تفريغ لاب تحليل آلي

اسم الموضوع:

Exp 5: Ultraviolet-Visible Spectroscopy - Effect of Solvent on λmax

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Aim of the experiment

- Study the effect of solvent polarity and pH on the UV spectrum in term of λ max and absorption intensity and explain the results by electronic transition.

Polarity & PH of solvent

أثروا على

λmax ← Absorption intensity

Qualitative
Quantitative

Experiment 5: Ultraviolet-Visible Spectroscopy – Effect of Solvent on λ_{max}

INTRODUCTION

Chromophore
→ Color يعطي ال
→ Absorption يعمل
electromagnetic ال
Radiation

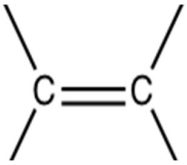
The part of the molecule that is responsible for imparting color to the to the molecule term chromophore. It is defined as any group which exhibits absorption of electromagnetic radiation in the visible or ultraviolet region.

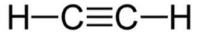
or π Bond non Bonding e⁻

e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

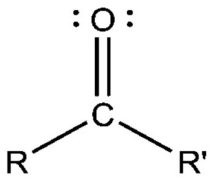
بصفة بناءً على Transitions type

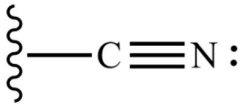
- Chromophores in which the group is having π electrons undergo **π → π*** transitions. Ex: ethylene, acetylenes.





- Chromophores having both π electrons and n electrons undergo two types of transitions: **π→ π*** and **n→ π***. Ex: carbonyl, nitrile.





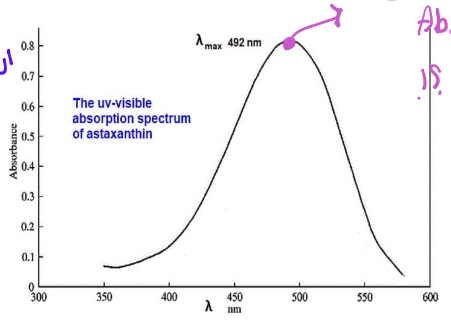
Chromophore shifts and effect of solvent on λ_{max}

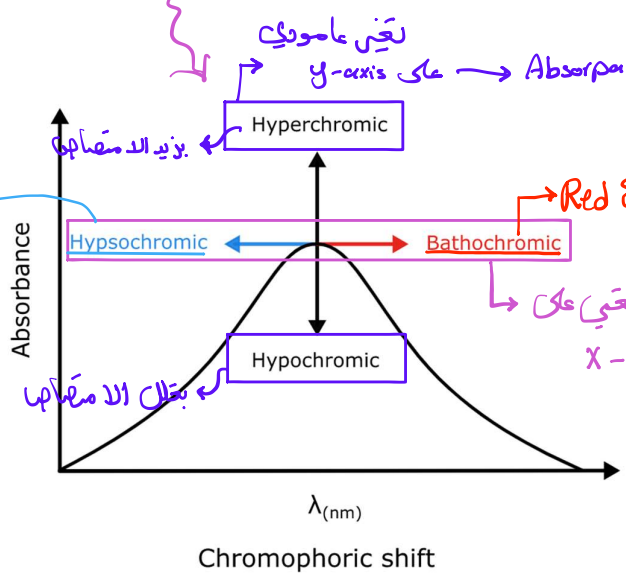
λ_{max} هي Peak اعلى
وبارتفاعها اعلى Absorbance
متفعتين !!

Peak قيمة λ عند اعلى ← Peak ارتفاع ال

Position of the absorption maximum wavelength (λ_{max}) and intensity of absorption can be modified in different ways by some ① structural changes or ② change of solvent.

Wavelength change is either **bathochromic** or **hypsochromic**, while absorbance intensity change is either **hyperchromic** or **hypochromic**.





Chromophoric shift

- **Bathochromic Shift or Red shift**

The shift of an absorption maximum towards longer wavelength or lower energy is called bathochromic shift. The red color has a longer wavelength than the other colors in the visible spectrum, therefore this effect is also known as red shift.

- **Hypsochromic Shift or Blue Shift**

The shift of absorption maximum towards the shorter wavelength or higher energy is called hypsochromic shift. The blue color has a lower wavelength than the other colors in the visible spectrum and hence this effect is also known as blue shift.

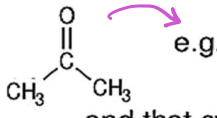
- **Hyperchromic Effect**

It is an effect that results in increased absorption intensity. The introduction of an auxochrome usually causes hyperchromic shift.

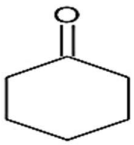
- **Hypochromic Effect**

An effect that results in decreased absorption intensity is called hypochromic effect. This is caused by a group which distorts the geometry of the molecule.

Structural change effect on λ_{max}

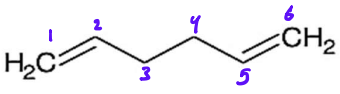


e.g. Acetone which has λ_{max} = 279 nm and that cyclohexane has λ_{max} = 291 nm.

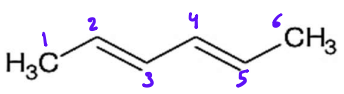


When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has λ_{max} = 178 nm
2,4 - hexadiene has λ_{max} = 227 nm



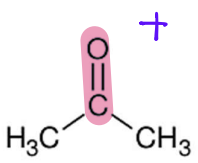
Not Conjugated



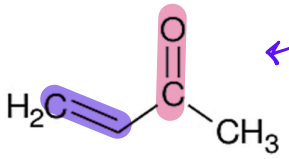
Conjugated

3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

e.g. Ethylene has λ_{max} = 171 nm
Acetone has λ_{max} = 279 nm



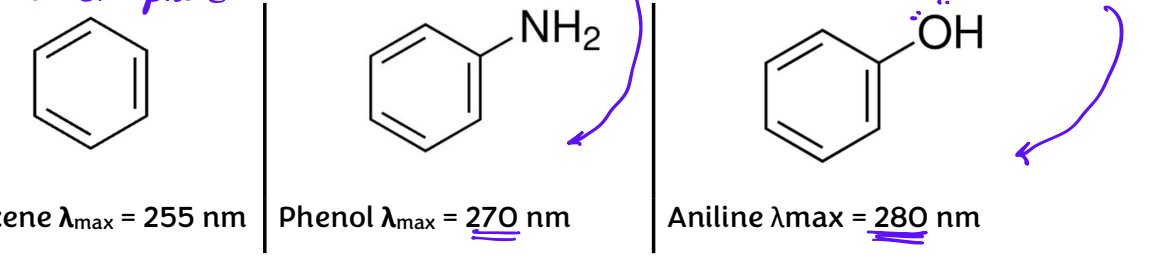
Crotonaldehyde has λ_{max} = 290 nm



Auxochrome is a functional group attached to the chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of the absorption.

It can also be defined as the functional group with **non-bonding electrons** that does not absorb radiation in near UV region but when attached to a chromophore **alters the wavelength** and intensity of absorption.

- Examples of auxochromes:



Benzene λ_{max} = 255 nm | Phenol λ_{max} = 270 nm | Aniline λ_{max} = 280 nm

- If an auxochrome is introduced to the compound the intensity of absorption increases causing a hyperchromic shift:

Pyridine
λ_{max} = 257 nm
ε = 2750

2-methyl pyridine
λ_{max} = 260 nm
ε = 3560

Solvent change effect on λ_{max}

Solvents play an important role in UV spectroscopy and the solvent for a sample should be selected in such a manner that it should neither absorb in the region of absorption nor affect the absorption of the sample. Common solvents used are water, methanol, ethanol, dilute acids and dilute alkalies.

The solvent exerts a profound influence on the quality and shape of spectrum. The absorption spectrum of pharmaceutical substance depends practically upon the solvent that has been employed to solubilize the substance.

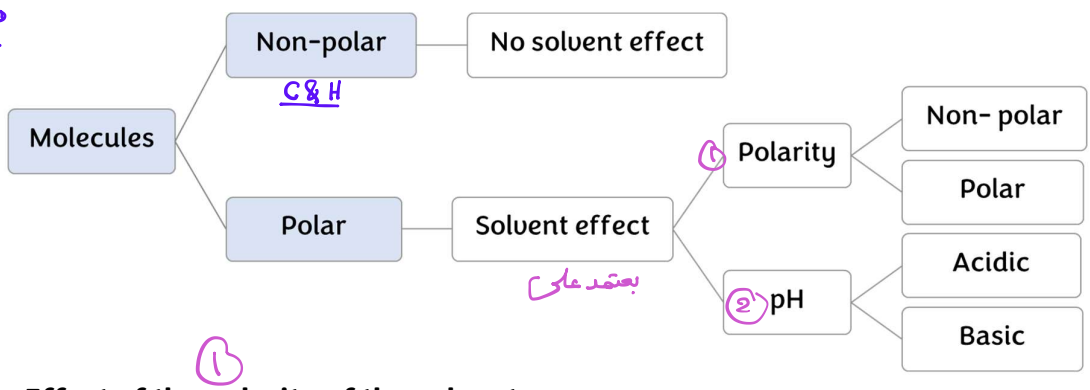
A drug may absorb a maximum radiation energy at particular wavelength in one solvent but shall absorb partially at the same wavelength in another solvent.

- Examples:

Bromophenol blue in HCL → λ_{max} at 437 nm

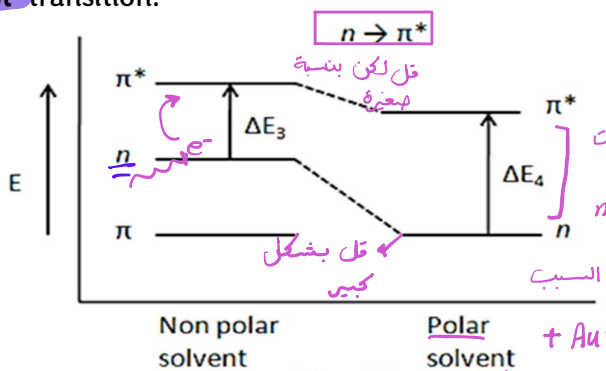
Bromophenol blue in distilled water → λ_{max} at 591 nm

Effect of solvent can be summarized in the following chart:



❖ Effect of the polarity of the solvent

Polarity causes a pronounced effect on the position and intensity of absorption bands. This increase is due to the **n→π*** and **π→π*** transitions. In the presence of polar hydrolytic solvent (i.e., water) hydrogen bonds form with the lone pair of electrons of auxochrome. As a result, the auxochrome's energy lowers to an equal amount of the bond formation energy, and hence the energy gap between n and **π*** increases, so, a hypsochromic shift is observed for **n→π*** transition.



$\Delta E_4 > \Delta E_3$

$\lambda_3 > \lambda_4$

Lowering of energy level of non-Bonding e- orbital

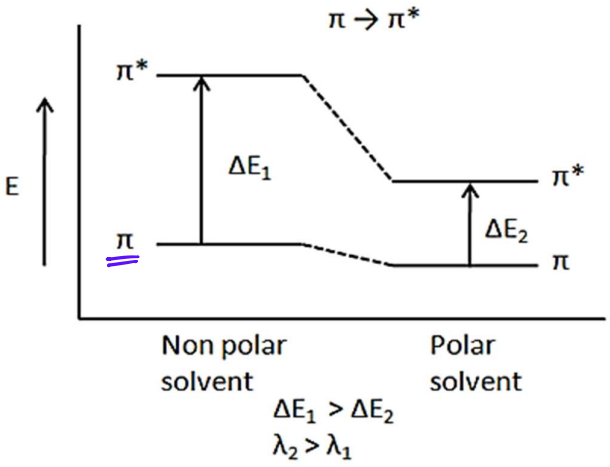
Hypsochromic Shift

$n \rightarrow \pi^*$ Transitions	Solvent	Absorption wavelength
	non-polar Hexane	279 nm
	Polar Methanol	270 nm
	more polar Water	264 nm

Polarity ↓ زيادة ↓ λ_{max} قلت

While for **π→π*** transition the **π*** orbital is more polar than **π** orbital therefore it is stabilized to a greater extent in the presence of a polar solvent. This will cause a bathochromic shift because the energy gap between **π→π*** is reduced due to the stability of the **π*** orbital.

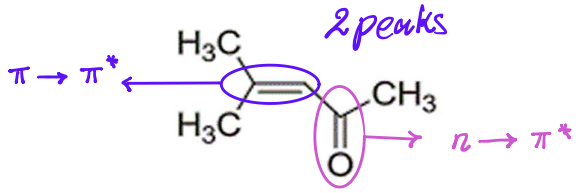
Red Shift
λ_{max} ↑



E↓ → λ↑

$\pi \rightarrow \pi^*$ Transitions	Solvent	Absorption wavelength
	Hexane	230 nm
	Water	243 nm

λ↑ مع زيادة Polarity ال



Effect of solvent on the electronic transition

Solvent	$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$	
	λ_{max}	ε	λ_{max}	ε
non-polar Hexane	230 ↓	↑ 12,600	327 ↑	↓ 98
Polar Ethanol	237 ↓	↑ 12,600	315 ↑	↓ 78
more polar Water	245 ↓	↑ 10,000	305 ↑	↓ 60

↓ intensity قلت

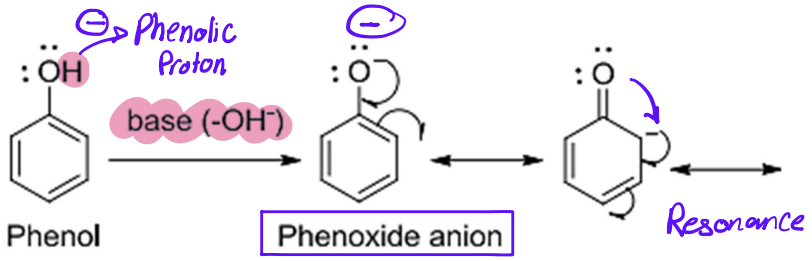
❖ **Effect of the solvent pH**

The pH of the sample solution can also have a significant effect on absorption spectra. The absorption spectra of certain aromatic compounds such as phenols and anilines change on changing the pH of the solution.

Phenols and substituted phenols are acidic and display sudden changes in their absorption's maxima upon the addition of a base. After the removal of the phenolic proton, we get phenoxide ion. In the phenoxide ion lone pairs on the oxygen is delocalized over the π-system of the aromatic ring and increases the conjugation of the same.

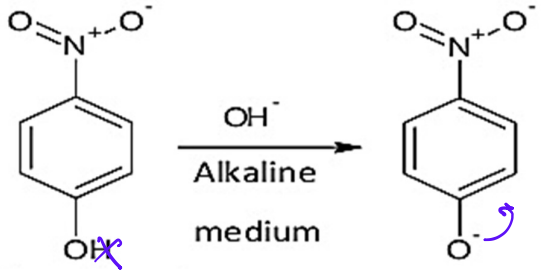
Extended conjugation leads to a decrease in the energy difference between **π→π*** orbitals, which results in red or bathochromic shift (to longer wavelength), along with an increase in the intensity of the absorption.

➢ Examples:



Neutral		**Basic**
λ_{max} = 210 (6200)	↑ λ_{max} ↑ intensity	λ_{max} = 235 (9400)
270 (1450)		287 (2600)

➢ In alkaline medium, **p-nitrophenol** shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electrons.

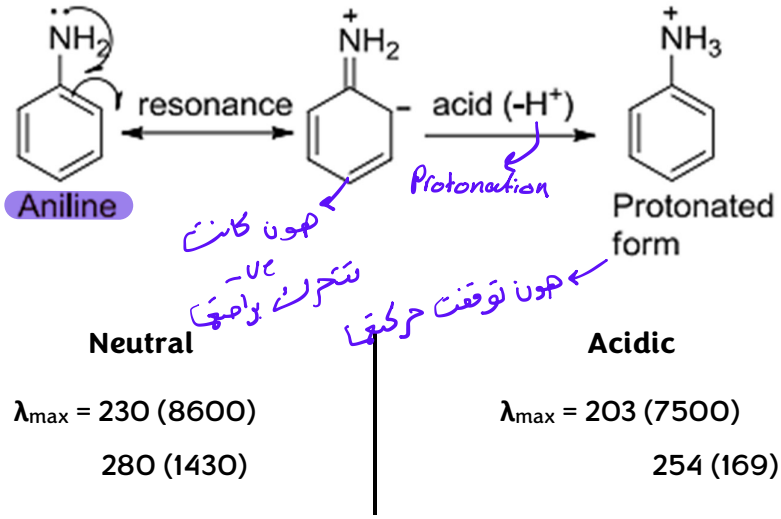


p-nitrophenol

λ_{max} = 255 nm → λ_{max} = 265 nm

Red Shift

- Similarly, an aromatic amine gets protonated in an acidic medium which disturbs the conjugation between the lone pair on nitrogen atom and the aromatic π-system. As a result, blue shift or hypsochromic shift (to shorter
- wavelength) is observed along with a decrease in intensity.



PRACTICAL PART

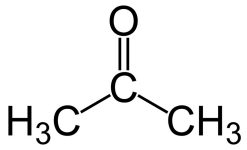
GLASSWARE	CHEMICALS
Volumetric flasks 50 & 10 ml	Paracetamol stock solution 1mg/ml
Beakers	Distilled water
Quartz cuvette	Acetone
Volumetric pipette 1, & 5 ml	Cyclohexane, heptane, or decan
Graduated pipette	0.1 M HCl
	0.1 M NaOH

AIM OF THIE EXPERIMENT

- *To Study the effect of solvent polarity and pH on the UV spectrum in term of λ_{max} and absorption intensity and explain the results by electronic transition.*

PROCEDURE

Part 1: Effect of solvent polarity on the λ_{max} of Acetone:



- Prepare the following solutions:

· Acetone in H2O (0.5% υ/υ)

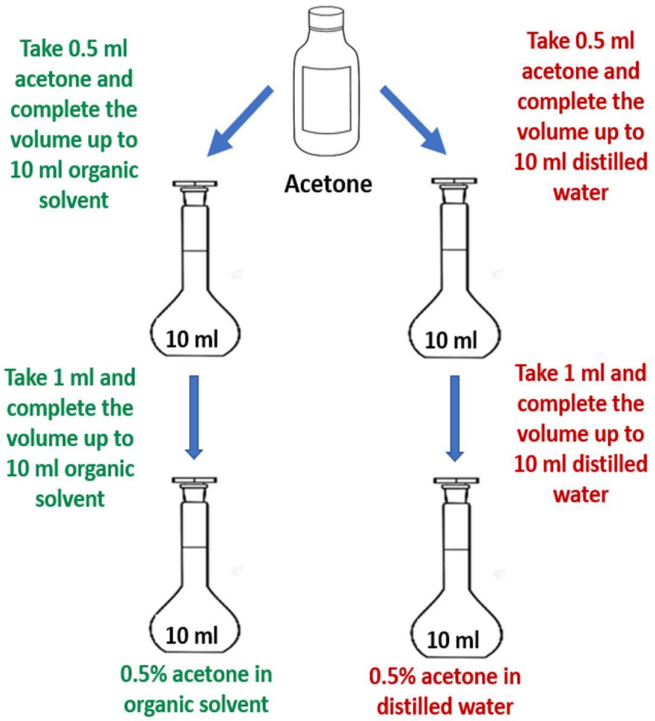
1. Take 0.5 ml of acetone into 10 ml volumetric flask and complete the volume up to the mark with distilled water.
2. Put 1 ml of the above solution into a 10 ml volumetric flask and complete the volume up to the mark with distilled water.

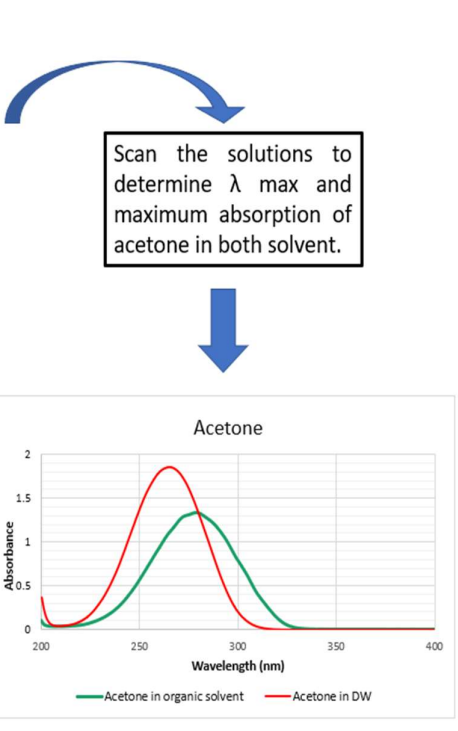
· Acetone in an organic solvent "cyclohexane, heptane or decan" (0.5% υ/υ)

1. Take 0.5 ml of acetone into 10 ml volumetric flask and complete the volume up to the mark with the chosen organic solvent.
2. Take 1 ml of the above solution into a 10 ml volumetric flask and complete the volume up to the mark with the same organic solvent.

- Scan (obtain UV spectrum) for each solution between 200-400nm.

PART 1 ROCEDURE DIAGRAM

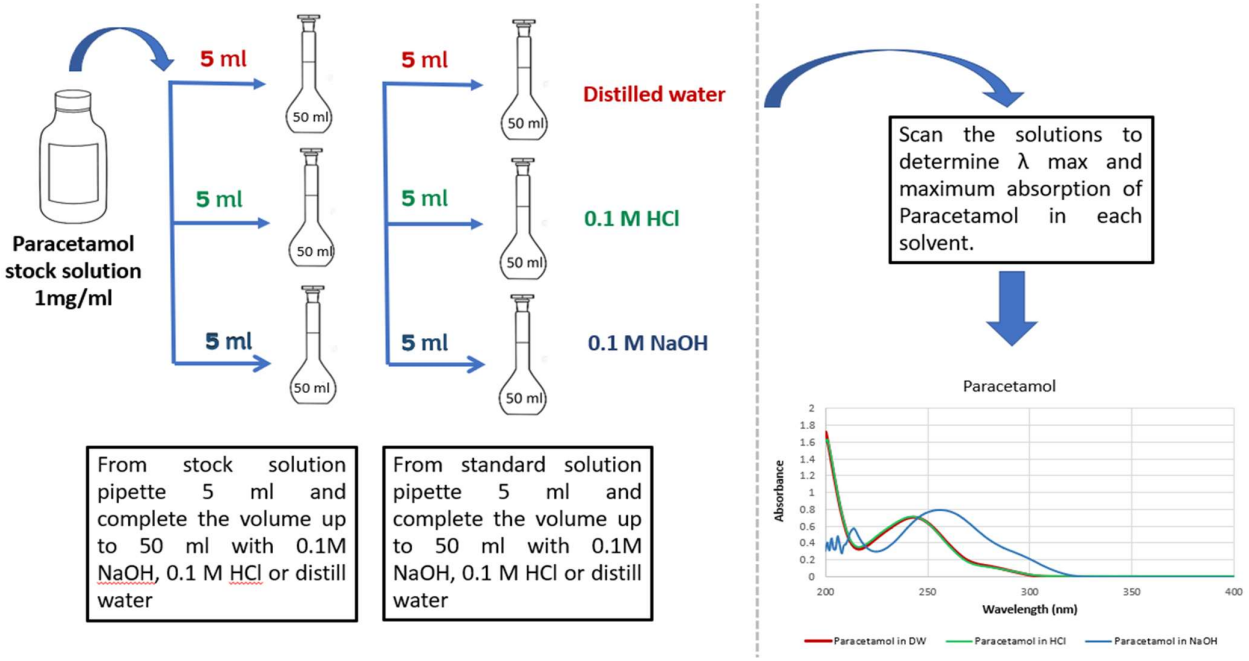




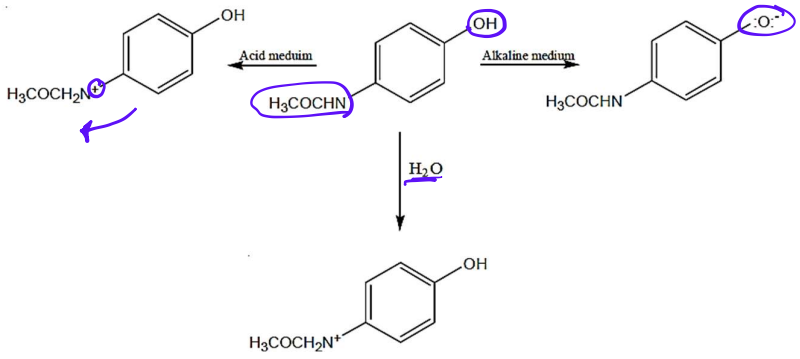
Part 2: Effect of solvent pH on the λ_{max} of Paracetamol:

1. Dissolve 50 mg paracetamol powder in a 50ml distilled.
2. Take 5ml of the above solution into 50ml volumetric flask and dilute up to volume with 0.1M NaOH.
3. Take 2.5 ml of the above solution into 25 ml volumetric flask and complete the volume up to the mark with 0.1M NaOH.
4. In the same way, prepare paracetamol solution in water and 0.1M HCl and record the weights in the report sheet.
5. Take each prepared solution, of the final concentration, and measure the absorbance at different wavelengths against the blank by scanning over the range (200 – 400) nm and record λmax and the absorbance value in the report sheet.

PART 2 ROCEDURE DIAGRAM



What happens with Paracetamol in different pH medium?



Chat GPT

في الصورة، يبدو أن هناك توضيحًا لكيفية تفاعل الباراسيتامول **(Paracetamol)** في بيئات مختلفة من حيث الرقم الهيدروجيني **(pH)**. التغيرات في بنية الباراسيتامول تؤثر على الامتصاصية **(Absorbance)** والطول الموجي **(λmax)** في الطيف فوق البنفسجي أو المرئي.

ماذا يحدث للباراسيتامول في أوساط مختلفة؟

1. في وسط حمضي:

- عند وجود وسط حمضي **(pH** منخفض)، قد يحدث بروتون**ation** (إضافة بروتون) إلى مجموعة الأميد **(-NH)** أو مجموعات أخرى في الجزيء. هذا قد يؤدي إلى تغيرات في الطيف الامتصاصي، حيث يحدث تغير في **λmax** بسبب التغيرات الإلكترونية في الجزيء.

2. في وسط قاعدي:

- في وسط قاعدي **(pH** مرتفع)، يحدث إزالة للبروتون **(Deprotonation)** من المجموعة الهيدروكسيلية **(-OH)** الموجودة على الحلقة العطرية. ينتج أيون فينولات **(Phenolate ion)**، وهو أكثر استقرارًا إلكترونيًا. هذا التغير يؤدي إلى زيادة في الامتصاصية **(Absorbance)** وقد يؤدي إلى تغير **λmax** باتجاه أطوال موجية أطول.

3. تفاعل مع الماء:

- إذا كان هناك تفاعل مع الماء في ظروف معينة، قد يحدث تحلل أو تغير إضافي في البنية الكيميائية للباراسيتامول.

تأثير ذلك على **λmax** والامتصاصية:

- **λmax** (الطول الموجي الأقصى):
  - في وسط قاعدي، يحدث انتقال للطول الموجي إلى أطوال أكبر **(Red shift)**، بسبب تكوين أيون الفينولات.
  - في وسط حمضي، قد يحدث انتقال للطول الموجي إلى أطوال أقصر **(Blue shift)**.
- الامتصاصية **(Absorbance)**:
  - الامتصاصية تزداد عادةً في الوسط القاعدي بسبب زيادة استقرار الفينولات. في المقابل، في الوسط الحمضي قد تتناقص الامتصاصية.