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Aim:- To Determine the Hammett constant of a given substituted benzoic acid by pH measurements.

Apparatus:- pH meter, glass and calomel electrodes or combined electrode, microburette, pipette, beakers etc.

Chemicals:- 0.02M benzoic acid, 0.02M substituted benzoic acid (p-nitro) in 50% ethyl alcohol water mixture, 0.2N NaOH solution.

Theory:- The effect of substituent at meta and para position of aromatic acids on its equilibrium constant can be studied by using Hammett equation. The equation is applicable to aromatic compounds having the same reaction centre present at a side chain and having a substituent in the m or p position to this reaction centre.

According to this equation, the equilibrium constant of the substituted compound $\log K'$ is related to the equilibrium constant of unsubstituted i.e. parent compound along with two constants ρ and σ . It can be given as

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$$\log K = \log K^0 + \rho \sigma$$

$$-\log K = -\log K^0 - \rho \sigma$$

$$pK = pK^0 - \rho \sigma \text{ or } pK^0 - pK = \rho \sigma$$

— where ρ and σ are constants, ρ is known as substituent constant because it depends only on the substituent, σ is known as the reaction constant which mainly depends on the solvent used.

— Therefore by knowing the values of ρ for the different substituents, the change in activity of the compound can be shown. substituents with positive ρ^+ values are stronger electron attractors and those with negative ρ^- values are weak electron attractors. Therefore the reaction with positive ρ^+ values are accelerated by electron withdrawal from benzene ring, whereas those with negative ρ^- value are retarded by electron withdrawal.

Procedure:-

- i) Prepare 0.02M solⁿ of benzoic acid and substituted benzoic acid in 50% ethyl alcohol water mixture.

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- 2) Pipette out 50 ml of 0.02M benzoic acid solution in 100 ml beaker and titrate against 0.2 N NaOH from burette.
- 3) similarly titrate 50 ml of substituted benzoic acid solution against the same NaOH solution.
- 4) Plot a graph, pH Vs Volume of NaOH added for both the acids.

calculations :-

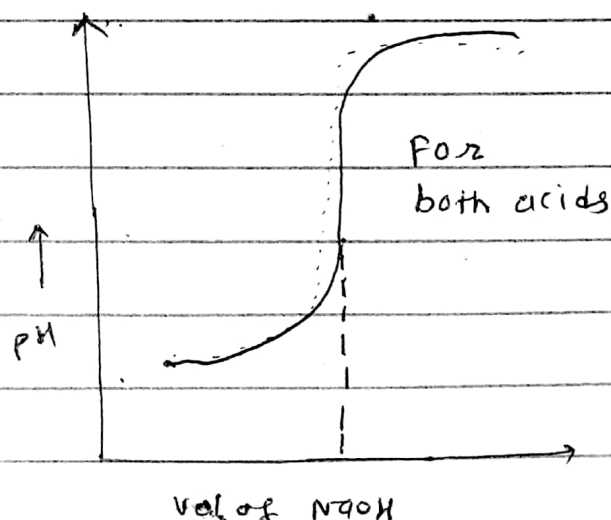
From the graph, determine the dissociation constant of benzoic acid (pK^0) and that of substituted benzoic acid (pK) from the values of pH at half neutralisation points.

Then calculate Hammett constants ' ρ ' by using the equation

$$pK^0 - pK = \rho \cdot \sigma$$

$$\sigma = \frac{pK^0 - pK}{\rho}$$

where $\rho = 1.65$ for
50% alcohol



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Observation table -

pH for benzoic Acid

pH for substituted benzoic Acid

Vol. of NaOH added	pH	Vol. of NaOH added	pH
0.0		0.0	
0.5		0.5	
1.0		1.0	
1.5		1.5	
2.0		2.0	
2.5		2.5	
3.0		3.0	
3.5		3.5	
4.0		4.0	
4.5		4.5	
5.0		5.0	
5.5		5.5	
1		1	
1		1	
1		1	
1		1	
15		15	

Result:- The Hammett constant of the given substituted benzoic acid is - - - -