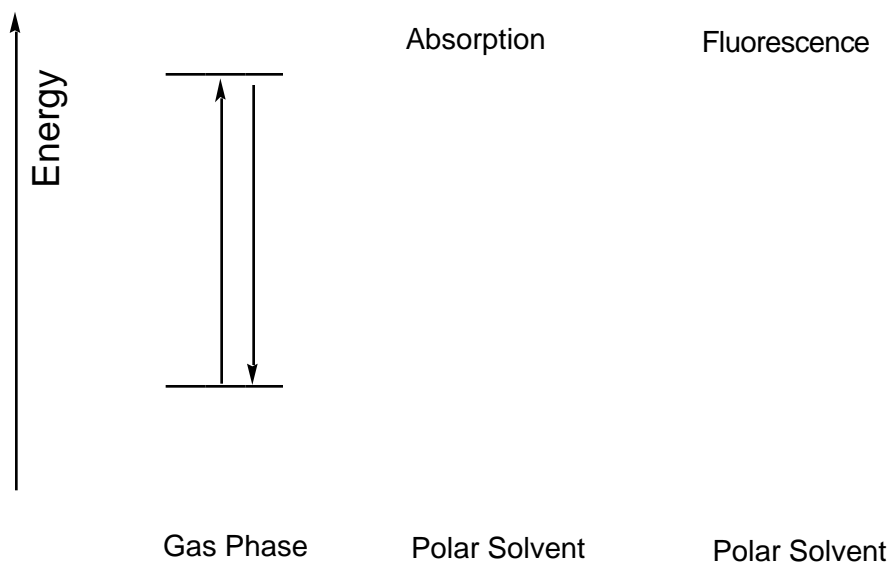
Question 3. Intra- and Intermolecular Charge Transfer.

Reichardt discusses in some detail the requirements that should be met by a positively or negatively solvatochromic compound for it to be useful for the establishment of a spectroscopically derived solvent polarity scale. One of these requirements states that the probe molecules should exhibit maximal sensitivity to changes in the surrounding medium. This behaviour is usually found for compounds for which the electronic excitation is associated with a high (a) intramolecular or (b) intermolecular charge transfer. Provide one example of your choice for each case with the only condition that the examples both must show *negative* solvatochromism. Give the structure of the probe and explain the charge transfer that occurs upon excitation. (6 points each)

(a) Negative solvatochromism because of INTRAmolecular charge transfer:

(b) Negative solvatochromism because of INTERmolecular charge transfer:

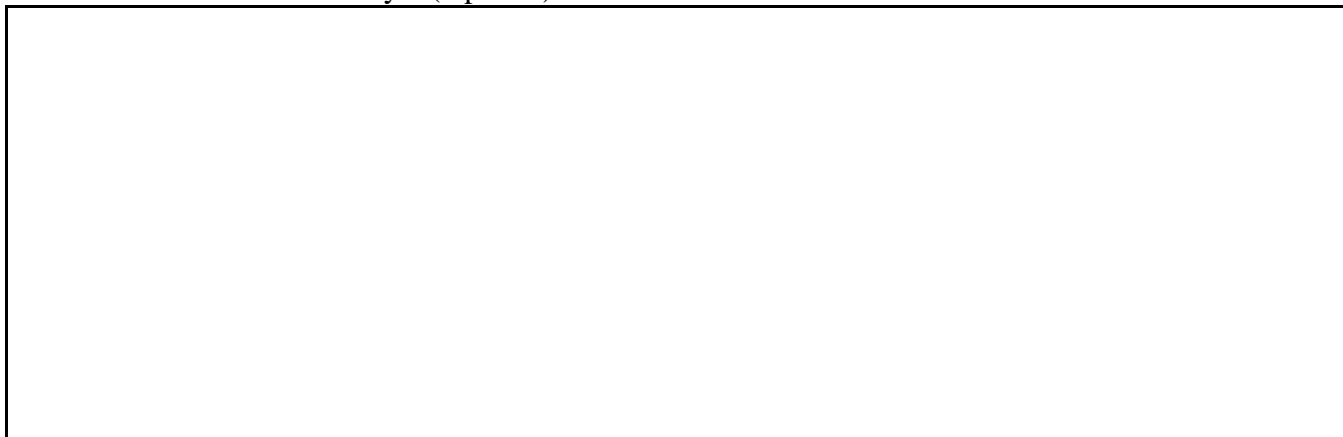**Question 4.** Reichardt's Dye and the E_T^N Scale of Solvent Polarity.

(a) Draw the structure of Reichardt's dye. (Yes, you should know this, especially since you just read Reichardt's review!) (2 points)

(b) What is the definition of the $E_T(30)$ value? Do not just give a formula, state in your own words what $E_T(30)$ is and what its units are. Also mention what the "30" stands for. (5 points)

(c) What is the definition of the E_T^N scale? What are the units of the E_T^N values? Why were the standards selected in this way? (5 points)

Question 5. Magnitudes and Trends in Empirical Solvent Polarity Paramters. (18 points)

You are given a copy of Table 2 of Reichardt's article. Look at the data and come up with <u>nine observations</u> that are based on these data. Each of your correct statements wins 2 points.

Example: The $E_T(30)$ values of homologous 1-alkanols, Me-$(CH_2)_n$-OH, indicate an exponential decrease as n is increased from 1 (methanol) to n = 11 (dodecanol).

The End