SUMMARY AND CONCLUSION
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The thesis is divided into three sections and an appendix. Section-I deals with equilibrium studies of the interaction between carbinol base of crystal violet and six aromatic carboxylic acids in benzene medium at temperatures 6.5°C, 10°C, 15°C, 20°C, 25°C, 30°C and 36°C. Section-II deals with kinetic studies of reactions between carbinol base of crystal violet and nine aromatic carboxylic acids in aprotic solvents (benzene, toluene, xylene) at temperatures 6.5°C, 10°C, 15°C, 20°C and 25°C. Section-III reports the results of absorption spectra of methylene blue in benzene. Appendix of thesis reports the results of photo-initiation of vinyl polymerisation by quaternary salts.

SECTION-I

Section-I comprises four Chapters. Chapter-I summarises briefly the developments of various acid-base theories. It also discusses briefly the various methods in particular the indicator method of determining the acid-base strengths in non-aqueous media. Such brief review shows that the relative order of acid strength determined by indicator method in non-aqueous media does not always run parallel with the order found in aqueous medium. Moreover, it is imperative to mention the reference base in reporting relative strengths of acid found by indicator method. Studies in various solvents suggest the formation of ion-pair and complications may arise at higher concentration due to the
formation of higher aggregates. Also, association of carboxylic acid molecules sometimes greatly influence the equilibrium of dye-base interaction.

Chapter-II deals with the general experimental procedure and method of calculation. It also includes the absorption spectra of crystal violet in different solvents and the determination of the total concentration of carbinol base. The extinction coefficient of carbinol base of crystal violet in benzene is also given.

Chapter-III shows the equilibrium results of six acids at temperatures 6.5 to 35°C in benzene medium and these results are discussed in Chapter-IV.

The main points of interest are summarised below:

1. The carbinol base of crystal violet reacts with an acid in benzene medium to give a coloured salt. The reaction reaches an equilibrium at a measurable rate.

2. The simple mass law equation is obeyed within experimental error at particular acid concentration, that is, the values of equilibrium constant $K_a$ are constant when the carbinol base concentration is varied at fixed acid concentration. But the mass law equation does not hold good when the acid concentration is varied at fixed carbinol base concentration and the values of $K_a$ increase rapidly with increase in acid concentration.
(3) The plot of log \((BH^+/A^-)/(B)\) vs -log (HA) for different acids, gives good straight lines with slope equal to 'n'. The value of 'n' varies from acid to acid and is always greater than unity.

(4) It is suggested that various associated forms of acid molecules such as acid-anion complexes in benzene medium provide a satisfactory explanation for the enhanced acidity of the above acids and also for the non-integral values of 'n'.

(5) A fairly good linear relationship is obtained for the above acids when log \(K_\text{a}\) values in benzene for different acids are plotted against the corresponding \(pK_\text{a}\) values in water.

(6) The results at different temperatures indicate that the values of \(K_\text{a}\) decrease with increase in temperature and which means that there is decrease in association of acid-anion complex. Thus, like all other acid-base reactions, the reaction between carbinol base and an acid is exothermic.

SECTION-II

Section-II consists of five Chapters. Chapter-V gives a brief review of current position dealing with kinetics of acid-base reactions. It discusses briefly various types of fast and slow acid-base reactions and the
techniques used for rate measurements. Special emphasis has been given on acid-base catalysed reactions in non-aqueous media. Such discussion reveals the fact that when water is replaced by aprotic solvents, all effects due to interionic or intermolecular attractions are greatly increased and thus inspite of the apparent chemical simplicity of the system, the kinetics of catalysis in aprotic solvents may be more complex than in aqueous medium.

Chapter-VI deals with experimental procedure, treatment of experimental data and method of calculation. Chapter-VII contains the results of kinetic studies at temperature 6.5 to 25°C and these results are discussed in Chapter-VIII. Chapter-IX gives a brief account of a consecutive reaction between catechol and carbinol base of crystal violet in benzene medium, which is visually observed as a slow development of a color which reaches a maximum and then goes on fading.

The main points of interest in this section are summarised below:

(1) The plot of \(-\log(x_e-x)\) vs time gives good straight lines under all conditions, that is, the course of the reaction is strictly unimolecular.

(2) The apparent velocity constant, \(k\) is constant within experimental error, when the concentration of carbinol base is varied at fixed acid concentration. Thus the reaction is strictly of first order with respect to carbinol base. But
The velocity constant (k) increases with increase in acid concentration and unlike the normal catalysed reactions, the first order rate constant is not directly proportional to the acid concentration. The results are expressible by a two-constant additive equation of the type:

\[ k = k_0 c + k_1 c^2 \]

or,

\[ k/c = k_0 + k_1 c \]

and the catalytic constant \( k_0 \) is evaluated graphically. The reaction shows the characteristics of "general acid catalysis" in aprotic media. Since the reaction fails to take place in the absence of the acid, the latter plays the dual role of both reactant and catalyst.

(3) It is believed that the variation of \( k/c \) with \( c \), the acid concentration, is due to the presence of acid-anion complex of carboxylic acids in the solution.

(4) The values of \( k_0 \) are independent of the solvent studied (benzene, toluene and xylene), and do not always run parallel with the acidic strengths of acids.

(5) When the values of \( k_0 \) for different acids are compared with corresponding \( K_a \) values in benzene and water, a fairly linear relationship is obtained for the above acids.

(6) A very good straight line is obtained when values of \( \log k_0 \) are plotted against Hammett's substitution constant \( \sigma \).
(7) The effect of temperature shows that the rate of reaction invariably increases with increase in temperature and the energies of activation of the reaction between carbinol base of crystal violet and various acids lie between 3.7 to 10.2 Kcal/mole.

(8) The individual rate constants ($k_1$ and $k_{-1}$) for dye-acid interaction have been determined by the method of Palit and Bhowmik. The degree of protonation by different acids depends at least partly on the rates of forward and reverse reactions.

(9) In the reaction between carbinol base of crystal violet and catechol, a violet colour develops slowly and reaches a maximum optical density of coloured salt and then starts losing its intensity and finally a colourless salt is obtained. It is a typical consecutive reaction, which can be shown as an interesting lecture demonstration.

SECTION-III

Chapter-X reports a brief study of absorption spectra of methylene blue in benzene. Following the dye extraction technique of Palit, methylene blue dye gives a red coloured extract in benzene. The absorption spectrum of red form of methylene blue has an absorption maxima at 515 m$\mu$. while the absorption maxima of methylene blue in water is at 665 m$\mu$. The red form of methylene blue can be recovered from benzene extract by freeze-drying technique. The absorption spectrum
of the red form of methylene blue in water shows an absorption peak at 620 m\(\mu\) which is exactly at the shoulder of absorption spectra of methylene blue in water and buffer. It is concluded that the red form of methylene blue is not a new form of dye as supposed by Lewis but is a dimer — its red colour in benzene being due to a solvent effect.

The absorption spectra of red form in benzene solution are highly sensitive to acids or polymers containing sulphate and similar endgroups and to comparatively high concentrations of hydroxylic compounds. The peak at 515 m\(\mu\) in benzene is not only shifted under such conditions to longer wavelengths but shows a number of subsidiary peaks.

**APPENDIX**

Appendix of the thesis reports vinyl polymerization in aqueous media by photochemical initiation with quaternary salts. The results show that no polymerisation has been noticed at concentration below C.M.C. of the detergents and \([\eta]\) is rather high, similar to that of emulsion polymerisation. The polymers give test for halogen endgroups by the dye partition technique. The mechanism suggested is of the electron transfer type; the micelles due to their large volume helping to accommodate the electron in the electron transfer mechanism; the solubilization of the monomers in the micelles is probably another favourable factor. In effect this may be regarded as photo-dissociation of the quaternary salts to produce initiating halogen radicals.