

Absorption of light (UV/Visible Spectroscopy)

(Item No.: P3070101)

Curricular Relevance



Difficulty



Intermediate

Preparation Time



10 Minutes

Execution Time



10 Minutes

Recommended Group Size



1 Student

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

Absorption of light, Electron excitation, Influence of solvents, Solvatochromic, hypsochromic and bathochromic shifts, Lambert-Beer's Law, Decadic molar extinction coefficient

Task and equipment

Introduction

Principle:

The structures of molecules are not changed by their chemical environment in the gas phase. In contrast to this, on transition to the condensed phase, in dilute solution, the solvent changes the binding state of the dissolved substance. One of the ways this influence makes itself shown is in the electron spectrum (solvatochromatic shift).

Tasks:

Plot and discuss UV-visible absorption spectra of methyl orange in various solvents.

From the decadic molar extinction coefficients of the bands in the visible range, determine the type of electron transition that causes these bands.

Plot the wavelengths of the absorption maxima in the visible range against the dielectric constants of the various solvents.

Note:

The graphical evaluation of the measured values can be very easily carried out by means of 'Measure' software. A downloadfile of this software is available as freeware for use in evaluating and graphically representing measured values under URL „www.phywe.com“.

Safety instructions



Ethanol

H225: Highly flammable liquid and vapour.

H319: Causes serious eye irritation.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

Ethylene glycol

H302: Harmful if swallowed

H372: Causes damage to organs through prolonged or repeated exposure

Methanol

H225: Highly flammable liquid and vapour.

H331: Toxic if inhaled.

H370: Causes damage to organs.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P233: Keep container tightly closed.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

N,N-Dimethylformamide

H226: Flammable liquid and vapour.

H360D: May damage the unborn child

P201: Obtain special instructions before use.

Equipment

Position No.	Material	Order No.	Quantity
1	Spectrophotometer 190-1100 nm	35655-99	1
2	Cell for spectrophotometer, quartz	35665-00	2
3	Volumetric flask 100 ml, IGJ12/21	36548-00	1
4	Volumetric pipette, 1 ml	36575-00	5
5	Pipettor	36592-00	1
6	Pipette dish	36589-00	1
7	Micro-l syringe, 100 micro-l	02606-00	1
8	Funnel, glass, top dia. 55 mm	34457-00	1
9	Weighing dishes, square shape, 84 x 84 x 24 mm, 25 pcs.	45019-25	1
10	Microspoon, steel	33393-00	1
11	Wash bottle, plastic, 500 ml	33931-00	1
12	Methyl orange soln., 0.1% 250 ml	31573-25	1
13	Methanol 500 ml	30142-50	1
14	Ethyl alcohol, absolute 500 ml	30008-50	1
15	Ethylene glycol 250 ml	30085-25	1
16	N,N-Dimethylformamide, puriss., 1 l	31259-70	1
17	Water, distilled 5 l	31246-81	1

Task

Plot and discuss UV-visible absorption spectra of methyl orange in various solvents.



Set-up and procedure



- The spectrophotometer that is required is shown in Fig. 1.
- Prepare the 0.001 molar methyl orange stock solution required for this experiment as follows: Weigh 33 mg of methyl orange into a 100 ml volumetric flask, dissolve it in distilled water and make it up to the mark with distilled water.
- Use a quartz cell for the recording of the spectra of methyl orange in the following solvents; water, methanol, ethanol, N,N-dimethylformamide and ethylene glycol. In each case, pipette 3 ml of the solvent into the quartz cell and carry out base line equalization.
- Then add 50 μl of the methyl orange stock solution with the microliter pipette and record the spectrum in the 800 to 200 nm range with the slowest scanning rate.
- Allow the software to determine the positions of the absorption bands (peaks) and record them together with the corresponding extinction values. Methyl orange has one adsorption band in each of the visible and ultraviolet ranges scanned.



Results and evaluation

Results

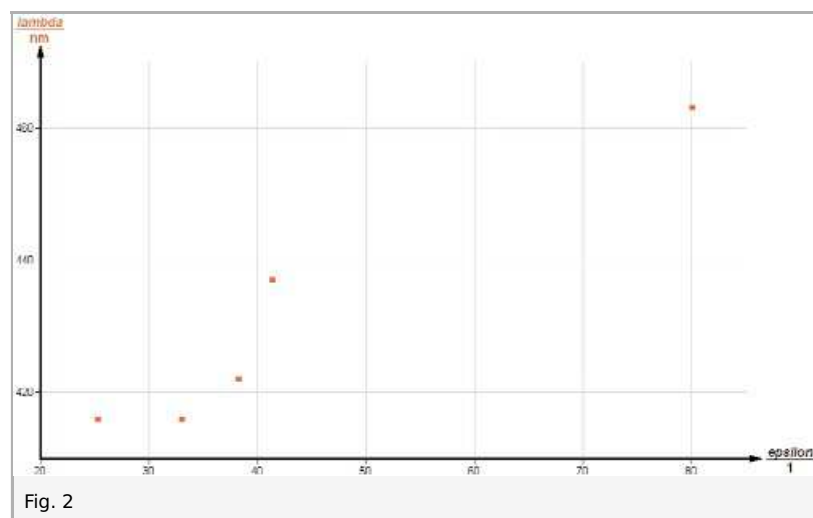
The relative dielectric constants of the solvents used:

Solvent	ϵ_r
Ethanol	25.3
Methanol	33.0
DMF	38.3
Glycol	41.4
Water	80.1

Table 1

Fig. 2 was created by this software.

Plot of the wavelenghts of the absorption maxima of methyl orange against the relative dielectric constants of various solvents:



Evaluation

In the UV-visible range of the electromagnetic spectrum, the energy of the light quanta is so high that the valency electrons in the s-bonds and und p-bonds of a molecule are excited, whereby the following electron transitions are of importance:

- between occupied and unoccupied π -energy levels: $\pi \rightarrow \pi^*$
- of n-electrons from nonbinding atomic energy state to unoccupied σ -energy levels: $n \rightarrow \sigma^*$
- of n-electrons from nonbinding atomic energy state to unoccupied π -energy levels: $n \rightarrow \pi^*$
- between occupied binding and excited σ -energy levels: $\sigma \rightarrow \sigma^*$

A band can be assigned to the type of electronic transition when the logarithm of the decadic molar extinction coefficient at the band maximum is determined.

$$\varepsilon_i = \frac{E_\lambda}{c_i d}$$

- ε_i Decadic molar extinction coefficient of substance i at awavelength of λ
 E_λ Extinction at a wavelength of λ
 c_i Concentration of substance i in $\frac{\text{mol}}{\text{l}}$
 d Layer thickness of the solution in cm

Values of $\log \varepsilon$ above 3 indicate a $\pi \rightarrow \pi^*$ -transition, values of $\lg \varepsilon$ less than 2 indicate a $n \rightarrow \pi^*$ -transition. The excitation of organic molecules is connected with electrical charge displacement, whereby polar solvents exert a strong influence on the excitation energy, and so on the position of the bands. As a rule, the polar excitation state of polar solvents is more strongly stabilised than the ground state, whereby $\pi \rightarrow \pi^*$ -transitions require less energy. This energy is brought by long wavelength radiation, with a resulting shift towards the red (bathochromic shift) on transition to polar solvents (positive solvatochromatic shift).

The band in the visible range of the methyl orange spectrum shows a more pronounced bathochromic shift with increasing polarity of the solvent. This connection is made very clear in Fig. 2, Results, where the wavelengths of the absorption maxima are plotted against the relative dielectric constants of the solvent (ε_r , Table 1, Results). The deviation shown by ethylene glycol is due to the influence of the water in the stock solution added.