CH1202

Physical Chemistry Laboratory

Experiment Number - 3

Determination of the pK_{in} value of an acid - base indicator by Spectrophotometric Method

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1 Principle

Spectrophotometric methods will be used to determine the acid dissociation constant of an acid-base indicator (Bromocresol green), the light absorption characteristics of its acid and base form. This experiment will provide you with opportunities to refine your understanding of absorption process while providing an opportunity to apply many aspects of acid - base chemistry.

2 Procedure

You will be provided with ≈ 0.5 N NaOH and ≈ 0.5 N acetic acid. Prepare 0.5 N oxalic acid (50 mL) and follow the procedure.

1. Standardisation of NaOH (≈ 0.5 N) using oxalic acid. Than standardise the acetic acid.
2. Prepare 50 mL of exact 0.4 N acetic acid ($pK^H = 4.74$ at $25°C$) and 50 mL of exact 0.4 N NaOH solutions separately by usual procedure.
3. Take 6 hard glass test tubes of uniform dimensions and label them from 1 to 6. Prepare the following series of solutions by proper mixing (experimental pH values may be obtained from chart below, or, may be determined using a pH meter).

Test Tube	Vol. of 0.4N Acetic Acid (mL)	Vol. of 0.4N NaOH (mL)	Volume of Water (mL)	pH (Expt.)	A	$\frac{A}{(A'-A)}$	$\log\frac{[In^-]}{[HIn]}$
1	5.0	0.5	4.5	3.72	0.0783	0.12	-0.92
2	5.0	1.5	3.5	4.27	0.2469	0.52	-0.28
3	5.0	2.5	2.5	4.63	0.3934	1.20	0.08
4	5.0	3.5	1.5	4.99	0.5168	2.53	0.40
5	5.0	4.5	0.5	5.57	0.7144	105.06	2.02
6	0.0	2.5	7.5		$A' = 0.7212$		

4. Add a few drops of bromocresol green indicator to test tube number 6 using a dropper.

5. Set spectrophotometer at 570 nm, adjust the transmittance of water to 100%.

6. Measure the transmittance of the solution in test tube 6. If the transmittance is below 15(i.e. Absorbance is above 0.82), take test tube 7 and add fewer number drops of the indicator to it and measure the transmittance. In this way by adjusting the number of drops of the indicator, adjust the transmittance of the alkaline form between 25 to 15 (absorbance is above 0.60 but below 0.82) using test tube numbers 6 to 8 as required.

7. Add the same number of drops of the indicator as adjusted in step 5 to each of test tubes 1 – 5 and measure their transmittance.

8. Calculate the absorbance (A) values of solutions 1 - 5 and the absorbance (A') of the alkaline solution of the indicator (6, 7 or 8) using the relation:

$$A = \log\frac{100}{T\%} = 2 - \log T$$

9. Plot pH against $\log_{10}\frac{A}{(A'-A)}$ and draw the best straight line of unit slope passing through the experimental points, using the same scale for pH and $\log_{10}\frac{A}{(A'-A)}$ axis. Find pK_{In} from the intercept on the pH axis.

3 Data tabulation and Calculations

3.1 Standardisation of NaOH using Oxalic Acid

Mass of Oxalic Acid (m) = 1.577g
Volume of Oxalic Acid taken (mL) = 50 mL
Strength of Oxalic Acid given = $\frac{m(g)}{V(L)} = 31.54gL^{-1}$

Sl. No.	Vol. of Oxalic Acid	Burette Reading (mL) initial	final	difference	Avg. Vol. (mL)
1	10	0	10	10	10.1
2	10	0	10.2	10.2	
3	10	0	10.1	10.1	

$$N_{Oxalic} \times V_{Oxalic} = N_{NaOH} \times V_{NaOH}$$
$$Strength\ of\ Oxalic\ Acid \times M_{NaOH} \times V_{Oxalic} = Strength\ of\ NaOH \times M_{Oxalic} \times V_{NaOH}$$
$$31.54(gL^{-1}) \times 40(g) \times 10(mL) = Strength\ of\ NaOH \times 90(g) \times 10.1(mL)$$
$$Strength\ of\ NaOH = 13.89gL^{-1}$$

3.2 Standardisation of Acetic acid using NaOH

Strength of NaOH = 13.89 gL^{-1}

Sl. No.	Vol. of Acetic Acid (mL)	Burette Reading (mL) initial	final	difference	Avg. Vol. (mL)
1	10	0	10	10	9.9
2	10	11	20.9	9.9	
3	10	0	9.9	9.9	

$$N_{Acetic} \times V_{Acetic} = N_{NaOH} \times V_{NaOH}$$
$$Strength\ of\ Acetic\ Acid \times M_{NaOH} \times V_{Acetic} = Strength\ of\ NaOH \times M_{Acetic} \times V_{NaOH}$$
$$Strength\ of\ Acetic\ Acid \times 40(g) \times 10(mL) = 13.89gL^{-1} \times 60(g) \times 9.9(mL)$$
$$Strength\ of\ Acetic\ Acid = 20.63gL^{-1}$$

3.3 Preparation of 0.4(N) NaOH (50mL)

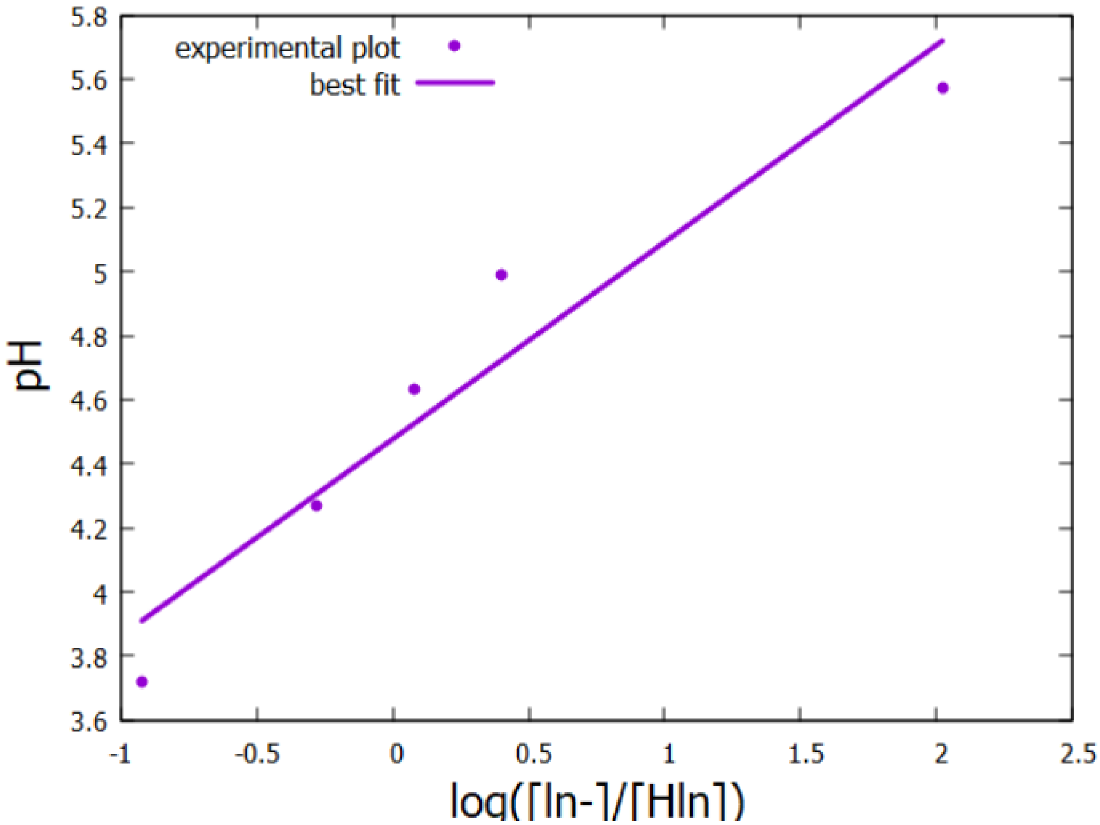
$N_{NaOH} \times M_{NaOH} \times V_{NaOH} = Strength\ of\ standardised\ NaOH \times V$
$0.4(N) \times 40g \times 50mL = 13.89gL^{-1} \times V$
$V = 57.59mL$
$Hence,\ 57.59mL\ of\ 13.89\ gL^{-1}\ NaOH\ is\ required\ to\ make\ 50\ mL\ of\ 0.4\ N\ NaOH$

3.4 Preparation of 0.4(N) Acetic Acid (50mL)

$N_{Acetic} \times M_{Acetic} V_{Acetic} = Strength\ of\ standardised\ acetic\ acid\ \times V$
$N_{Acetic} \times M_{Acetic} \times V_{Acetic} = Strength\ of\ standardised\ acetic\ acid\ \times V$
$V = 58.17ml$
Hence, 58.17 mL of 20.63 gL^{-1} Acetic Acid is required to make 50 mL of 0.4N Acetic Acid.

3.5 Calculation of pK_{In}

Using the equation $pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$ and the above table, we plot a graph of $pH vs. \log \frac{[In^-]}{[HIn]}$:



The y intercept of the above plotted graph is found out to be 4.48 ± 0.1. Therefore the $pKln = 4.48 \pm 0.1$.

4 Conclusion

pK_{In} of Bromocresol Green is 4.48 ± 0.1.