

CHAPTER-II

EXPERIMENTAL

SECTION-I

Materials

(i) Processing of Vinyl Monomers

The stabilised vinyl monomers such as methylmethacrylate, methylacrylate, styrene were all washed with two to five percent caustic soda solution until free of stabilisers and then rendered free of alkali by repeated washing with distilled water and then kept over fused calcium chloride for twenty four hours. The dried monomers were then distilled under vacuum; the middle fraction being collected in each case for experimental processes.

Acrylonitrile was free from inhibitor by washing with one sodium carbonate solution, then with one percent sulfuric acid solution and finally with distilled water. Washed monomer was dried over fused calcium chloride and then monomer was collected by double ordinary distillation. Acrylic acid and methacrylic acid monomers were purified by freezing in a refrigerator and finally by distillation, the major middle fraction being collected in each case³⁵.

Vinyl acetate was freed from inhibitor by two to three percent sodium hydroxide solution and then washed with distilled water, dried over fused calcium chloride for twenty four hours. It was then refluxed in an atmosphere of nitrogen with a little benzoyl peroxide catalyst⁹⁵. When the mixture become moderately polymerised, it was distilled finally in an atmosphere of nitrogen at atmospheric pressure. The fraction boiling between 72.8 - 73°C was collected. Purified monomers were all preserved in well stoppered glass bottles in a refrigerator at 5°C.

(ii) Purification of Solvents

Solvents used were of reagent grade. They were purified by the usual methods and fractionally distilled before use.

(iii) Initiators used in Polymerization Experiments

A large number of organic and inorganic compounds was used as initiators of polymerization both in aqueous and non-aqueous media, mentioned in respective chapters. E. Merck (Pro analysis) or Analar B.D.H. products were used as far as possible.

(iv) Purification of Water as a Polymerization Medium

Water used for polymerization experiments must be free from other electrolytes and gases in order to avoid

complications which may arise due to their presence. The ordinary distilled water was redistilled from alkaline potassium permanganate solution in all glass distillation unit and the middle fraction was always used for experiments. The dissolved oxygen was removed by nitrogen flashing.

(v) Purification of Nitrogen Used in the Polymerization Experiments.

Oxygen acts as an retarder of polymerization as studied by Bacon⁵⁸, So all aqueous polymerization experiments were carried out in nitrogen atmosphere (unless mentioned otherwise). Traces of oxygen present in the commercial nitrogen were removed by passing the gas through towers containing oxygen absorbing "Fieser's solutions"⁹⁶. It was prepared by dissolving hundred parts carefully boiled distilled water, four parts by weight of sodium anthraquinone β -sulphonate, sixteen parts by weight of caustic soda and thirteen parts by weight of sodium hydrosulfite. The nitrogen free of oxygen was dried by passing through a tower containing concentrated sulfuric acid before passing into the polymerization vessel.

(vi) Other Materials Used

Pure pyridine supplied by E. Merck or Fisher and B.D.H. phthalic anhydride were used without any further purification.

Dyes used for endgroup analysis were calcozine rhodamine 6GX (Conc.) (C.I. No. 45160), methylene blue (chloride), disulfine blue VN 150. All these were supplied in very pure form but were recrystallised before use.

SECTION-II

(1) Preparation of Polymers

(a) Preparation of Polymers in Bulk or in Non-aqueous Solution

Pyrex glass sealing tube were used in these experiments. They were thoroughly cleaned with chromic acid, washed with water, followed by subsequent rinsing with sulfurous acid solution and finally washed with distilled water and dried in an air oven. Required amount of monomer and other necessary reagents were taken in the sealing tube, flushed with purified nitrogen, frozen in liquid oxygen and sealed under vacuum. The sealed tubes were then kept in a thermostatic bath at a desired temperature or in presence of mercury arc u-v lamp as required by respective experiments and the polymerization was allowed to continue to suitable conversions which were judged approximately by noting the consistency of the polymer formed. The tubes were taken out, cooled if necessary and carefully broken open. The polymers were then isolated by precipitating the contents with a suitable non-solvent.

(b) Preparation of Polymer in Aqueous Solution

Aqueous polymerization was carried out in well-cleaned 150 ml pyrex conical flasks fitted with rubber stopper. First water was thoroughly flashed with nitrogen for fifteen minutes and then required quantities of vinyl monomer, initiator and activator (if any) were added in proper order. The mouth of the flask was then fitted with a cleaned rubber stopper while nitrogen was still passing. The contents were then shaken carefully avoiding contamination with the stopper. Then was allowed to stand at room temperature or at constant temperature bath or in sunlight or in presence of u-v light, whichever the case may be, until the polymerization was apparently complete.

Polymers obtained in the precipitated phase were filtered, washed thoroughly with warm water until free of soluble impurities. Polymers obtained in emulsion or in colloidal phase were coagulated by salting out method and then filtered, washed thoroughly with water as above. The washed polymers were then dried in an air oven at temperature range of 45 - 50°C and weighed.

(ii) Purification of Polymers

Dye tests for endgroups were highly sensitive to even traces of impurities. The polymers obtained, therefore, were subjected to purification before using for endgroup analysis. This was carried out by a method



of repeated precipitation using benzene as the solvent and a mixture of alcohol and petroleum ether as the non-solvent and finally twice precipitation from benzene solution using petroleum ether alone as the non-solvent.

The polymers obtained in bulk or in solution recovered, purified in the same way by a suitable non-solvent, and then as above by repeated precipitation technique.

SECTION-III

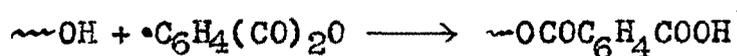
Chemical Transformation of Endgroups (Non-responsive to the Dye Tests) to Suitable Dye-responsive Groups

It has been found that hydroxyl endgroups or halogen atom endgroups in polymers are non-responsive to the ionic dye reagents in a dye test for endgroup analysis evidently due to their being non-ionic in nature. They may, however, be converted to suitable dye responsive ionic groups by chemical transformations, such as transformation of hydroxyl endgroup to carboxyl endgroup and halogen atom to quaternary pyridinium halide endgroups.

(a) Transformation of Hydroxyl Endgroup to Carboxyl Endgroup (Phthalation Technique)

Conversion of neutral hydroxyl endgroups to carboxyl endgroups was carried out by treatment with an anhydride of a dibasic acid such as phthalic anhydride⁹⁷.

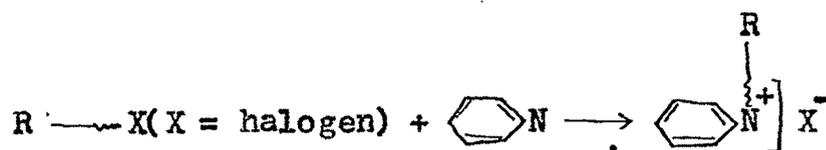
About 0.1 to 0.2 gm of a polymer containing hydroxyl endgroup and 0.5 gm of phthalic anhydride were dissolved in 10 ml pyridine in a 50 ml capacity round bottom flask with a standard joint neck. This was then refluxed on a water bath for six hours in a standard joint refluxing unit. After this, esterification:



the polymer was precipitated with petroleum ether and dissolved in benzene four to five times, each time precipitating with petroleum ether alone for complete separation of any unreacted phthalic anhydride. Finally, the benzene solution of the polymer was filtered and purified by repeated precipitation method as described earlier.

(b) Transformation of Halogen Atom Endgroup to Quaternary Pyridinium Halide Groups

The halogen endgroups, non-responsive to dye test were converted to dye responsive pyridinium halide groups by the method of Saha, Ghosh and Palit³³. About 0.2 to 0.3 gm of the polymer was dissolved in 2 to 5 ml of pyridine in a pyrex sealing tube. The tube was sealed after freezing the contents in liquid oxygen. The sealed tube was then placed in a thermostatic bath maintained at $90 \pm 0.5^\circ\text{C}$ and the process of quaternisation stopped after 90 hours.



The quaternised polymers were purified by the usual method of repeated precipitation. The purified polymers were dried and subjected to dye partition test using aqueous disulfine blue VN 150 dye reagent for the determination of halogen atom endgroups (transformed to quaternary pyridinium halide endgroups).

SECTION-IV

Determination of Intrinsic Viscosity and Molecular Weight of Polymers

The molecular weights of polymers were determined by viscometric method. The viscosity measurement was carried out with benzene solution of polymethylmethacrylate and polystyrene at $35 \pm 0.01^\circ\text{C}$ using an Ostwald capillary viscometer. Intrinsic viscosity was obtained by extrapolating the η_{sp}/C against C curves to zero concentration (where $\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0}$ where η and η_0 are viscosities and t and t_0 the times of flow of the solution and solvent respectively and C is the concentration of the solute expressed in gms per 100 ml of the solvent. The number average molecular weights (\bar{M}_n) for polymethylmethacrylate and polystyrene were calculated from the respective values with the use of following equations:-

$$\text{Polymethylmethacrylate}^{98} \quad \bar{M}_n = 2.81 \times 10^5 \times [\eta]^{1.32}$$

$$\text{Polystyrene}^{99} \quad \bar{M}_n = 1.84 \times 10^5 \times [\eta]^{1.40}$$

SECTION-V

Endgroup Analysis by the Application of Dye Techniques

Palit²⁴ has recently introduced two sensitive dye techniques viz. (i) dye partition technique and (ii) dye interaction technique which have opened the possibility of rapid detection of polymer endgroups and their quantitative estimation. The principle of these two dye techniques has already been described in Chapter I, Section IV.

For dye partition technique, methylene blue was chosen in all experiments for testing sulfoxy endgroups while disulfine blue VN 150 was chosen for testing quaternary halide endgroups and amino endgroups.

For dye interaction technique, calcozine rhodamine 6GX conc. was chosen for anionic endgroups present in polymers.

SECTION-VI

Determination of Endgroups

(A) Dye Partition Test

1) Dye Partition Method for the Detection and Determination of Sulfate and other Anionic Sulfoxy Endgroups

Aqueous methylene blue (chloride) dye reagent for the detection of strong acid endgroups such as sulfate,

sulfonate and the like in polymers was prepared by dissolving 20 mg of purified methylene blue (chloride) dye in a litre of 0.01 M aqueous hydrochloric acid solution. The color of the reagent is blue. Chloroform solutions of polymer bearing anionic sulfoxy endgroups, such as sulfate and sulfonate when shaken with the aqueous methylene blue reagent in partition experiments, the chloroform layer turned blue. But when a blank experiment was conducted in a similar fashion, no color change was noticed in chloroform layer.

For quantitative measurements, a known amount of the purified polymer is dissolved in 10 ml of chloroform taken in a 25 ml stoppered centrifuge tube and then well-shaken for one to two hours with an equal volume of an aqueous methylene blue dye reagent prepared for the purpose. The biphasic system is then allowed to stand for two hours. A distinct blue color in the chloroform layer indicates the presence of sulfoxy endgroups in the polymer. This dye partition test is only specific for anionic strong acid endgroups (sulfoxy endgroups) and weak acid endgroups such as carboxyl (COOH) fail to give any response.

The chloroform layer is then separated from the aqueous layer and then centrifuged ; if necessary to get a clear solution and the color developed is measured in a Hilger Uvispek photoelectric spectrophotometer at 660 m μ

with the use of 1 cm cells. The polymer endgroup is obtained by comparing the experimental optical density values with a calibration curve (Fig.1) of pure sodium lauryl sulfate, obtained by following a similar procedure³¹.

ii) Dye Partition Method for Determination of Halogen Endgroups Transformed to Quaternary Halide Endgroups

For the determination of halogen endgroups in polymers, disulfine blue reagent is prepared by dissolving 80 mg disulfine blue VN 150 dye in a litre of 0.01 M aqueous hydrochloric acid solution. Color of the aqueous dye reagent is green. Tests for quaternary halide endgroups in polymers are carried out in non-aqueous solution (chloroform) and such solutions are mixed with the dye reagent and shaken with the chloroform layer, the organic layer becomes blue. A similar partition in the absence of polymer or detergents produce no color in the organic layer.

The determination of quaternary halide endgroups aqueous disulfine blue (vide Chapter II, Section IIIb) was used in dye partition test in the same way as for the determination of sulfoxy endgroups with aqueous methylene blue reagent. The color developed in the chloroform layer is measured after centrifugation in a Hilger Uvispek spectrophotometer at 630 m μ with the use of 1 cm cells. The quantity of halogen endgroup present in the polymer is obtained by comparing the experimental optical density

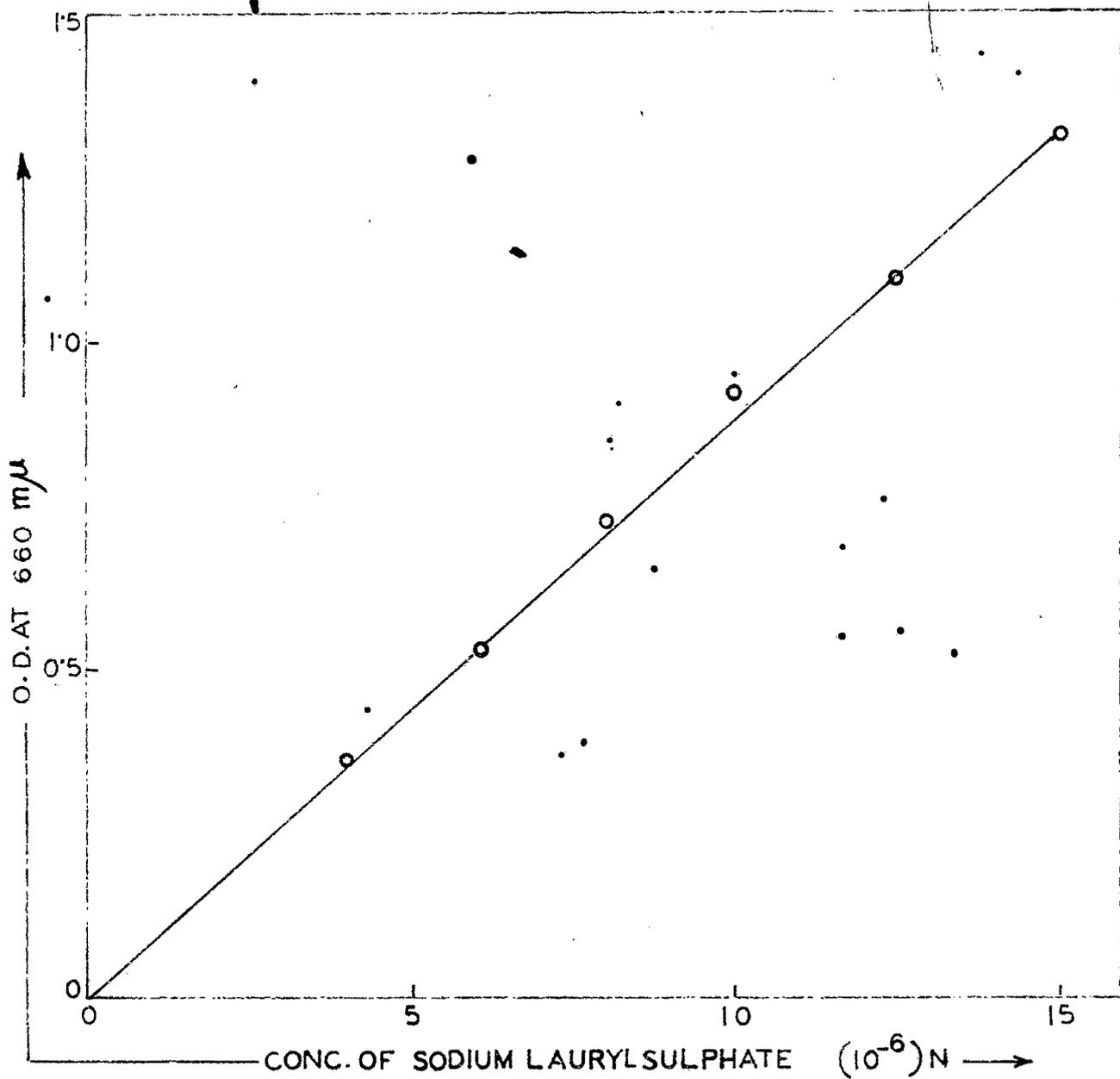


Fig. 1 - Optical density Vs. concentration of sodium lauryl sulfate (using methylene blue reagent)

values with a calibration curve (Fig.II) of pure lauryl pyridinium bromide (LPB), obtained by following a similar procedure³³.

iii) Dye Partition Method for Determination of Amino Endgroups

Recently dye partition experiment is extended for the determination of amino endgroups in polymers^{100, 101}. Disulfine blue VN 150 dye reagent was found to give response to long chain aliphatic amines and also to amino endgroups in polymers. For this experiment disulfine blue VN 150 dye was prepared as described above. The experiment is also the same as described for the determination of quaternary halide endgroups.

The quantity of amino endgroup present in the polymer is obtained by comparing the experimental optical density values with a calibration curve (Fig.III) of pure dodecylamine.

B. Dye Interaction Test

Determination of (anionic) Acidic Endgroups such as Carboxyl by Dye Interaction Test

Calcozine Rhodamine 6GX dye used for the dye interaction test is prepared in the following way :

3-4 mg of the dye was dissolved in 3-4 ml of a phosphate buffer of pH 10-12 and was immediately extracted with 100 ml of benzene with thorough shaking. The orange

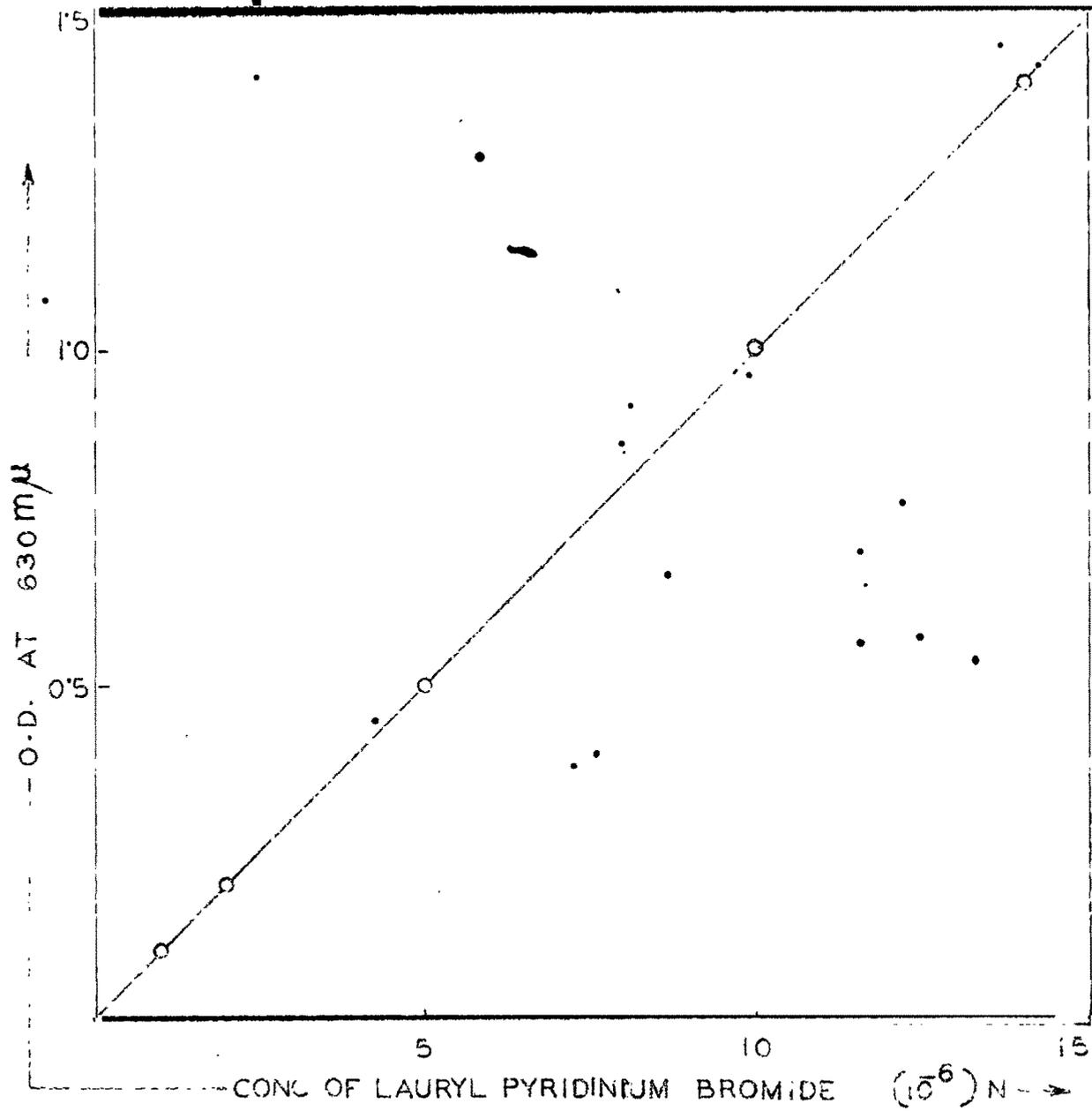


Fig.II - Optical density Vs. concentration of lauryl pyridinium bromide (using disulfine blue reagent).

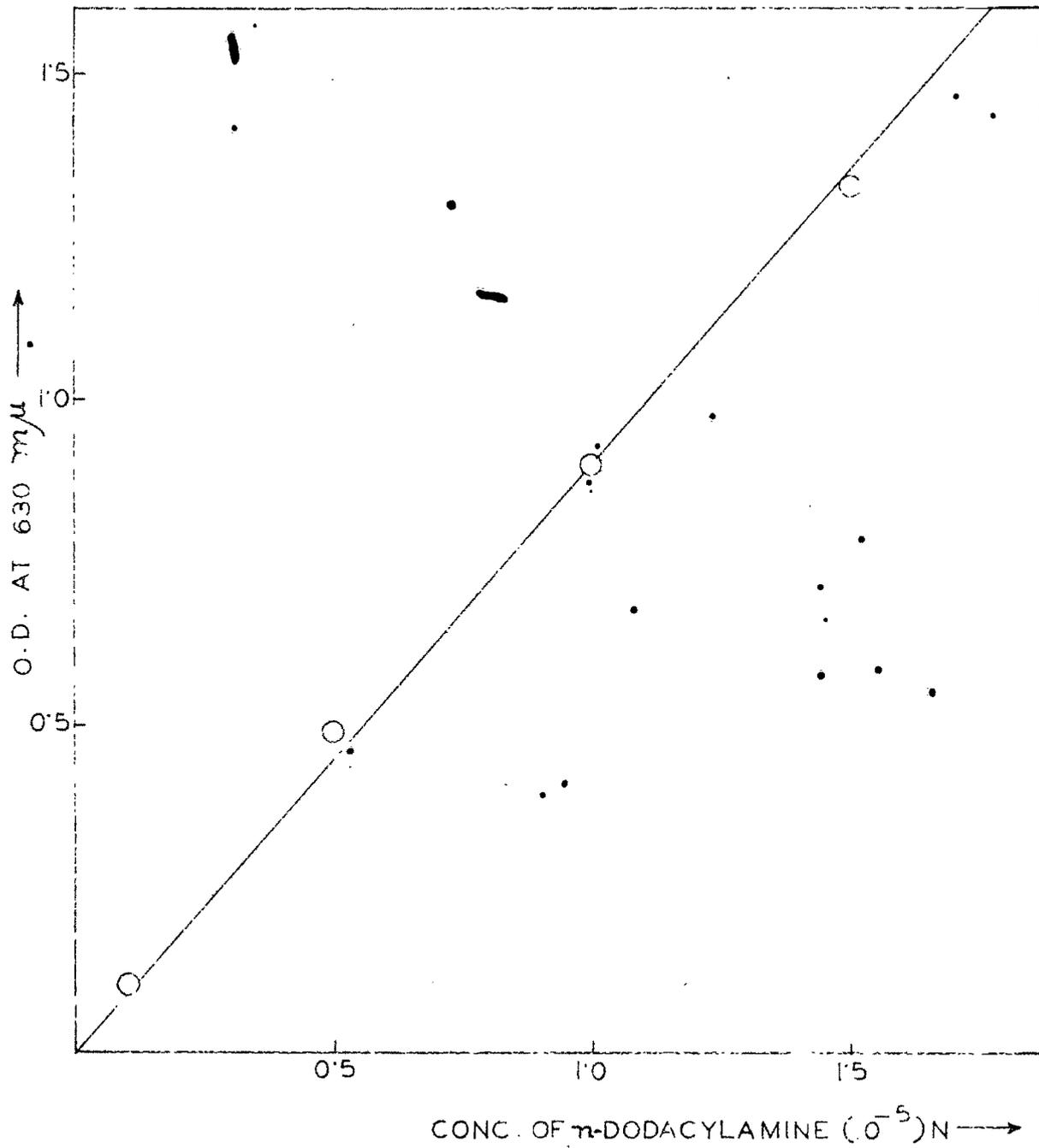


FIG. III - Optical density Vs. concentration of n-dodacylamine (using disulfine blue reagent)

yellow benzene extract thus obtained was used as the desired sensitive dye reagent. The reagent can be preserved for months by keeping over a few beads of sodium hydroxide in dark at room temperature (25-30°C). The orange yellow color of the dye reagent changed to pink on the addition of benzene solution of polymers bearing anionic endgroups such as carboxyl, sulfate, sulfonate etc.

Dye interaction test with rhodamine reagent for the determination of carboxyl endgroups and hydroxyl endgroups after conversion to carboxyl endgroup was carried out by following the method as described by Palit and Ghosh³⁵. Measurements of the change in color of the dye reagent by the addition of benzene solutions of polymer containing acidic endgroup were made in Hilger Uvispek spectrophotometer using 1 cm cells. Equal volumes of the dye reagent (rhodamine reagent) and polymer solution of known concentrations were added together in specially cleaned pyrex test tubes and thoroughly mixed together. The original orange yellow color of the dye reagent changes to pink, thereby indicating the presence of anionic endgroups in the polymers. A measure of the color change gives the amount of anionic endgroups in the polymers and is carried out at 515 m μ . The optical density of the blank dye has been maintained at 0.40 ± 0.005 for convenience in comparison. The quantity of the carboxyl endgroups

present in a polymer was obtained by comparing the experimental optical density values with a calibration curve of formic acid (Fig. IV) obtained by following a similar procedure³⁵. The suitability of formic acid as a basis for comparison for carboxyl groups in polymers has already been advocated.

Some uncertainty may appear in the absolute values of the amount of endgroups estimated since the values are dependent on the basis of comparison with arbitrary standard substances (e.g. carboxyl endgroups have been estimated by comparing with a calibration curve obtained with the use of formic acid and sulfate or sulfonate, by comparing with that of sodium lauryl sulfate). Again, the quantitative figures have been obtained on the basis of viscometric determination of number-average molecular weight \bar{M}_n and the equations (relating $[\eta]$ with \bar{M}_n) used may not be sufficiently correct in all molecular weight ranges investigated. The results of quantitative endgroup estimation are probably correct within ± 20 percent. The relative quantitative values for each initiator system are representative and reproducible.

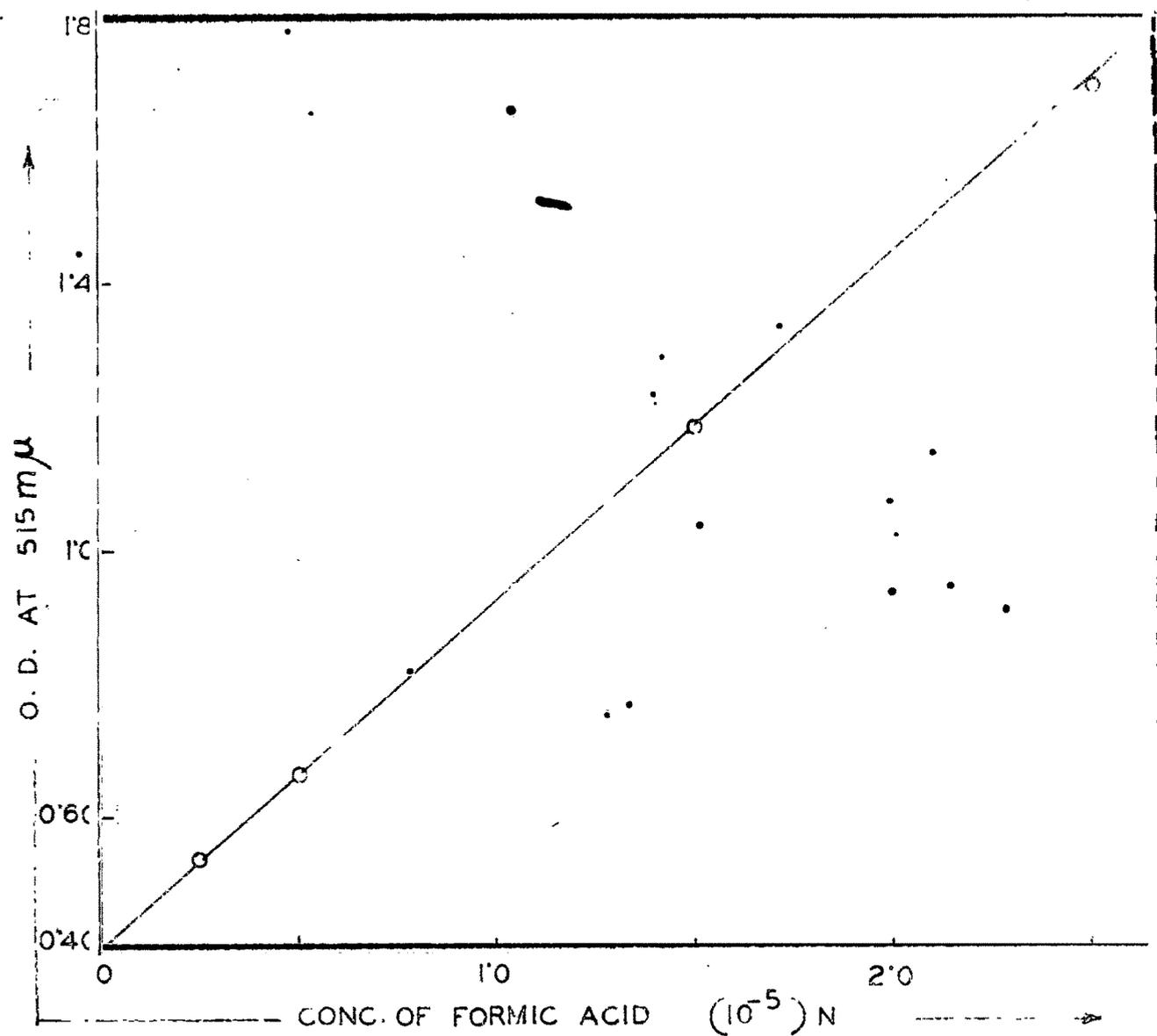


Fig.IV - Optical density Vs. concentration of formic acid (using rhodamine reagent)