

Laboratory Courses in Physical Chemistry  
for students the study courses chemical engineering  
Technische Universität München SS 2003

# **Elaboration of the experiment 7.1**

## **Light Absorption**

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## 1 Problem

In this experiment, we measured the constant of balance of the methyl red indicator. To obtain that, we measured the light absorption of methyl red in solutions with different pH values.

## 2 Theory

### 2.1 The Lambert-Beer Law

The amount of light penetrating a solution is known as transmittance  $T$ , which is to be expressed as the ratio of the intensity of the transmitted light  $I_t$ , and the initial light intensity of the light beam  $I_0$  through the thickness  $d = \int dx$ :

$$\frac{dI}{I} = -\alpha dx \Rightarrow \frac{I_t}{I_0} = e^{-\alpha d} = T_\lambda \quad (1)$$

Equation (1) is known as the *Lambert Law*. The relationship between transmittance  $T$  and absorbance  $E$  is inverse and logarithmic (base 10):

$$E_\lambda = \log \frac{1}{T_\lambda} \quad (2)$$

The extinction coefficient  $\alpha$  of a dissolved substance is a linear function of its concentration  $c$ , the so-called *Beer Law*, and the molar extinction coefficient  $\epsilon$  determine the slope of the linear plot. A complete description of the extinction is hard.  $\alpha$  is often a very complex function of the frequency.

$$\alpha = \epsilon c \quad (3)$$

With the equations (1) and (3) we finally get the *Lambert-Beer Law*:

$$\frac{I_t}{I_0} = e^{-\epsilon c d} = T_\lambda \quad (4)$$

And for the absorption:

$$E_\lambda = \log \frac{I_0}{I} = \log(e^{\epsilon c d}) \quad (5)$$

The Lambert-Beer law however is valid only for diluted solutions. The limits for its validity differ for different materials. As a general rule, one can understand that every material showing an absorption of up to 0.5 - 0.6 still obeys the Lambert-Beer Law.

### 2.2 UV/visible Spectroscopy

When light, either visible or ultraviolet, is absorbed by valence (outer) electrons these electrons are promoted from their normal (ground) states to higher energy (excited) states. The energies of the orbitals involved in electronic transitions have fixed values. Because energy is quantised, it seems safe to assume that absorption peaks in a UV/visible spectrum will be sharp peaks. However, this is rarely, if ever, observed. Instead the spectrum has broad peaks (Fig. 3). This is because there are also vibrational and rotational energy levels available to absorbing materials (Fig. 1).

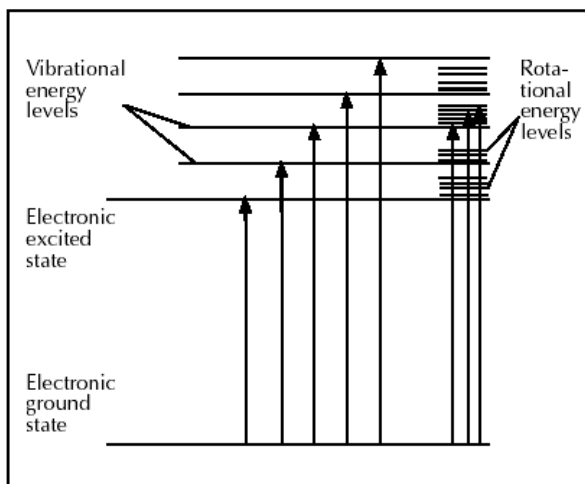


Figure 1: Energy levels

Because light absorption can occur over a wide range, light from 190 nm to 900 nm is usually used. Valence electrons are found in three types of electron orbitals. Single, or  $\sigma$ , bonding orbitals; double or triple ( $\pi$  bonding orbitals); and non-bonding orbitals (lone pair electrons). Sigma ( $\sigma$ ) bonding orbitals tend to be lower in energy than  $\pi$  bonding orbitals, which in turn are lower in energy than non-bonding orbitals. When electromagnetic radiation of the correct frequency is absorbed a transition occurs from one of these orbitals to an empty orbital, usually an antibonding orbital,  $\sigma^*$  or  $\pi^*$  (Fig. 2). Most of the transitions from bonding orbitals are too high frequency (too short a wavelength to measure easily), so most of the absorptions involve only  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \sigma^*$  and  $n \rightarrow \pi^*$  transitions.

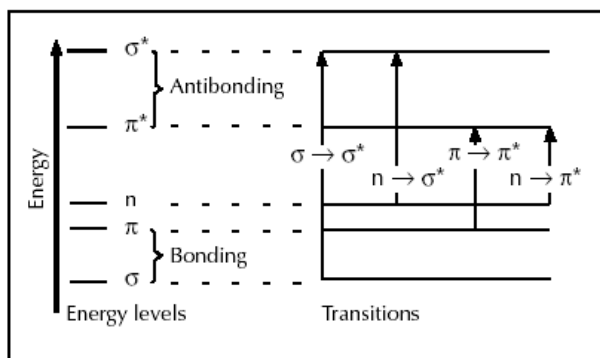


Figure 2: Orbital transitions

The exact energy differences between orbitals varies. In organic molecules double bonds which are next to each other can conjugate, join together and delocalise the electrons over all of the atoms. This lowers the energy needed to promote the outer electrons. As a consequence molecules with many conjugated double bonds can be coloured because they absorb energy in the visible as well as the ultraviolet part of the spectrum.

### 3 Experiment

#### 3.1 Procedure

First we prepared five solutions of different pH values with the indicator methyl red in 10 ml pistons:

- 1 ml 0,1 n HCl
- 1 ml 0,1 n Natrium acetate
- 1 ml buffer solution pH 4.6
- 1 ml buffer solution pH 5.0
- 1 ml buffer solution pH 5.4

In each of these solutions, we put in 1 ml of indicator (methyl red) and then filled it up to 10 ml with distilled water. Then we filled the solutions in quartz cuvettes and measured the absorption between the wavelengths of 320 nm and 630 nm in a spectrometer. To calibrate the spectrometer, we used the solvent which is in our case distilled water and racked out the concerning wavelengths.

## 3.2 Evaluation

### 3.2.1 Analysing the data

We got absorption spectra plotted in figure 3.

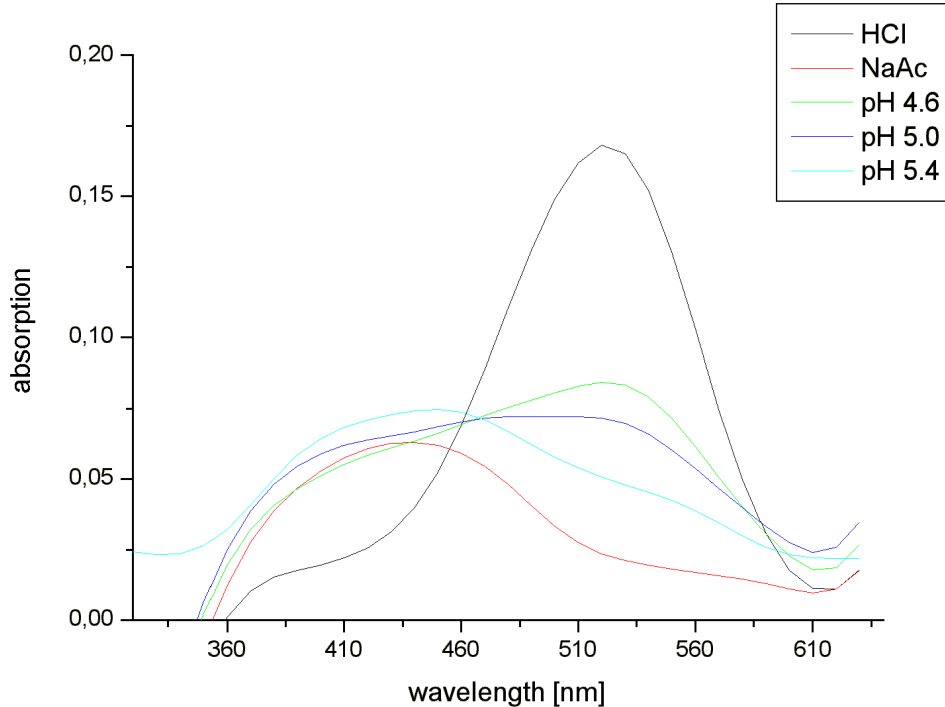


Figure 3: Absorption spectra for methyl red

We used the FFT filtering algorithm for smoothing the curves, in the appendix you will find the original curves.

All of the mixtures except the mixture of pH value 5.4 show negative absorption values up to 360 nm. This is quite interesting because it would mean the mixtures are emitting light instead of absorbing it. We can explain this phenomenon because we used a normal glass cuvette instead of a quartz cuvette for the calibration with distilled water. So, all values are afflicted with a systematic error.

In the acid solution all the indicator (methyl red) is protonised. In the basic NaAc solution all of the methyl red should be deprotonised. This means, that in the theory the absorption curve should be exactly the inverse to the acid solution curve, maxima and minima should occur at the same wave length. In our case, the maximum of the HCl solution is at  $\lambda_2 = 520$  nm and of the NaAc solution, it is  $\lambda_1 = 440$  nm. The literature values are 523-526 nm for acid and 427-437 nm for alkaline which nearly fit our results.

For 520 nm, our values are matching the theoretical data. The absorption of the HCl solution has got a maximum and the NaAc solution nearly a minimum. Between these two curves (see

Fig. 3), the curves of the solutions with the different pH values are in the right order: the solution with the lowest pH value is the closest to the curve of the acid solution in opposition to curve with the highest pH value which is close to the alkaline solution.

For 440 nm, our values does not match the expected values. Although the 3 buffer solutions in the right order relative to each other, the basic NaAc solution has a far to low absorption curve for wavelength under 460 nm. The curve should show up a the highest peak for 420 nm. In our case, it is the lowest curve of all curves. This is quite illogical and an explanation is quite difficult to find. Perhaps the normal glas cuvette used to calibrate the system with water had an higher absoption value for light with wavelength under 460 nm.

### 3.2.2 Determination of the constant of balance

We can calculate the percentage of the protonised and deprotonised methyl red with following formulas:

$$\begin{aligned} \%I^- &= \frac{E_{\lambda_1}(\text{solution})}{E_{\lambda_1}(I^-_{\text{pure}})} \cdot 100\% \\ \%IH &= \frac{E_{\lambda_2}(\text{solution})}{E_{\lambda_2}(IH_{\text{pure}})} \cdot 100\% \end{aligned}$$

with  $E_{\lambda_1}(I^-_{\text{pure}}) = 0,065$  and  $E_{\lambda_2}(IH_{\text{pure}}) = 0,175$  we get the results of table 1.

solution	$E_{\lambda_1}(\text{solution})$	$\%I^-$	$E_{\lambda_2}(\text{solution})$	$\%IH$
4,6	0,064	98,46154	0,087	49,71429
5,0	0,067	103,07692	0,073	41,71429
5,4	0,075	115,38462	0,051	29,14286

Table 1:  $\%I^-$  and  $\%IH$  in the buffer solutions

We can calculate the pKc value with:

$$pKc = pH - \log \frac{[I^-]}{[IH]} = pH - \log \frac{\%I^-}{\%IH} \quad (6)$$

And so we obtain the values of table 2.

solution	$\%I^-$	$\%IH$	pKc
4,6	98,46154	49,71429	4,30321
5,0	103,07692	41,71429	4,60712
5,4	115,38462	29,14286	4,80238

Table 2: pKc values of buffer solutions

The middle value is  $pKc = 4,57091$ .

By adding up the protonised and deprotonised indicator we should obtain 100%. As you can see in the table 3 below, this is not the case in our case. The values for %I<sup>-</sup> are partly over 100% because, like described in the analysis of the data, the NaAc curve shows up abnormal behavior for wavelengths under 460 nm.

solution	%I <sup>-</sup>	%IH	pKc
4,6	98,46154	1,53846	2,79382
4,6	50,28571	49,71429	4,59504
5,0	103,07692	-3,07692	
5,0	58,28571	41,71429	4,85472
5,4	115,38462	-15,38462	
5,4	70,85714	29,14286	5,01415

Table 3: Error discussion for table 2

It does not make any these to calculate further with these values so we have a look at the exacter formulas which should give us better results, which take case that some I<sup>-</sup> is till absorbing light in the acid solution:

$$E = E_{IH} + E_{I^-} \quad (7)$$

Taking into account this fact we get the following fomulas:

$$E_{\lambda_1}(IH) = E_{\lambda_1}(IH_{\text{pure}}) \cdot \frac{E_{\lambda_2}(\text{mix})}{E_{\lambda_1}(IH_{\text{pure}})} \quad (8)$$

$$E_{\lambda_1}(I^-) = E_{\lambda_1}(\text{mix}) - E_{\lambda_1}(IH) \quad (9)$$

$$\%I^- = \frac{E_{\lambda_1}(I^-)}{E_{\lambda_1}(I^-_{\text{pure}})} \cdot 100\% \quad (10)$$

$$\%IH = 100\% - \%I^- \quad (11)$$

solution	$E_{\lambda_1}(\text{mix})$	$E_{\lambda_1}(I^-)$ (8 + 9)	%I <sup>-</sup> (10)	%IH (11)	pKc
4,6	0,064	0,04561	70,16264	29,83736	4,22865
5,0	0,067	0,05157	79,33187	20,66813	4,41585
5,4	0,075	0,06422	98,79560	1,20440	3,48603

Table 4: Exact calculation 1

$$E_{\lambda_2}(I^-) = E_{\lambda_2}(I^-_{\text{pure}}) \cdot \frac{E_{\lambda_1}(\text{mix})}{E_{\lambda_1}(I^-_{\text{pure}})} \quad (12)$$

$$E_{\lambda_2}(IH) = E_{\lambda_2}(\text{mix}) - E_{\lambda_2}(I^-) \quad (13)$$

$$\%IH = \frac{E_{\lambda_2}(IH)}{E_{\lambda_2}(IH_{\text{pure}})} \cdot 100\% \quad (14)$$

$$\%I^- = 100\% - \%IH \quad (15)$$

solution	$E_{\lambda 2}(\text{mix})$	$E_{\lambda 2}(\text{IH})$ (12 + 13)	%IH (14)	%I <sup>-</sup> (15)	pKc
4,6	0,087	0,06435	36,77363	63,22637	4,36464
5,0	0,073	0,04929	28,16703	71,83297	4,59342
5,4	0,051	0,02446	13,97802	86,02198	4,61084

Table 5: Exact calculation 2

The pKc value (3,48603) of the buffer solution at pH 5.4 seems to be wrong. The reason for the bad value could be a bad solution or a bad cuvette of the pH 5.4 buffer solution.

Considering the exact values we finally get an average value of  $\text{pKc}_{\text{exact}} = 4,28324$ .

### 3.2.3 Error calculation

The main error is due to the measurement of the extinction values. With *Kortuem* we get the following error:

$$\frac{dE}{E} = \pm \frac{\log e}{E} \cdot \frac{dT}{T} \quad (16)$$

With  $dT = 1\%$  we get on the basis of the error curve of figure 4 with a minimum at  $E = 0,4343$  an error of  $dE/E = \pm 2,72\%$  which is set arbitrary to  $dE/E = 1$ .

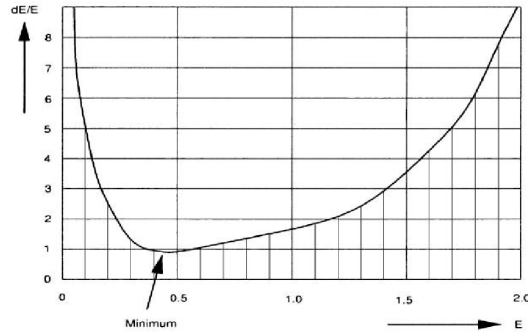


Figure 4: Error curve

From these  $dE/E$  errors we can also calculate the errors of the pKc-terms. Therefore we have to combine the equations (10) and (14) with (6):

$$\begin{aligned}
 \text{pKc} &= \text{pH} - \log \frac{\%I^-}{\%HI} \\
 &= \text{pH} - \log \frac{E_{\lambda 1}(I^-) \cdot E_{\lambda 2}(\text{IH}_{\text{pure}})}{E_{\lambda 1}(I_{\text{pure}}^-) \cdot E_{\lambda 2}(\text{IH})} \\
 &:= \text{pH} - \log \frac{E_1 \cdot E_2}{E_3 \cdot E_4}
 \end{aligned}$$

With the gaussian error propagation and  $d(\log_a x)/dx = 1/(x \ln a)$  following maximum error is given:

$$\begin{aligned}
\Delta pKc &= \sum_{i=1}^n \left| \frac{\partial pKc}{\partial E_i} \cdot \Delta E_i \right| \\
&= \left| \frac{\partial pKc}{\partial E_1} \cdot \Delta E_1 \right| + \left| \frac{\partial pKc}{\partial E_1} \cdot \Delta E_1 \right| + \left| \frac{\partial pKc}{\partial E_1} \cdot \Delta E_1 \right| + \left| \frac{\partial pKc}{\partial E_1} \cdot \Delta E_1 \right| \\
&= \left| \frac{\Delta E_1}{\ln 10 E_1} \right| + \left| \frac{\Delta E_2}{\ln 10 E_2} \right| + \left| -\frac{\Delta E_3}{\ln 10 E_3} \right| + \left| -\frac{\Delta E_4}{\ln 10 E_4} \right|
\end{aligned}$$

	$E$ (abscissa)	ordinate	$dE/E$	$\Delta pKc$
	$E_2 = 0,175$	2,8	0,07616	
	$E_3 = 0,065$	6,0	0,16320	
4,6	$E_1 = 0,064$	6,0	0,16320	$\pm 0,23862$
	$E_4 = 0,087$	5,4	0,14688	
5	$E_1 = 0,067$	6,0	0,16320	$\pm 0,24216$
	$E_4 = 0,073$	5,7	0,15504	
5,4	$E_1 = 0,075$	5,7	0,15504	$\pm 0,25988$
	$E_4 = 0,051$	7,5	0,20400	

Table 6: Error calculation for pKc

As a result we got a maximum error for pKc of  $\pm 0,25988$  (Table 6) and a final result for the exact calculation of the constant of balance of the metyl red indicator of  $pKc_{exact} = 4,28 \pm 0,26$ .

## 4 Appendix

wavelength	$E_{HCL}$	$E_{NaAc}$	$E_{pH4.6}$	$E_{pH5.0}$	$E_{pH5.4}$
320	-0,09	-0,09	-0,09	-0,09	0,025
330	-0,056	-0,058	-0,045	-0,036	0,025
340	-0,019	-0,021	-0,007	0,001	0,021
350	-0,004	0	0,009	0,002	0,021
360	0,003	0,014	0,021	0,03	0,03
370	0,003	0,023	0,026	0,034	0,035
380	0,021	0,047	0,048	0,056	0,058
390	0,022	0,047	0,048	0,058	0,062
400	0,02	0,056	0,053	0,06	0,065
410	0,019	0,057	0,054	0,061	0,067
420	0,022	0,06	0,057	0,062	0,07
430	0,03	0,064	0,062	0,067	0,075
440	0,037	0,065	0,064	0,067	0,075
450	0,05	0,064	0,066	0,069	0,076
460	0,066	0,06	0,069	0,07	0,074
470	0,087	0,055	0,072	0,071	0,072
480	0,11	0,051	0,077	0,074	0,069
490	0,132	0,04	0,077	0,072	0,062
500	0,154	0,032	0,081	0,072	0,057
510	0,169	0,025	0,083	0,072	0,052
520	0,175	0,023	0,087	0,073	0,051
530	0,17	0,02	0,085	0,07	0,048
540	0,158	0,017	0,08	0,066	0,044
550	0,14	0,022	0,081	0,068	0,047
560	0,107	0,016	0,055	0,049	0,036
570	0,07	0,016	0,055	0,049	0,036
580	0,04	0,014	0,038	0,038	0,03
590	0,022	0,012	0,026	0,03	0,025
600	0,014	0,011	0,02	0,027	0,02
610	0,012	0,011	0,019	0,025	0,022
620	0,012	0,011	0,018	0,025	0,022
630	0,01	0,011	0,018	0,024	0,022

Table 7: Original values of the spectras

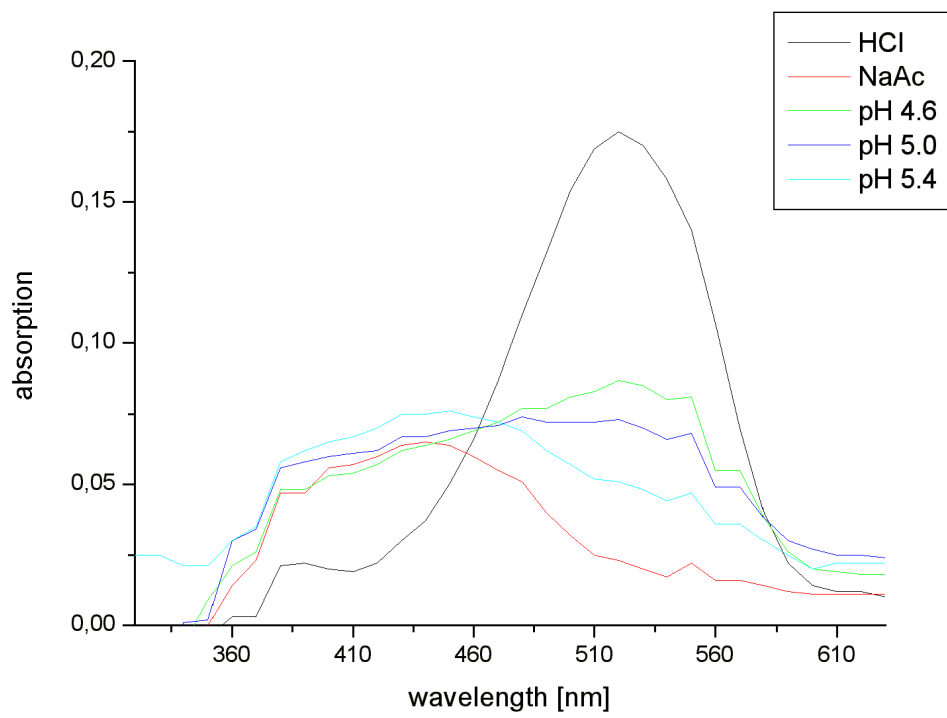


Figure 5: Original absorption spectras for methyl red