

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING

**TITLE: ELECTRONIC ABSORPTION SPECTRA OF SOME Cu(II)
COMPLEXES.**



NAME: AMPAW-ASIEDU, MERCY
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I.D. NO: 3643609
T.A.: NESTA BOTEY- SAM
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Aims and Objectives:

- 1 To determine the acid dissociation constant of the indicator, phenol red using the Spectrophotometer method.
- 2 To learn how to use the pH-meter to determine the pH of a solution.
- 3 To learn how to use the spectrophotometer to measure the absorbance of a given solution.

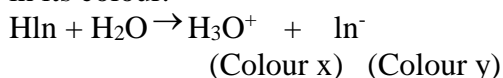
INTRODUCTION

An acid-base indicator is a weak organic acid or base added to a solution to indicate by colour change the point at which equivalent amounts of the acid has reacted with equivalent amount of the base. Acid base indicators can exist in either an acid or base form. The two forms have different colours. Thus the indicator turns one colour in an acid and turns another colour in a base. Knowledge of the pH at which the indicator turns from one form to the other can help one to tell whether a solution has a lower or higher pH (i.e. acidic or basic).

HOW AN ACID-BASE INDICATOR WORKS

An acid-base indicator can also be defined as weak organic acid or base that contains a highly delocalised planar pi-bonding system. In a sufficiently acidic solution the indicator is protonated (say HIn). In a sufficiently basic solution the indicator is converted to its conjugate base (say In⁻).

The deprotonation of HIn changes the structure of the indicator, which alters the pattern of electron delocalisation in the pi system. This change in the indicator's delocalised pi system also causes a change in its colour.



The concentration of an indicator is negligible compared to the concentration of the solution to which it is added. Indicators are also usually present as minor species in the solution. Therefore the colour change is often determined by the dominant equilibrium. Hence in a sufficiently acidic solution, the equilibrium will shift to the left, producing colour 'x', while in a sufficiently basic solution the equilibrium shifts to the right to give colour 'y'.

Indicators are weak acids or bases, therefore they dissociate partially in aqueous solution.

From the equation above the acid dissociation constant, K_a is given by

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

Rearranging and taking logs gives:

$$\text{pH} = \text{p}K_a + \frac{\log [\text{In}^-]}{[\text{HIn}]}$$

As the two forms the indicator has different colours, with the help of the spectrophotometer, absorbance measurement can be used to determine the $\text{p}K_a$ of the indicator from the equation

$$\text{pH} = \text{p}K_a + \log \frac{(A - A_{\text{HIn}})}{(A_{\text{In}} - A)}$$

Where "A" is the absorbance at a wavelength of 558nm

A_{HIn} is the minimum absorbance

A_{In} is the maximum absorbance

APPARATUS AND CHEMICALS

0.067 mol dm⁻³ KH₂PO₄
0.067 mol dm⁻³ NaHPO₄

0.025 mol dm⁻³ NaB₄O₃ . 10H₂O
0.025 mol dm⁻³ NaHCO₃

0.1 mol dm⁻³ HCl
Spectrophotometer
pH meter

0.025 mol dm⁻³ Na₂CO₃

PROCEDURE

- 1) The required amounts of each of the solutions provided were measured into a beaker to prepare the buffer solution.
- 2) Exactly 1 cm³ of phenol red was added to 25 cm³ of each of the buffers prepared and their pH was measured (using the pH meter) and recorded.
- 3) Later with the help of the spectrophotometer, the absorbance of each of the solutions in the range 350 to 650 nm was measured and recorded.
- 4) Also the absorbance of each of the solutions was measured at a wavelength of 558 nm.
- 5) Using A_{HIn} as the minimum absorbance and A_{In} as the maximum absorbance value the quantity $\log [(A - A_{HIn}) / (A_{In} - A)]$ was calculated.
- 6) A graph of pH against $\log [(A - A_{HIn}) / (A_{In} - A)]$ was plotted and y-intercept was determined.
- 7) $\log [(A - A_{HIn}) / (A_{In} - A)]$

TABLE OF VALUES

pH	Buffer /cm ³	350λ	400λ	450λ	500λ	550λ	600λ	650λ	558λ
6.0	KH ₂ PO ₄ /Na ₂ HOP ₄	3.9999	0.3784	0.3010	0.2385	0.2010	0.1730	0.1490	0.1952
6.4	KH ₂ PO ₄ /Na ₂ HOP ₄	3.9999	0.0466	0.0330	0.0254	0.0256	0.0238	0.0214	0.0240
6.8	KH ₂ PO ₄ /Na ₂ HOP ₄	3.9999	0.0618	0.0330	0.0216	0.0132	0.0107	0.0821	0.0121
7.2	KH ₂ PO ₄ /Na ₂ HOP ₄	0.0000	0.0227	0.0168	0.0118	0.0016	-0.0045	-0.0040	-0.0023
7.6	KH ₂ PO ₄ /Na ₂ HOP ₄	3.9999	0.5288	0.5579	0.5541	0.5574	0.6573	0.5402	0.5540
8.0	KH ₂ PO ₄ /Na ₂ HOP ₄	0.0477	0.0273	0.0241	0.0471	0.0143	0.0023	0.0070	0.0051
8.4	HCl/Borax/H ₂ O	3.9999	0.0826	0.1007	0.1277	0.0811	0.0774	0.0726	0.0811
8.8	HCl/Borax/H ₂ O	0.0000	0.6181	0.0450	0.813	0.0385	0.0200	0.0194	0.0280
9.0	HCl/Borax/H ₂ O	0.3008	0.0935	0.1041	0.1405	0.0974	0.0792	0.0886	0.0826
10.0	NaHCO ₃ / Na ₂ CO ₃	-0.3008	0.0417	0.0544	0.0469	0.0214	0.2050	0.3010	0.0214

Ph	Wavelength (λ)	Absorbance A	A - A _{HIn}	A _{In} - A	$\frac{A - A_{HIn}}{\log A_{In} - A}$
6.0	558	0.1952	0.1975	0.3594	-0.2600
6.4	558	0.0240	0.0263	0.5310	-1.3051
6.8	558	0.0121	0.0144	0.5429	-1.5763
7.2	558	-0.0023	0.0000	0.5573	0.0000
7.6	558	0.5540	0.5563	0.0000	0.0000
8.0	558	0.0051	0.0074	0.5499	-1.8711
8.4	558	0.0811	0.0834	0.4739	-0.7545
8.8	558	0.0280	0.0303	0.5270	-1.2404
9.0	558	0.0826	0.0849	0.4724	-0.7454
10.0	558	0.0214	0.0237	0.5336	-1.3525

$$\frac{A - A_{HIn}}{\log A_{In} - A}$$

From the equation $\text{pH} = \text{pKa} + \log \frac{A - A_{HIn}}{A_{In} - A}$ $y = mx + c$
Using the method of least squares in which

$$\sum y = m \sum x + nc \dots\dots\dots (1)$$

$$\sum xy = m \sum x^2 + c \sum n \dots\dots\dots (11)$$

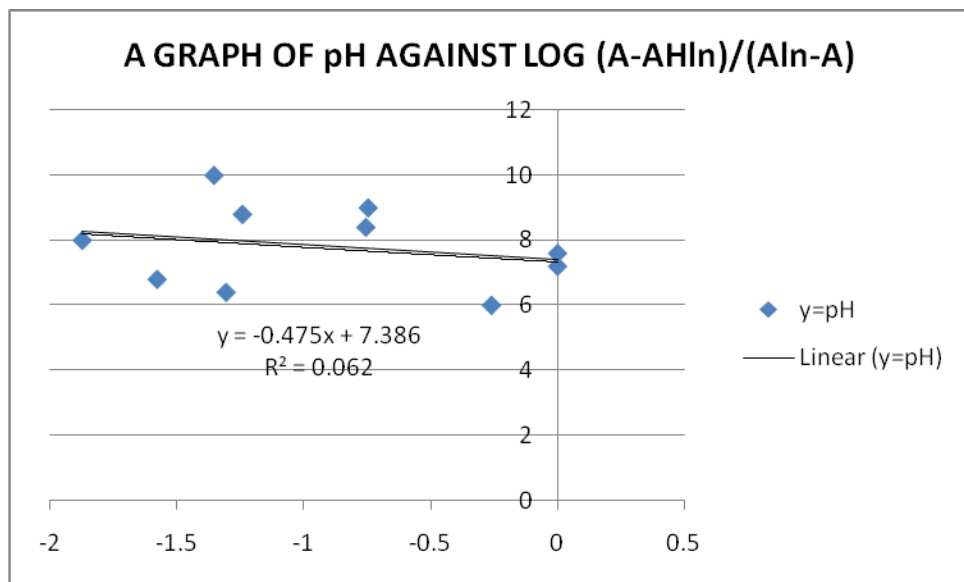
The gradient m is calculated from

$$m = \frac{n \sum xy + (\sum x)(\sum y)}{n \sum x^2 + (\sum x)^2} \dots\dots\dots (I)$$

and the intercept, c = $\frac{\sum y - m \sum x}{n}$ (11)

where n = number of terms

X = $\log \frac{A - AHIn}{AIn - A}$	y=pH
-0.2600	6.0
-1.3051	6.4
-1.5763	6.8
0.0000	7.2
0.0000	7.6
-1.8711	8.0
-0.7545	8.4
-1.2404	8.8
-0.7454	9.0
-1.3525	10.0

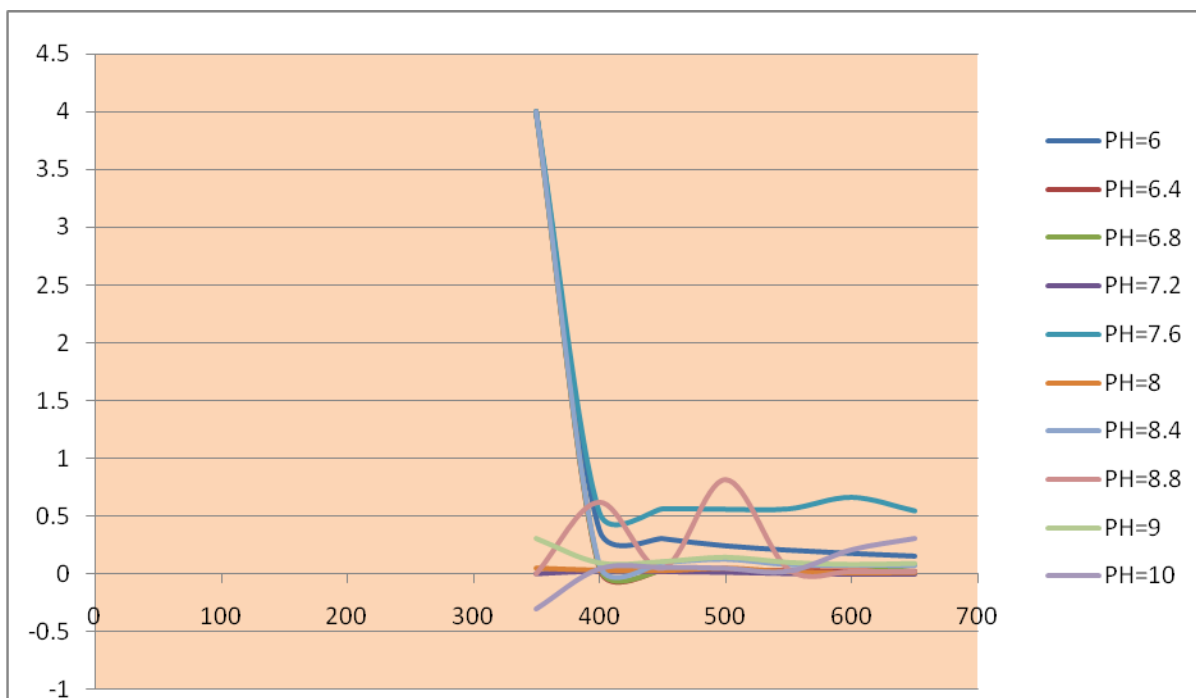


From the graph, the equation of the graph is $y = -0.475x + 7.386$

Therefore the slope of the graph is **-0.475**.

The pKa = the y- intercept = **7.386**

The Ka = $10^{-7.40} = \mathbf{4.111 \times 10^{-8}}$



DISCUSSION

Through research, information was gathered concerning the experiment, it was seen that, the absorbance of buffers increased with increasing pH. Therefore, it can be concluded that the absorbance of a given solution is directly proportional to its pH.

Again, in acidic medium, a buffer solution with pH below 7, the colour of the unionized form of the phenol red is dominant. As the intensity increases, the yellow colour also intensifies as the corresponding pH moves to the acidic medium. This indicates that phenol red changes to yellow in the acidic medium.

Whilst, in the basic medium, the pink colour, that is the basic form of the phenol red becomes dominant. The pink intensified with an increase in pH. The purple colour obtained at higher pH when pink intensifies. Also it was observed that the colour of the indicator (phenol red) in a sufficiently acidic solution (i.e. $\text{pH} < 7$) was yellow. This colour changed to red and to deep red as the pH of the buffers increased above 7. The pK_a of phenol red determined from the graph is 7.40. This value deviated from the true value (i.e. 7.9) appreciably.

POSTLAB

In spectroscopy, an isobestic point is a specific wavelength at which two chemical species have the same molar absorptivity.

The pK_a value is the logarithmic measure of the acid dissociation constant.

-The isobestic point is that point at which most of the curves on the graph meet.

According to the graph the isobestic point is (400nm)

ERROR ANALYSIS

- 1 The concentrations of the solutions prepared may be less, or greater than the assumed values.
- 2 The spectrophotometer may give wrong readings which can affect the results.
- 3 The pK_a value obtained experimentally from the true value due to a defect in the spectrometer thus not recording accurate values.

PRECAUTIONS

- a) It was ensured that the spectrophotometer reading was at zero before any measurement was taken.
- b) It was ensured that the glass wares were thoroughly washed before and after use.
- c) It was ensured that the solutions prepared were not spilled on the tables.

CONCLUSION

The literature pKa value is 7.9 and the experimental value from the calculations is 7.40. The Ka value is 4.111×10^{-8} .

The absorbance of a solution is directly proportional to its pH. The colour of phenol red indicator is yellow in a sufficiently acidic solution and red in a sufficiently basic solution.

The pKa of phenol red indicator can be determined graphically and by calculation.

The working range of phenol red is within the range 4.8-8.0

REFERENCES

Chemistry the central science 7th edition by Brown Lemay Bursten (Page 597-8)

Chemistry the molecular science by Olmsted and Williams (803-5).

