

Related topics

Absorption of light, electron excitation, solvent influence, solvatochromism, hypsochromic and bathochromic shifts, Lambert-Beer law, decadic molar extinction coefficient.

Principle and task

In the gas phase the structure of molecules is not altered by their chemical environment. In contrast, on transition to the condensed phase in dilute solution, the solvent changes the binding relationships of the dissolved substances. This influence shows itself in the electron spectrum (solvatochromism).

Equipment

Spectrophotometer, 200-1100 nm	35653.97	1
Program pack spectrum analysis	35653.01	1
Cells f.spectrophotom., quartz, 2	35665.02	1
Volumetric flask 100 ml, IGJ12/21	36548.00	1
Volumetric pipette, 1 ml	36575.00	5
Pipettor	36592.00	1
Pipette dish	36589.00	1
Micro-l syringe, 100 micro-l	02606.00	1
Funnel, glass, top dia. 55 mm	34457.00	1
Laboratory balance, data outp. 620g	45023.93	1
Weighing dishes, 85×85× 7 mm, 100	45019.01	1
Microspoon, special steel	33393.00	1

Wash bottle, plastic	500 ml	33931.00	1
Methyl orange, powder	25 g	30144.04	1
Methanol	500 ml	30142.50	1
Ethyl alcohol, absolute	500 ml	30008.50	1
Ethylene glycol	250 ml	30085.25	1
Dimethylformamide	250 ml	31259.25	1
Water, distilled	5 l	31246.81	1

Problems

Record and discuss UV-VIS-absorption spectra of methyl orange in different solvents.

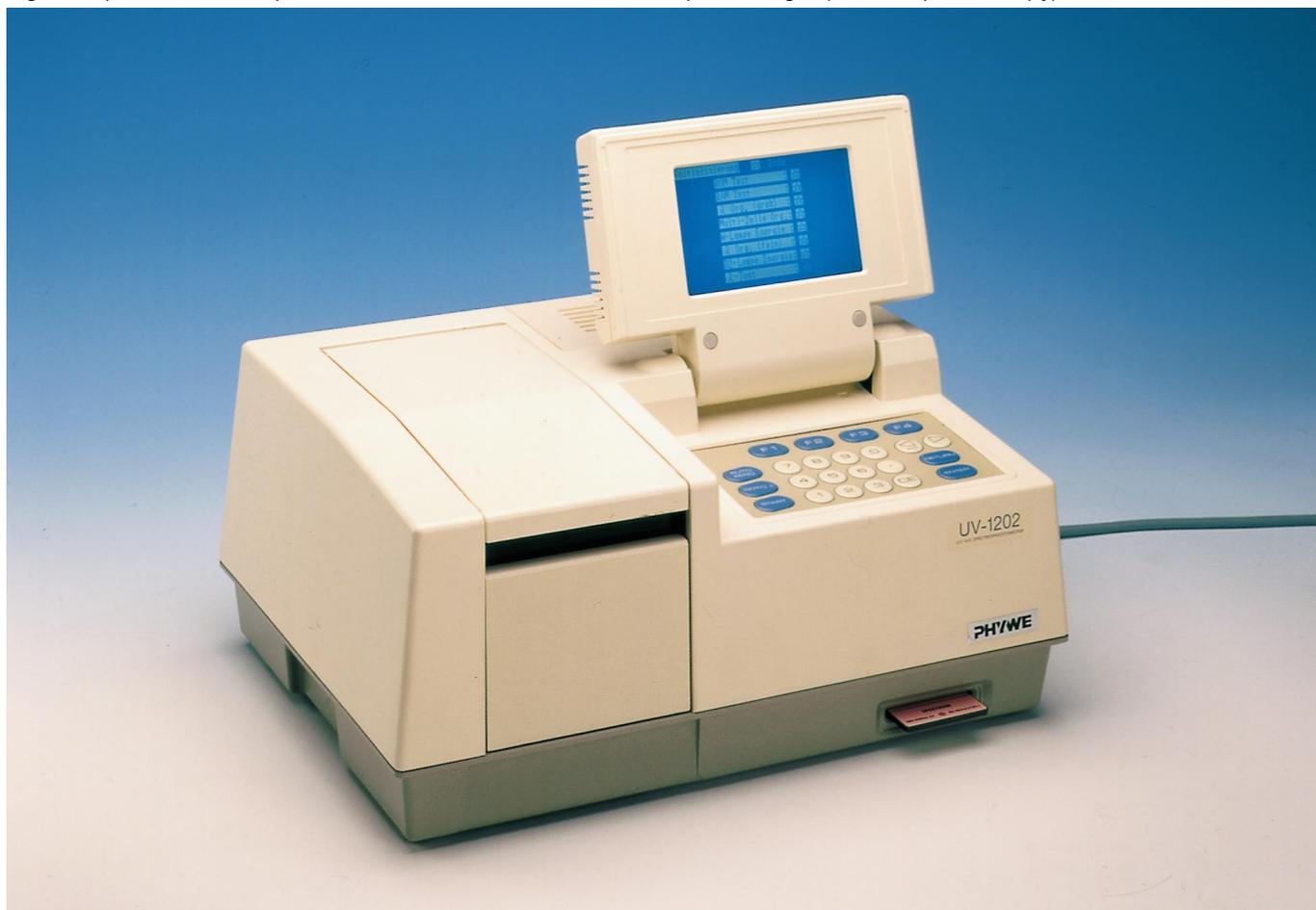
Determine the type electron transition which causes the bands in the visible region of the electromagnetic spectrum via the decadic molar extinction coefficient. Plot the wavelengths of the absorption maximum in the visible region of the spectrum against the dielectric constant of the respective solvent.

Set-up and procedure

Perform the experimental set-up according to Fig. 1. Prepare the methyl orange stock solution required for the experiment as follows:

- 0.001 molar methyl orange solution: Weigh 33 mg of methyl orange into a 100 ml volumetric flask, dissolve it in distilled water, and fill the volumetric flask with distilled water to the calibration mark.

Fig. 1: Experimental set-up: Transmission of colour filters – absorption of light (UV-VIS spectroscopy).



Record the spectra in a quartz cell. Equip the spectrometer with the spectrum program pack. Record the spectrum of methyl orange in the following solvents: water, methanol, ethanol, dimethylformamide, and ethylene glycol. To perform the measurements, pipette 3 ml of the respective solvent into the quartz cell in each case and perform the base line adjustment. Subsequently add 50 μl of the methyl orange stock solution and record the spectrum in the region between 800 and 200 nm with the lowest scanning rate. Use the software to determine the position of the absorption bands and record them with the corresponding extinction values. Methyl orange has one absorption band in the visible region and one in the investigated ultraviolet region of the spectrum.

Theory and evaluation

In the UV-VIS region of the electromagnetic spectrum, the energy of the light quanta is so high that the valence electrons in the σ - and π -bonds of a molecule can be excited. On doing so, the following electron transitions are of importance:

- Those between occupied and unoccupied π -energy levels: $\pi \rightarrow \pi^*$
- Those involving n electrons of non-binding atomic energy states in vacant σ -energy levels: $n \rightarrow \sigma^*$
- Those involving n electrons of non-binding atomic energy states in vacant π -energy levels: $n \rightarrow \pi^*$
- Those between occupied binding and excited σ -energy levels: $\sigma \rightarrow \sigma^*$

A band can be assigned to the type of electron transition, if the logarithm of the decadic molar extinction coefficients are determined at the band maxima.

$$\varepsilon = \frac{E}{c \cdot d} \quad (1)$$

where

ε = decadic molar extinction coefficient

E = extinction

c = concentration in mol/l

d = layer thickness of the liquid in cm

Values of $\lg \varepsilon$ greater than 3 indicate $\pi \rightarrow \pi^*$ -transitions, those less than 2 indicate $n \rightarrow \pi^*$ -transitions.

The excitation of organic molecules is linked with an electrical charge transfer, whereby polar solvents exert a strong influence on the excitation energy and thus on the position of the bands. As a rule, the polar excitation state is more strongly stabilised by polar solvents as the ground state; as a consequence, $\pi \rightarrow \pi^*$ -transitions require less energy. This energy is provided by radiation of longer wavelengths; which results in a red shift (bathochromic shift) in the transition to polar solvents (positive solvatochromism).

Data and results

The bands in the visible region of the methyl orange spectrum show a pronounced bathochromic shift with increasing polarity of the solvent. Plotting the wavelengths of the absorption maxima against the relative dielectric constants (ε_r) of the solvents (Table 1) illustrates this correlation very clearly (Fig. 2). The deviation which occurs with ethylene glycol is caused by the influence of the water in the stock solution.

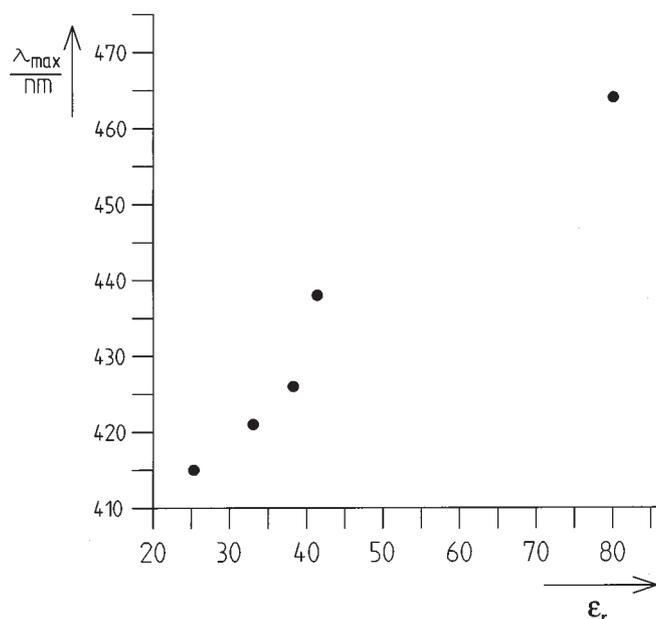


Fig. 2: Plot of the absorption maxima of methyl orange against the relative dielectric constants of different solvents.

Table 1: Relative dielectric constants of the solvents used

Solvent	ε_r
Methanol	33
Ethanol	25.3
Glycol	41.4
Water	80.1
DMF	38.25