A STRUCTURAL STUDY OF 66 NYLON FIBERS AND FILMS BY IODINE SORPTION

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by
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AND FILMS BY IODINE SORPTION
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A STRUCTURAL STUDY OF 66 NYLON FIBERS AND FILMS BY IODINE SORPTION

ABSTRACT

A structural investigation of drawn and undrawn 66 nylon by sorption of iodine from I_2-KI solutions, density measurements, optical microscopy, and infrared absorption studies is presented.

A detailed investigation of the sorption of iodine from I_2-KI solutions on drawn and undrawn 66 nylon fibers as a function of concentration, temperature, and time is made. Also densities of drawn and undrawn fibers were measured and compared. Penetration of cross-sections of iodine treated filaments was studied by optical microscopy and solubility studies in concentrated I_2-KI solutions at room temperature and elevated temperature were made. Finally the infrared spectra of untreated and iodine treated nylon films were obtained, indexed, and compared for indications of structural changes.

The results of this study show that the amount of iodine sorbed increases with concentration, temperature, and time. Sorption isotherms suggest that the iodine sorption process is not a simple adsorption process. The results of the penetration studies, the solution behavior, density and rate studies of iodine sorption on drawn and undrawn fiber, and the shift of the 3290 cm^{-1} N-H hydrogen banding stretching frequency gives very strong evidence that the major swelling and dissolving, and iodine sorption process is predominantly an absorption process.

It is suggested that the I_3^- ion makes possible a breaking of hydrogen bonds followed by a bridging of an I_2 molecule between adjacent chains

through the carbonyl oxygen. It is suggested further that this is the mechanism of solution of 66 nylon in highly polar solvents, such as phenol and formic acid, for example.

CHAPTER I

INTRODUCTION

66 nylon, a condensation polymer, has commerical importance in textile fibers and in molded articles. The physical and mechanical properties of the polymer are closely related to the structure of the molecules within the polymer. As a result of this relationship, a knowledge of this structure is of importance.

Purpose of the investigation. The purpose of this study is to investigate the structure of 66 nylon by the use of iodine sorption as a function of concentration, temperature and time, together with optical microscopy studies and infrared absorption studies.

CHAPTER II

LITERATURE REVIEW

PREPARATION OF 66 NYLON

The two general methods of polymerization are addition polymerization and condensation polymerization. This investigation deals with a product of the latter.

The type of reaction in which products of high molecular weight are formed by the repetitive splitting out of small molecules such as water or alcohol, is known as condensation polymerization. The structural requirement for condensation polymerization is that both molecules involved must be at least bifunctional, for then their reaction product will be bifunctional and the reaction can continue. If there are just two functional groups in each molecule, the long-chain compounds of high molecular weight are the normal products (8).

Condensation polymerization of the type just described has led to the development of a number of important synthetic fibers. One of these fibers, 66 nylon, is produced from the polyamide resulting from the interaction of hexamethylene diamine and adipic acid (8).

$$nH_2N\text{-}(CH_2)_6\text{-}NH_2 + nHOC\text{-}(CH_2)_4\text{-}COH \rightarrow n[\text{Salt}]$$

$$n[\text{Salt}] \xrightleftharpoons{\Delta} H\text{-}\left[HN(CH_2)_6NHC(CH_2)_4C\right]\text{-}nOH + nH_2O$$

The polyamide melts at about 260°C, and the molten material can be drawn into fine threads (17).

THE TWO PHASE CONCEPT IN 66 NYLON

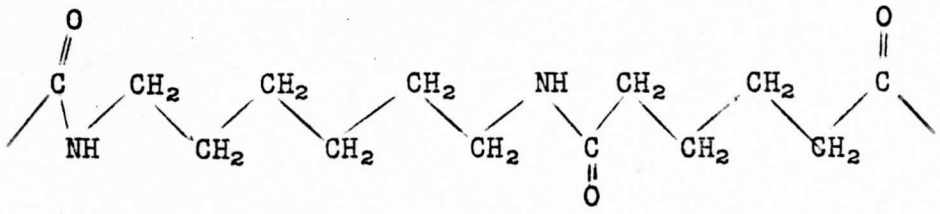
66 nylon has an order-disorder structure much the same as polyethylene terephthalate, stereoregular polypropylene, polyethylene, and cellulose. According to the two phase concept there are regions in the polymer where the molecules are aligned with respect to each other at well defined distances and in three dimensional order. These regions are the crystalline part of the material. There are also other regions in which the polymer molecules have little or no alignment with respect to each other. These regions of no order are known as the amorphous regions.

Physical and mechanical properties of nylon films and fibers are related to the degree of the order-disorder structure of the polymer. Because of this relationship, desired physical and mechanical properties can be induced in the polymer by appropriate treatment. The degree of crystallinity is determined by the method of preparation, and by thermal and mechanical treatments applied to the polymer.

Due to the fact that the order-disorder structure has an effect on the properties of the polymer, it is of importance to know and understand the structure and intermolecular forces present in the polymer.

AN ANALYSIS OF THE BONDS AND INTERMOLECULAR FORCES IN 66 NYLON

Bunn and Garner give the repeat distance of the 66 nylon molecule along the fiber axis as 17.2Å. (5).



17.2Å

If it is assumed that the long molecules are parallel to the fiber axis, the repeat distance suggests that the chains must be fully extended, or very nearly so. They must be plane or very nearly plane zigzags. Any considerable rotation around any of the bonds to give a non planar chain would shorten the repeat distance (5).

There are two types of bonds acting in 66 nylon to hold the films and fibers together. These are primary valence bonds and secondary valence bonds.

Primary valence forces. The atoms which compose the backbone of the nylon chain are carbon and nitrogen. The chain is made up largely of C-C bonds (1.54Å) and a lesser amount of C-N bonds (1.39Å). These C-C and C-N bonds are of the primary valence type. These bonds are probably neither pure covalent or pure ionic, but are between the two extremes. Primary valence bonds are also involved in attaching atoms to the polymer backbone, such as C-H(1.12Å), C=O (1.25Å) and N-H (1.03Å) (5).

Secondary valence forces. It is readily seen that the forces which hold the atoms within the chain together are primary valence forces. However, in terms of structure the answer to the question, "What holds the chains together?" is equally important.

Polymer films and fibers have their chain molecules united to each other by secondary valence forces. Secondary valence forces are of the electrostatic type. These can be either hydrogen bonding or dipolar interactions. In order to answer the question and to help establish chain

conformation it is necessary to know which type of secondary valence forces exist in the polymer.

Hydrogen bonding. The secondary valence forces which seems responsible for intermolecular attraction in 66 nylon is that of hydrogen bonding. Various polyamides, including 66 nylon, have been studied by X-ray diffraction (4, 5, 7, 10, 12, 14) and by infrared spectroscopy (4, 9, 10, 19, 21) which indicate that hydrogen bonding takes place in polyamides.

In an x-ray investigation of 66 nylon, Bunn and Garner found that in the α structure the oxygen of one molecule is opposite the nitrogen of the next. The distance between these two atoms is 2.8Å. The van der Waals radius of N-H is about 1.8Å and that of oxygen is 1.35Å, hence if there were no electrostatic interactions the N to O distance would be expected to be 3.15A. The shorter distance found, 2.8Å, is characteristic of hydrogen bond formation. It is in good agreement with the N-O distances found in glycine and acetamide (5).

Infrared spectroscopy also gives information that suggest hydrogen bonding in 66 nylon. The strong band at 3290 cm^{-1} is due to the N-H valency vibration (4, 9, 21). Measurements made on solid N-mono-substituted amides at widely different concentrations in chloroform, indicate that "free N-H groups" have a valency vibration of about 3430 cm^{-1}. In conditions most favorable to hydrogen bonding (i.e., in the solid), a single band appears at about 3270 cm^{-1}. In concentrated solutions both bands appear simultaneously. The presence of a single band at 3290 cm^{-1} in nylon therefore indicates that the degree of hydrogen bonding taking place is very considerable, and probably nearly complete (9).

Another interesting feature of the infrared spectra is the displacement of the carbonyl group band from its usual position at 1720-1740 cm^{-1} to about

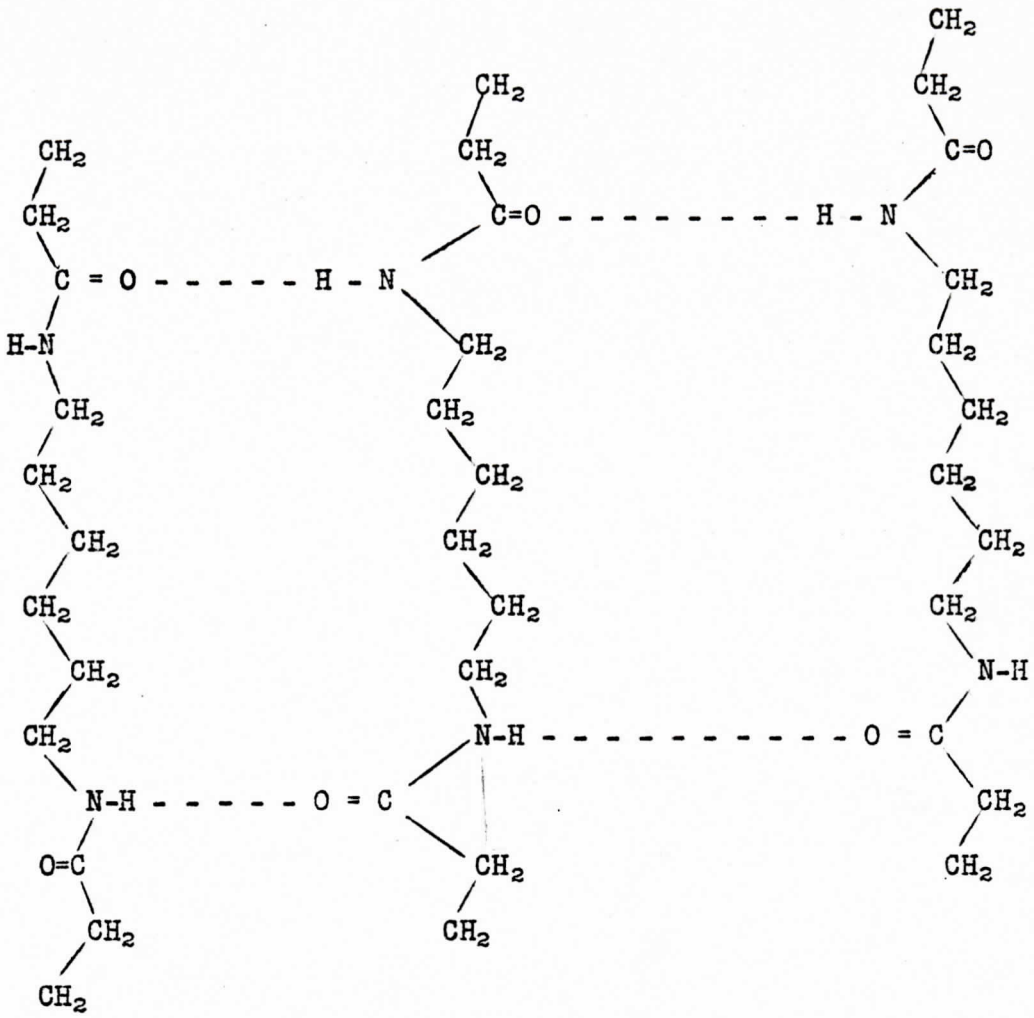
1630 cm^{-1}. This occurs with amides in general, and must arise from some form of interaction between the carbonyl group and the NH group. In the case of 66 nylon hydrogen bonding of the type C=O - - - H-N- may be formed by interaction between units of different chains (9, 21).

STRUCTURE OF 66 NYLON

After a determination of the primary and secondary valence forces acting in nylon and determination of the conformation of the chain molecule, a structure of the polymer can be realized.

Apart from the hydrogen bond distance between N and O atoms, all the other distances between atoms of neighboring molecules are the normal ones characteristic of the van der Waals forces. The hydrogen bonds link molecules together in sheets; but the links in other directions are much weaker, and the whole structure is thus a pronounced layer like type (5). It is this feature which is responsible for the plane orientation in rolled and pressed sheets. The sheets of molecules linked together by hydrogen bonds are found parallel to the plane of the sheet of the material.

The illustration below shows how sheets of 66 nylon are held together by hydrogen bonding (12).



In general, the high tensile strength of nylon owes something to the hydrogen bonds. When a fiber is broken individual chains are not broken, but the crystals are pulled apart by molecules slipping past each other. This would be more difficult, the stronger the forces holding the molecules side by side.

THE SORPTION OF IODINE ON NYLON FIBERS

There have been several studies made of the sorption of iodide by polyamide fibers (1, 2, 3, 4, 6, 10, 13, 20, 22, 23). These include fibers other than 66 nylon and solutions other than I_2-KI solutions.

The most complete study of the sorption of iodine by a polyamide fiber was made by Arimoto (1, 2, 3, 4). The fiber used was 6 nylon which sorbed iodine from I_2-KI solutions.

Some of the conclusions reached by Arimoto are that (1) iodine enters into the crystalline part of 6 nylon and co-ordinates to the oxygen of the amide group to form a definite complex, and (2) co-ordination occurring on the oxygen brings about dissociation of hydrogen bonds between amide groups. Iodine enters into the crystal lattice through the space between the hydrogen-bonded molecular sheets and co-ordinates to the oxygen of the amide groups to form a halogen-molecule bridge between the amide groups lying in the adjacent sheets. The hydrogen bond is broken and the amide group is twisted to a direction perpendicular to the molecular sheet. (4)

Although there is no direct evidence to support the halogen-molecule bridge between the amide groups, the X-ray data on the acetone-bromine system and the change of the amide I, a band in nylon an adsorption of iodine suggest this bridge (4).

In the other studies no mention of the dissolving or partial dissolving of nylon in I_2-KI solution was made. However, in the present study, partial solution of nylon in I_2-KI solution was accomplished. Whether a crystalline or amorphous material will dissolve in a given liquid depends upon whether the molecular forces between the material and solvent are greater or less than the intermolecular forces in the solid (5).

CHAPTER III

EXPERIMENTAL

MATERIALS AND EQUIPMENT

The materials used for this study were 66 nylon fiber (undrawn, 240 denier) obtained from the Chemstrand Research Center, U. S. P. grade iodine, and Fisher Certified potassium iodide, sodium thiosulfate, formic acid, toluene, and carbon tetrachloride. Also employed were copper wire, Duco cement, a pycnometer, 125 ml Erlenmeyer flasks, and 3" X 3" glass plates.

The equipment used for maintaining constant temperature, carrying out necessary weighings, optical studies, and infrared absorption studies were a thermoregulated constant temperature water both assembly, a Mettler Gram-atic balance, a Bausch and Lomb Polarizing Microscope, and a Beckman Infrared Spectrophotometer, Model IR-7 with Beam condenser, respectively.

PREPARATION OF SAMPLES

Three types of 66 nylon samples were used in this investigation. These were (1) undrawn fibers, (2) drawn fibers, and (3) solution cast films.

Undrawn tow was prepared for analysis by wrapping tow in loops weighing approximately 100 mg each. Finish was removed by immersing the loops in benzene. The samples were then dried and weighed to the nearest 0.1 mg.

Drawn fibers of 66 nylon were obtained by elongating the benzene treated

undrawn fibers to a draw ratio of 2.5x (final length - initial length) / initial length).

66 nylon films were prepared from 1%, by weight, nylon-formic acid solution. 66 nylon films were prepared for the infrared investigation in the following manner.

The prepared solution is heated on a steam bath and 3" X 3" glass plates are heated in an oven maintained at 115° C. A thin layer of the solution is poured on the plate. The plate is returned to the oven whose initial temperature is 115°C. The oven door is left open and solvent is evaporated by fanning. After all solvent is removed, the films are removed from the plates by a stream of cold water. By this method reasonably clear films, less than 0.01 mm thick, are obtained. In this method rapid evaporation of solvent is essential for obtaining transparent films.

EXPERIMENTAL INVESTIGATION OF THE SORPTION OF IODINE BY 66 NYLON

The experimental work in this study consisted of determining the amount of iodine sorbed by undrawn and drawn 66 nylon fibers as a function of concentration, temperature, and time from solutions of iodine dissolved in aqueous potassium iodide. In addition the structural changes as revealed by optical studies, infrared absorption spectroscopy and density measurements were studied.

THE SORPTION OF IODINE ON UNDRAWN 66 NYLON FIBERS

This portion of the study consist of determining the amount of iodine sorbed by undrawn 66 nylon fibers as a function of concentration, temperature and time.

Concentration as a variable. Solutions of iodine with concentrations of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 16, 18, 20, 22, and 24 grams

of iodine per liter of 0.2N potassium iodide were prepared. Accurately weighed samples of undrawn fibers, approximately 100 mg, were immersed in 50 ml of the above concentrations for a period of thirty minutes at temperatures of 15.0°, 30.0°, 45.0°, 60.0°, and 75.0°C. The sorption was carried out in 125 ml Erlenmeyer flask which were immersed in a constant temperature water bath.

After a period of thirty minutes, the samples were rinsed in tap water and dried at room temperature for twenty-four hours. The samples were reweighed and the amount of iodine sorbed per gram of nylon was calculated. All determinations were made in duplicate, thus the amount of iodine sorbed is taken as an average of the two determinations.

Temperature as a variable. The data obtained from the above work was utilized to give the amount of iodine sorbed as a function of temperature.

Time as a variable. Solutions of 5, 10, and 20 grams of iodine per liter of 0.2N potassium iodide were prepared. Accurately weighed loops of undrawn fiber were immersed in 50 ml of the above concentrations for periods of 1, 3, 5, 10, 15, 20, 30, 40, 50, and 60 minutes at a temperature of 58.2°C. After the specified period the samples were rinsed in tap water, dried at room temperature for twenty-four hours, and the amount of iodine sorbed was determined.

However, it was found that the nylon sorbed the iodine so rapidly that it was necessary to reduce both the time and temperature. Using the same concentrations as above, a different method for the time study was used.

600 ml of each concentration were brought to a temperature of 30.5°C. Accurately weighed loops were immersed in the appropriate solution for periods of 10, 30, 60, 90, 120, 150, 180, 240, 300, 360, 420, 480, and 540 seconds. After the specified time the samples were rinsed in tap water,

dried at room temperature for twenty-four hours, and the amount of iodine sorbed was determined.

THE SORPTION OF IODINE ON ON DRAWN 66 NYLON FIBERS

The purpose of this investigation was to determine the amount of iodine sorbed by drawn 66 nylon fibers as a function of concentration, temperature, and time.

Concentration as a variable. Solutions of 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, and 24 grams of iodine per liter of 0.2N potassium iodide were prepared. Weighed samples of drawn nylon fibers previously described were immersed in 50 ml of the above solutions for a period of thirty minutes at temperatures of 15.0°, 30.5°, 43.7°, 58.2° and 73.0°C. The sorption was carried out in 125 ml Erlenmeyer flasks which were immersed in a constant temperature water bath. After the specified time the samples were rinsed in tap water, dried at room temperature for twenty-four hours and the amount of iodine sorbed was determined.

Temperature as a variable. The data obtained from the concentration study was utilized to give the amount of iodine sorbed as a function of temperature.

Time as a variable. Solutions of 5, 10, and 20 grams of iodine per liter of 0.2N potassium iodide were used. 600 ml of the solutions of the above concentrations were brought to a temperature of 30.5°C. Loops of drawn fiber were immersed in the appropriate solutions for periods of 10, 30, 60, 90, 120, 150, 180, 240, 300, 360, 420, 480, and 540 seconds. After the specified time the samples were rinsed in tap water, dried at room temperature for twenty-four hours, and the amount of iodine sorbed was calculated.

SORPTION OF IODINE FROM IODINE-CARBON TETRACHLORIDE SOLUTION

A saturated solution of iodine in carbon tetrachloride was prepared. Nylon fiber was immersed in the solution for one hour at about 60°C. However, when the fiber was rinsed no iodine remained on the fiber. Thus indicating no iodine sorption.

INFRARED INVESTIGATION OF 66 NYLON WITH RESPECT TO IODINE SORPTION

The infrared study will be divided into three parts: (1) spectra of untreated 66 nylon (2) spectra of 66 nylon with a mild treatment of iodine. (3) spectra of 66 nylon with a heavy treatment of iodine.

Spectra of untreated 66 nylon. A film of 66 nylon was prepared by a method described earlier. The film was placed in an IR-7 infrared spectrophotometer and the region between 2.5μ and 15.0 μ was scanned. A speed of 20 cm^{-1} / minute was used to give maximum resolution.

Spectra of mildly treated 66 nylon. The film from the above work was placed in an I_2-KI solution at room temperature for a period of twenty-four hours. The solution was eight grams of iodine per liter of 0.2N potassium iodide. The sample was rinsed, dried and remounted in the spectrophotometer and a similar spectra obtained.

Spectra of heavily treated 66 nylon. The film used in the mild treatment was then treated with a more concentrated solution of I_2-KI. The film was dipped for one minute at room temperature into a solution of 445 grams of iodine per liter of saturated potassium iodide. There was partial dissolving of the film. At this point, the film was so dark that it was necessary to use a beam condenser in the spectrophotometer. A Beckman Beam Condenser, Model 18601 with KBr plates, was installed and the reference beam partially blocked. With these modifications, the region was again

scanned at a speed to give maximum resolution.

The point of interest is the N-H stretching frequency band which appears at 3290 cm^{-1} in the untreated sample.

PENETRATION OF IODINE IN 66 NYLON FIBERS

This investigation was carried out to determine the depth of penetration of iodine through-out the cross section of the fiber.

Sections of undrawn nylon yarn were dipped into an I_2-KI solution of various concentrations for a period of thirty minutes at a temperature of 30.0°C. After drying, the yarn was held in a stretching frame and coats of Duco cement were applied and allowed to harden. By cutting a thin slice from the cross-section and viewing the filaments under a microscope (250X) the depth of penetration was determined.

In addition, the change in filament diameter was observed on fibers treated with iodine solutionand fibers treated with a five percent phenol-water solution. These treated filaments were compared to untreated filaments.

PARTIAL SOLUTION OF NYLON IN IODINE-POTASSIUM IODIDE SOLUTION

A very concentrated I_2-KI solution was prepared by adding iodine to 25 ml of saturated potassium iodide until saturation occurred.

With the I_2-KI solution at about 80°C, dissolving of nylon would occur. However, at room temperature the fibers just fused together.

DENSITY OF DRAWN AND UNDRAWN FIBERS

Density measurements on drawn and undrawn fibers were made by a floatation method. A small knot of fiber was placed in a test tube which was immersed in a water bath at 30.5°C. Carbon tetrachloride and

toluene were added until the sample was suspended half-way in the solution. The density of the solution was determined with a pycnometer. The density of the solution is the density of the fiber. From the density of the fiber the percent crystallinity was calculated.

CHAPTER IV

RESULTS

EFFECT OF CONCENTRATION, TIME, AND TEMPERATURE

Tables I, II, III, IV, and V list the grams of iodine sorbed per grams of 66 fiber from I_2-KI solutions ranging in iodine concentrations from 1 to 24 g/l using a constant immersion time of thirty minutes and temperatures of 15.0°, 30.0°, 45.0°, 60.0°, and 75°C, respectively.

These data are shown graphically by Figures 1, 2, 3, 4, and 5, respectively. Here, grams of iodine sorbed per gram of fiber are plotted verses concentrations of I_2-KI solutions.

Figure 1, corresponding to the 15.0°C sorption isotherm, shows that the amount of sorption increases in an approximately sigmoidal manner. From 0 to 10 g/l the amount sorbed increases gradually. From 10g/l to 24g/l, the increase in the amount of iodine sorbed increases much more rapidly.

Figure 2, corresponding to the 30.5°C sorption isotherm, shows a similar type of sigmoid shaped curve. It is interesting to observe that the amounts of iodine sorbed at this higher temperature are not significantly different from those amounts obtained for the lower temperature.

Figure 3, corresponding to the 45°C isotherm, also shows the sigmoid curve. However, here it appears to be losing some of this character as is evident by a more gradual increase in the slope of the curve from 10 g/l to 24 g/l. It is to be observed also that at this temperature less iodine is being sorbed at the very highest concentrations than is the case for the lower temperature isotherms.

Fugures 4 and 5 show increased leveling out effects at even higher temperature isotherms. Also the maximum amount of iodine sorbed appears to be about the same for these two higher temperature isotherms as for the lower temperature isotherm shown by Figure 3.

TABLE I

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 15.0°C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
1	0.048
2	0.081
3	0.105
4	0.106
5	0.137
6	0.137
7	0.138
8	0.142
9	0.146
10	0.170
11	0.173
12	0.250
14	0.250
16	0.279
18	0.440
20	0.431
22	0.455
24	0.523

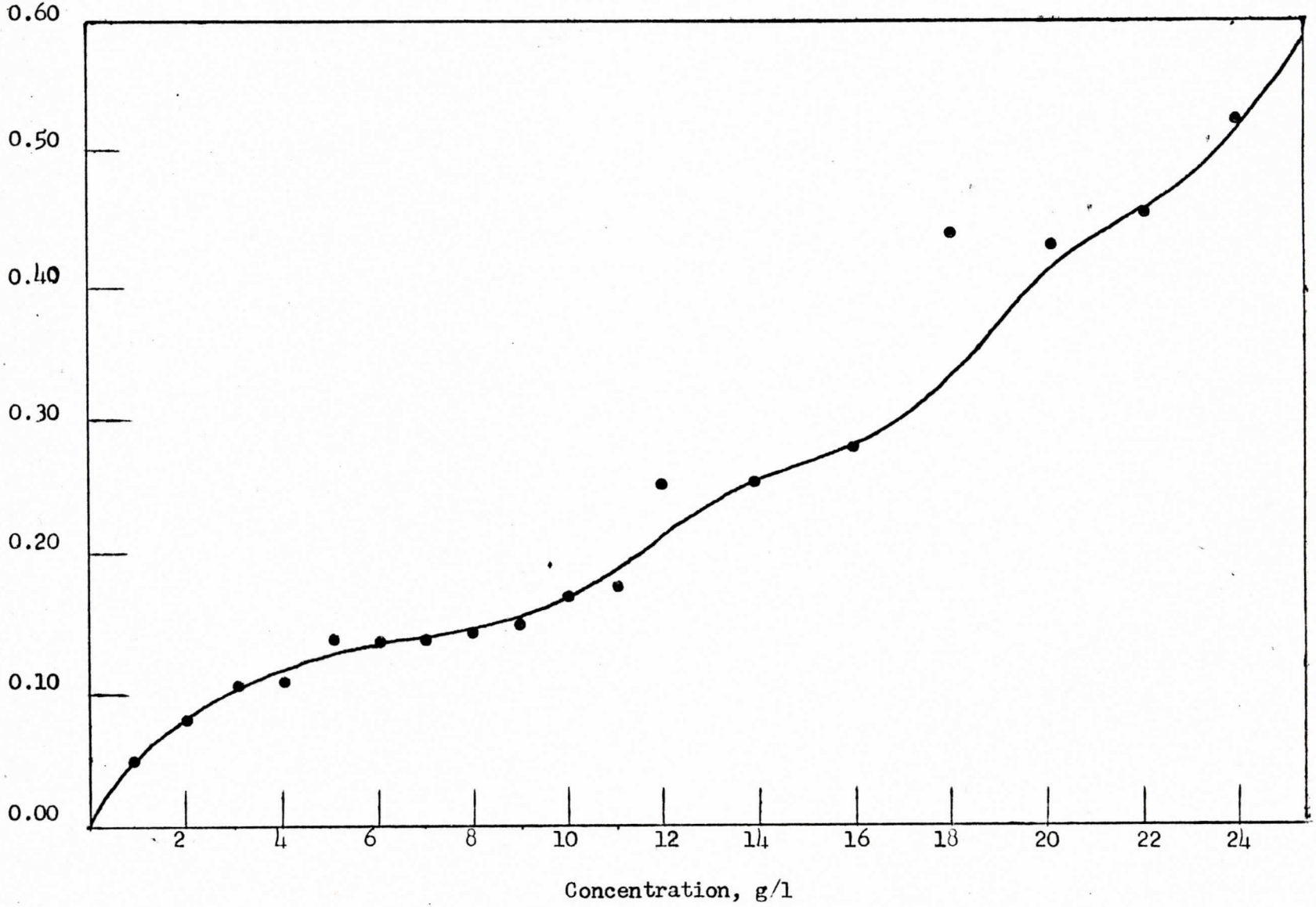


Figure 1. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at a Temperature of 15.0°C and over a Period of Thirty Minutes

TABLE II

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 30.0°C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
1	0.048
2	0.086
3	0.101
4	0.122
5	0.150
6	0.171
7	0.200
8	0.232
9	0.220
10	0.178
11	0.206
12	0.192
14	0.206
16	0.237
18	0.279
20	0.333
22	0.404
24	0.514

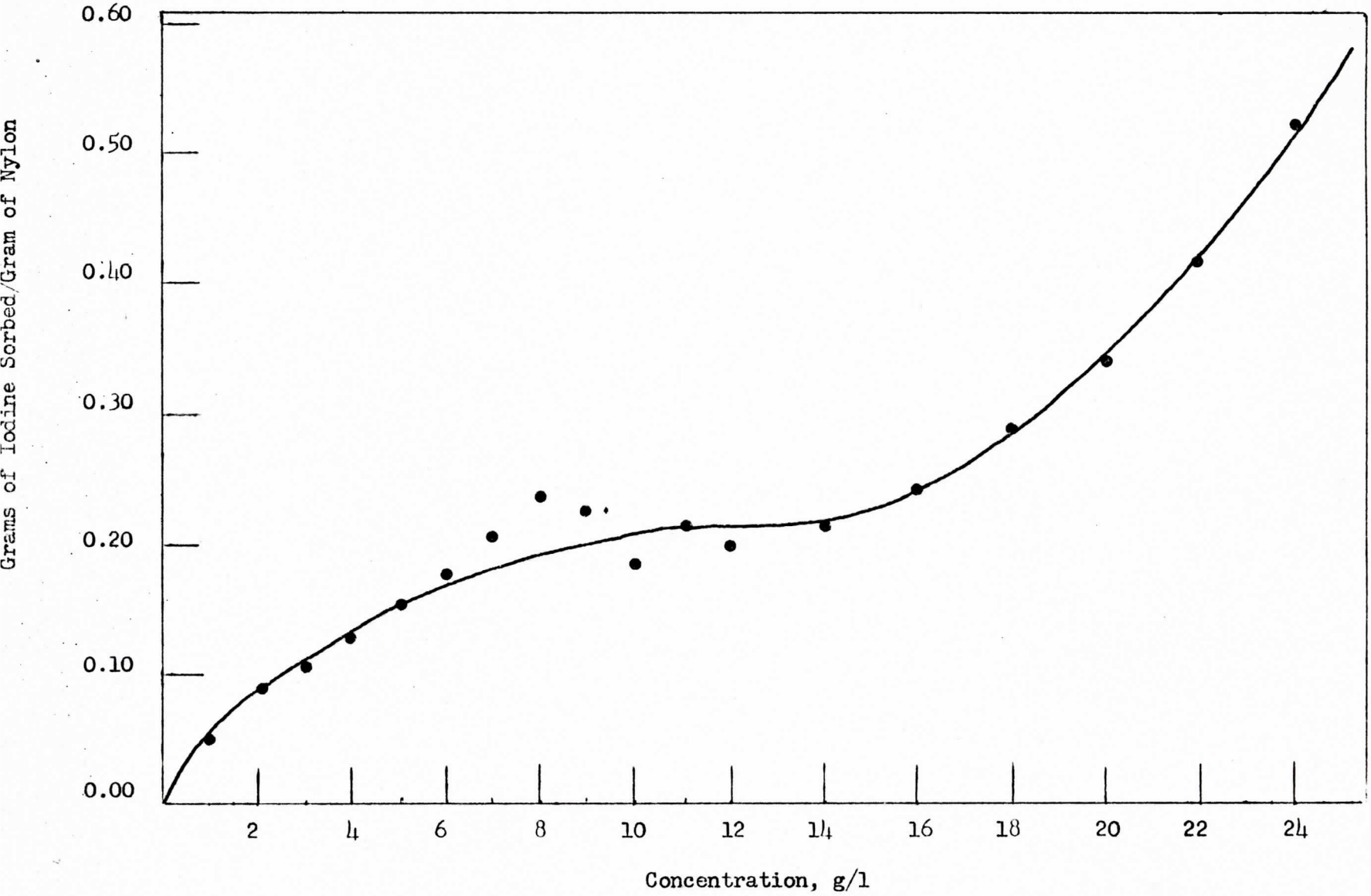


Figure 2. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fiber from I_2-KI Solutions of

TABLE III

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 45.0° C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
1	0.068
2	0.096
3	0.110
4	0.126
5	0.131
6	0.183
7	0.178
8	0.236
9	0.208
10	0.214
11	0.242
12	0.230
14	0.229
16	0.273
18	0.355
20	0.361
22	0.396
24	0.395

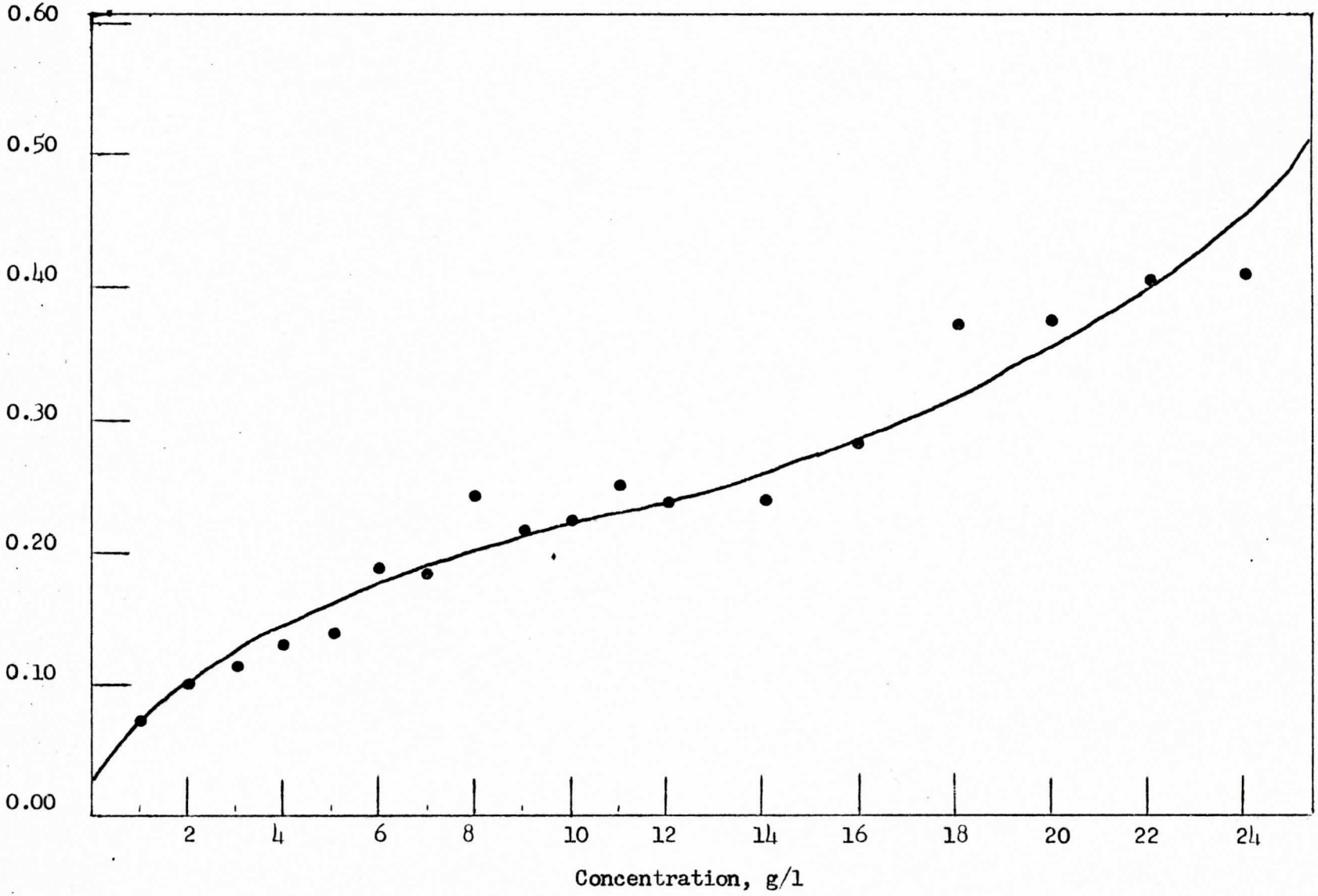


Figure 3. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at a Temperature of 45.0°C and over a Period of Thirty Minutes.

TABLE IV

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 60.° C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
1	0.034
2	0.064
3	0.081
4	0.107
5	0.137
6	0.129
7	0.136
8	0.151
9	0.246
10	0.254
11	0.252
12	0.308
14	0.333
16	0.345
18	0.355
20	0.410
22	0.400
24	0.416

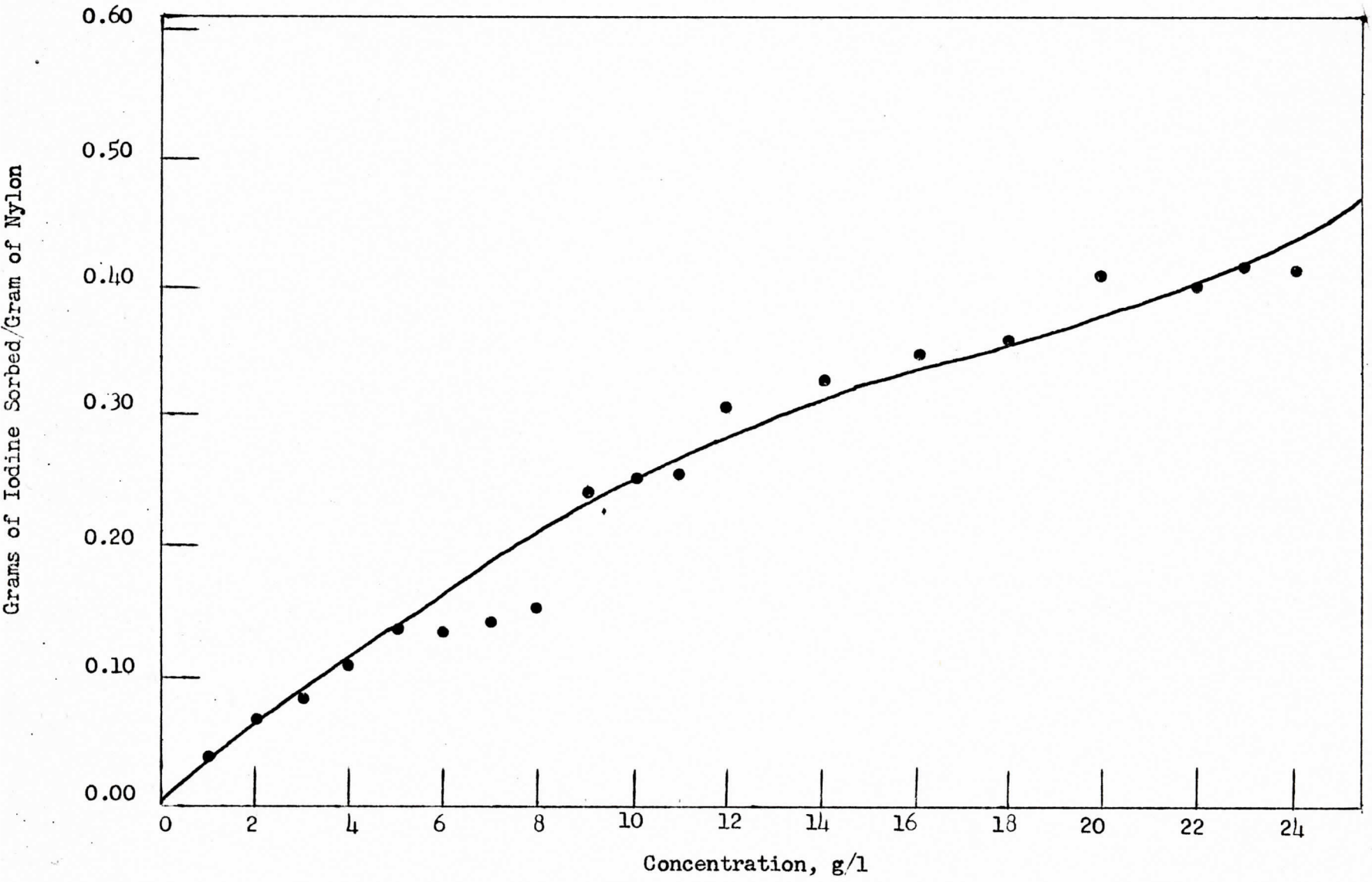


Figure 4. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at a Temperature of 60.0°C and over a Period of Thirty Minutes

TABLE V

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 75.0 C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
1	0.042
2	0.071
3	0.114
4	0.147
5	0.147
6	0.166
7	0.196
8	0.212
9	0.256
10	0.245
11	0.285
12	0.293
14	0.327
16	0.362
18	0.407
20	0.428
22	0.473
24	0.483

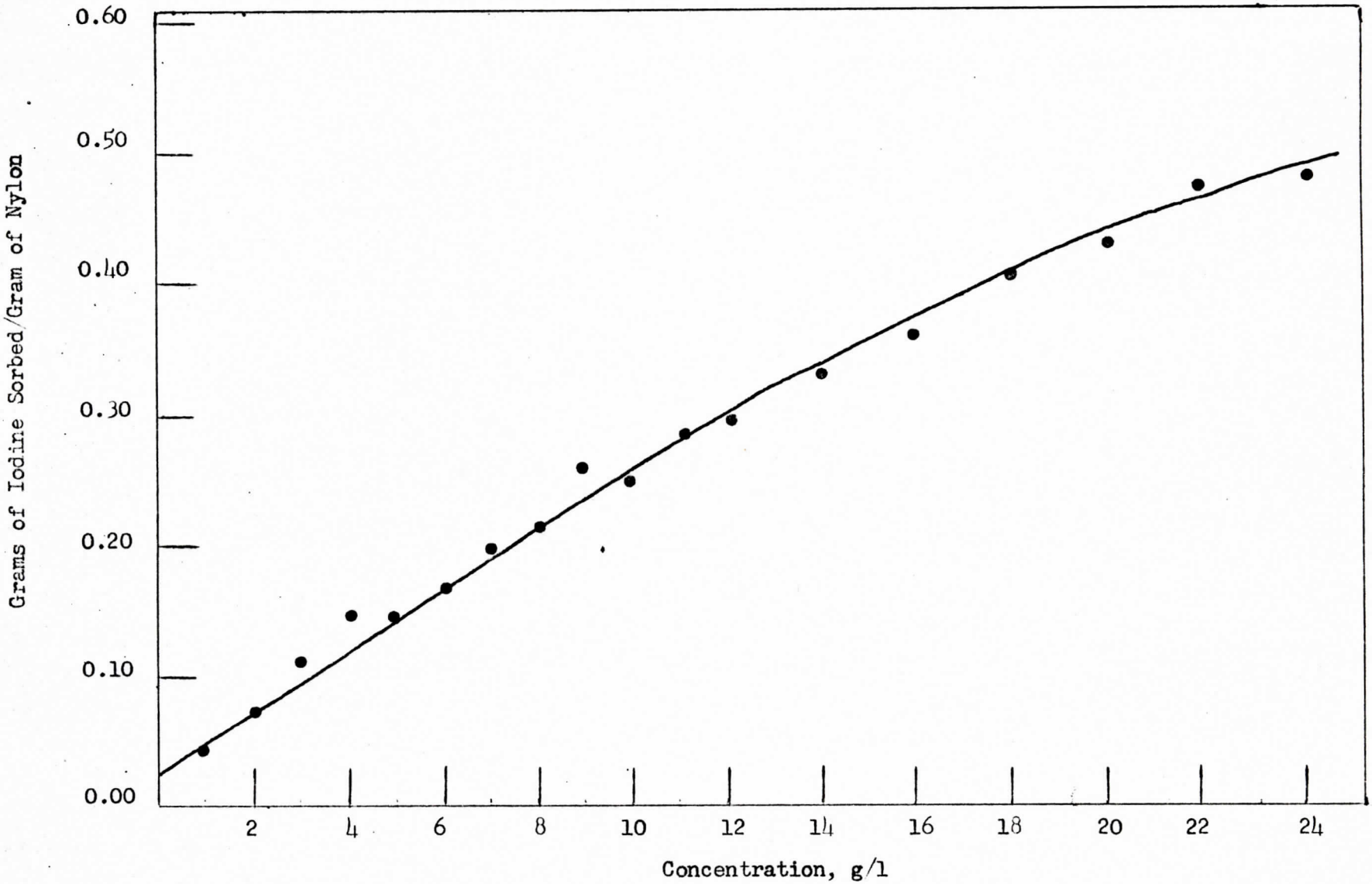


Figure 5. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at a Temperature of 75.0°C and over a Period of Thirty Minutes

In Table VI the sorption data for the undrawn nylon yarn is rearranged to show more conveniently the effect of increasing temperature of sorption.

Figure 6 shows graphically the grams of iodine sorbed per gram of nylon verses the temperature of sorption. In this plot curves for low concentrations, 1 and 3 g/l, and moderate concentrations, 9 and 18 g/l, I_2-KI solutions are shown. The 1 and 3 g/l plots show no dependence upon temperature. The 9 and 18 g/l plots, on the other hand, show that the amount sorbed increases with increasing temperature. There appears to be a linear dependence on temperature.

Table VII gives the grams of iodine absorbed at 58.2°C from 5, 10, and 20 g/l solutions of I_2-KI for various immersion times. These data are plotted in Figure 7. It is seen that the amount absorbed increases rapidly with time. After a time of about 15 minutes maximum sorption is reached after which time no further increase is observed.

Table VIII and Figure 8 show data obtained for a similar time study carried out on the undrawn fiber at a lower temperature, 30.5°C, and over a shorter period of time.

Tables IX, X, XI, XII, and XIII give data on sorption of iodine by drawn fibers for various I_2-KI concentrations sorbed at temperatures of 15.0, 30.5, 43.7, 58.2, and 73.0°C, respectively. These data are shown graphically in Figures 9, 10, 11, 12, and 13, respectively.

As shown by Figures 9, 10, 11, 12, and 13, sigmoid shape curves are obtained. However, the slope is much more gradual than is shown by the undrawn fibers. The curves show that the amount sorbed is tending to approach more of a linear relationship with I_2-KI concentration.

Table XIV and Figure 14 show that the amount of iodine sorbed by the drawn fibers has no simple dependence on temperature. Although there is

TABLE VI

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT VARIOUS TEMPERATURES AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams Sorbed at 15.0°C	Grams Sorbed at 30.0°C	Grams Sorbed at 45.0°C	Grams Sorbed at 60.0°C	Grams Sorbed at 75.0°C
1	0.048	0.048	0.068	0.034	0.042
2	0.081	0.086	0.096	0.064	0.071
3	0.105	0.101	0.110	0.081	0.114
4	0.106	0.122	0.126	0.107	0.147
5	0.137	0.150	0.131	0.137	0.147
6	0.137	0.171	0.183	0.129	0.166
7	0.138	0.200	0.178	0.136	0.196
8	0.142	0.232	0.236	0.151	0.212
9	0.146	0.220	0.208	0.246	0.256
10	0.170	0.178	0.214	0.254	0.245
11	0.173	0.206	0.242	0.252	0.285
12	0.250	0.192	0.230	0.308	0.293
14	0.250	0.206	0.229	0.333	0.327
16	0.279	0.237	0.273	0.345	0.362
18	0.440	0.279	0.355	0.355	0.407
20	0.431	0.333	0.361	0.410	0.428
22	0.455	0.404	0.396	0.400	0.483
24	0.523	0.514	0.395	0.416	0.483

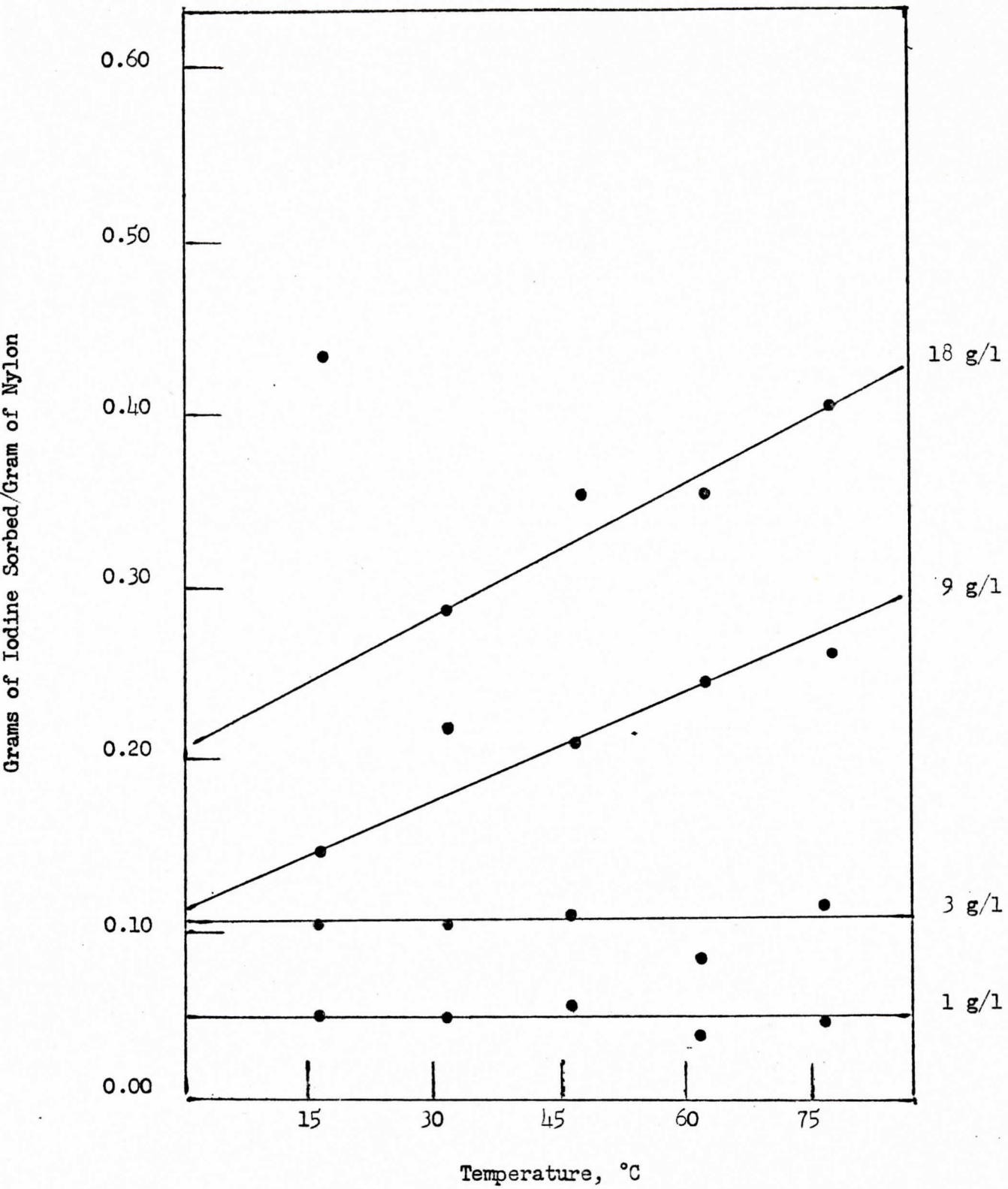


Figure 6. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at Various Temperatures and over a Period of Thirty Minutes

TABLE VII

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 58.2°C AND AT VARIOUS TIMES

Concentration, g/l	Time, Minutes	Grams I_2 Sorbed / Gram of Nylon
5	1	0.052
5	3	0.099
5	5	0.117
5	10	0.145
5	15	0.154
5	20	0.162
5	30	0.149
5	40	0.143
5	50	0.145
5	60	0.162
10	1	0.113
10	3	0.143
10	5	0.145
10	10	0.208
10	15	0.208
10	20	0.201
10	30	0.186
10	40	0.196
10	50	0.199
10	60	0.191
20	1	0.187
20	3	0.275
20	5	0.275
20	10	0.266
20	15	0.299
20	20	0.368
20	30	0.294
20	40	0.282
20	50	0.295
20	60	0.335

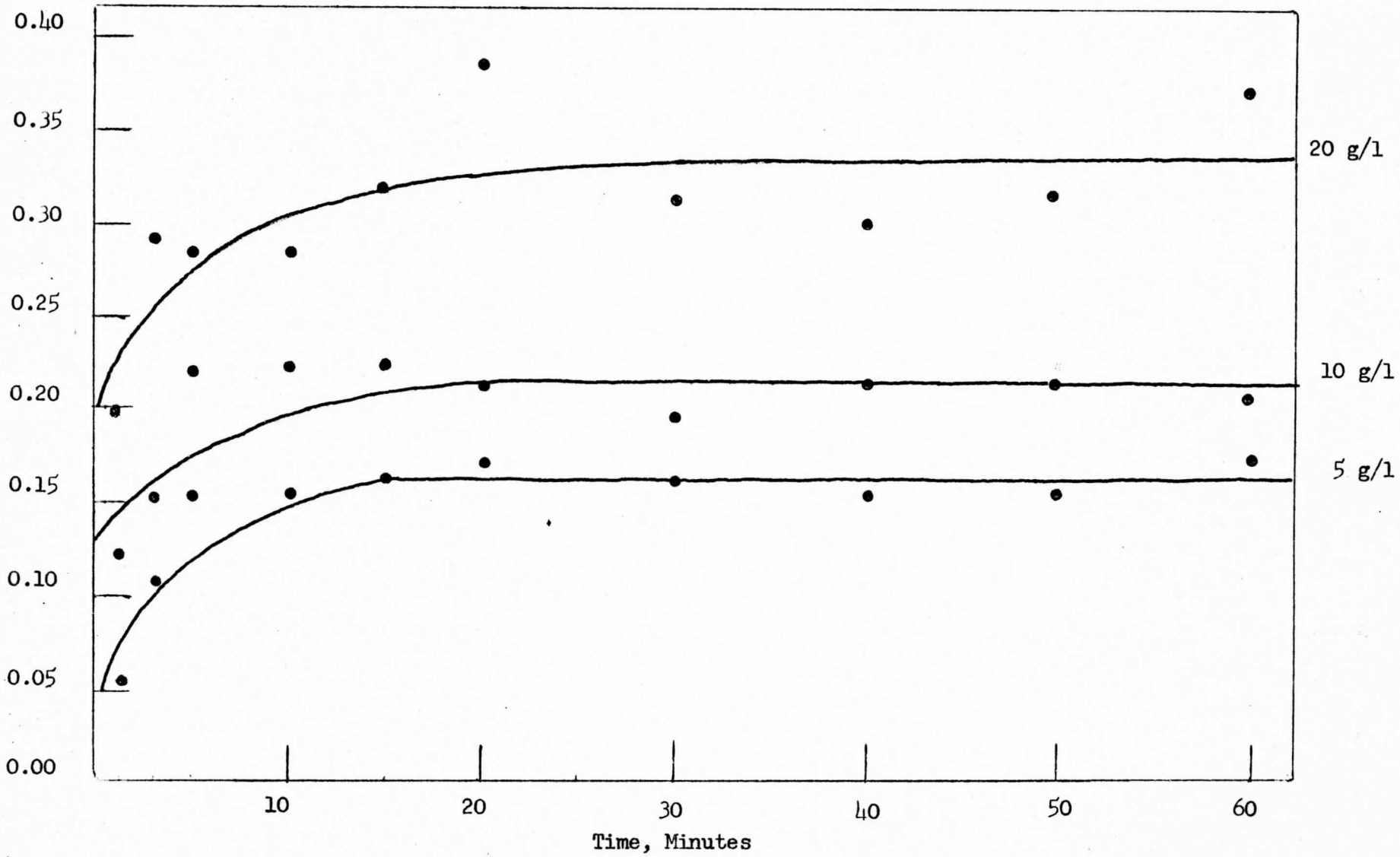


Figure 7. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at a Temperature of 58.2°C and at Various Times

TABLE VIII

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 30.5°C AND AT VARIOUS TIMES

Concentration, g/l	Time, Seconds	Grams I_2 Sorbed / Gram of Nylon
5	10	0.010
5	30	0.020
5	60	0.027
5	90	0.039
5	120	0.045
5	150	0.055
5	180	0.054
5	240	0.065
5	300	0.076
5	360	0.079
5	420	0.081
5	480	0.119
5	540	0.123
10	10	0.024
10	30	0.038
10	60	0.050
10	90	0.058
10	120	0.083
10	150	0.101
10	180	0.102
10	240	0.121
10	300	0.131
10	360	0.174
10	420	0.161
10	480	0.198
10	540	0.197
20	10	0.062
20	30	0.090
20	60	0.124
20	90	0.151
20	120	0.171
20	150	0.210
20	180	0.257
20	240	0.243
20	300	0.279
20	360	0.288
20	420	0.293
20	480	0.280
20	540	0.279

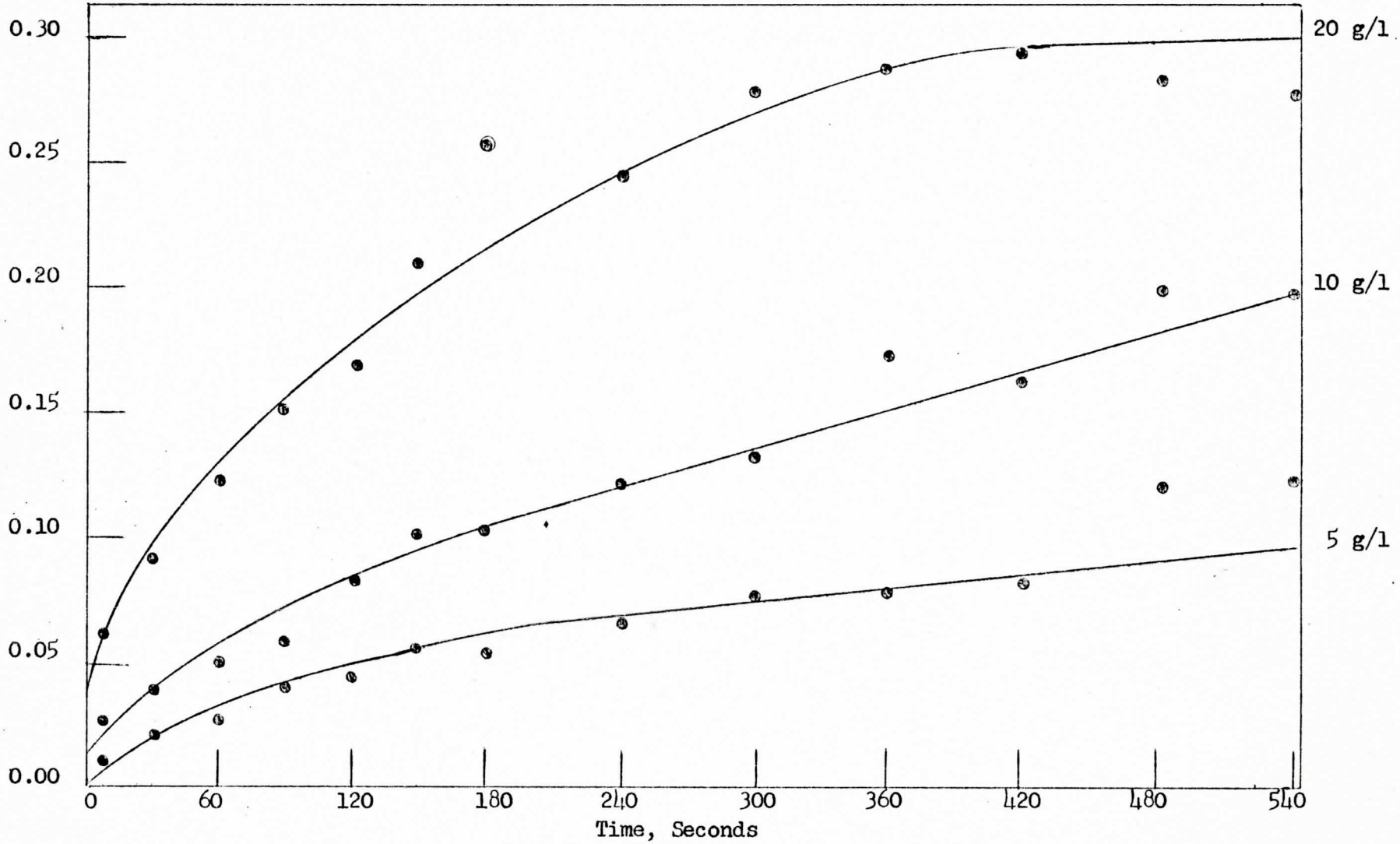


Figure 8. Grams of Iodine Sorbed Per Gram of Undrawn 66 Nylon Fibers from I_2-KI Solutions of Various Concentrations at a Temperature of 30.5°C and at Various Times

TABLE IX

GRAMS OF IODINE SORBED PER GRAM OF DRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 15.0 C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
2	0.062
4	0.096
6	0.133
8	0.189
10	0.233
12	0.280
14	0.290
16	0.330
18	0.407
20	0.405
22	0.413
24	0.492

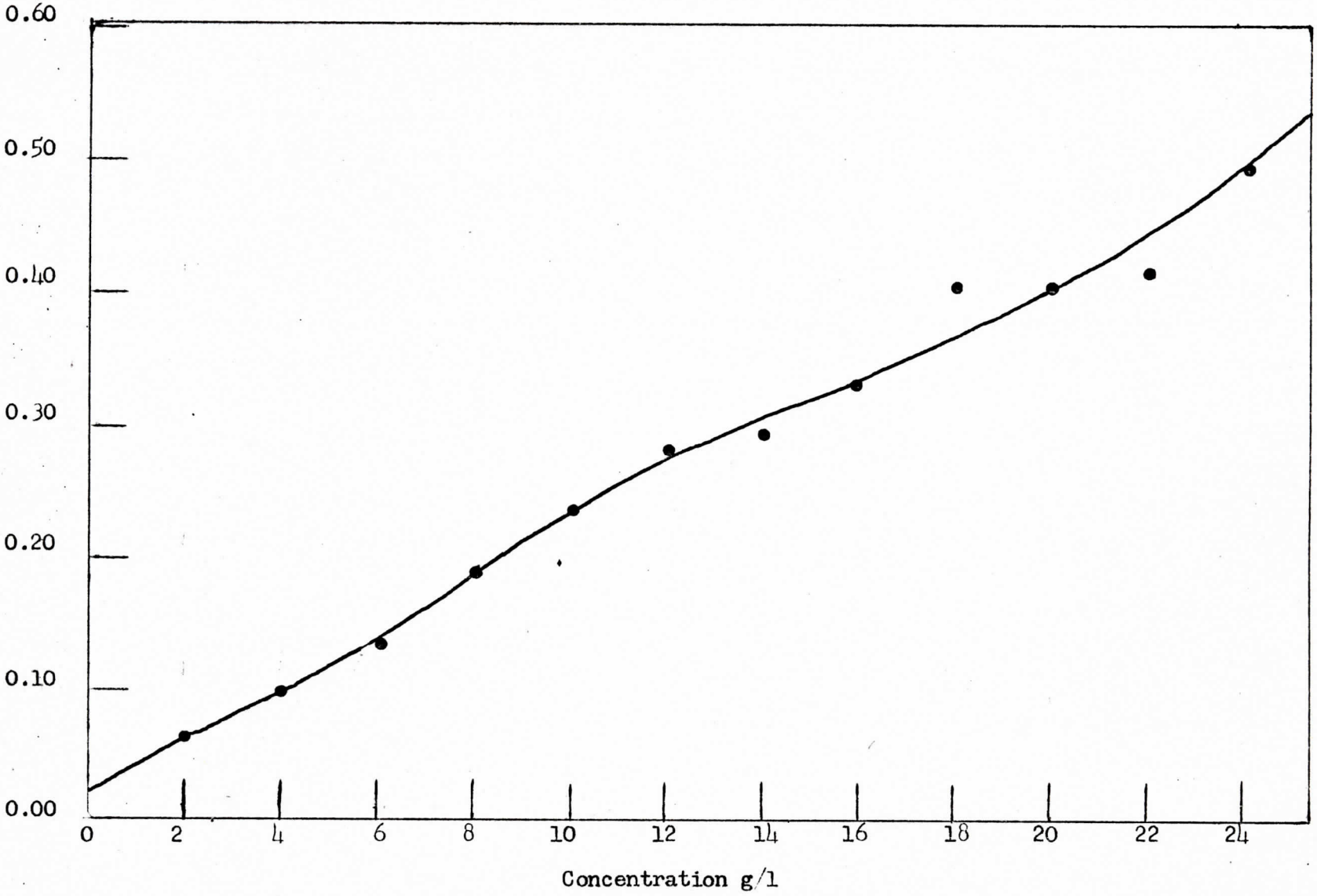


Figure 9. Grams of Iodine Sorbed Per Gram of Drawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at a Temperature of 15.0°C and over a Period of Thirty Minutes

TABLE X

GRAMS OF IODINE SORBED PER GRAM OF DRAWN 66 NYLON FIBER FROM I_2- KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 30.5 C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
2	0.095
4	0.133
6	0.165
8	0.193
10	0.258
12	0.270
14	0.282
16	0.308
18	0.341
20	0.374
22	0.445
24	0.500

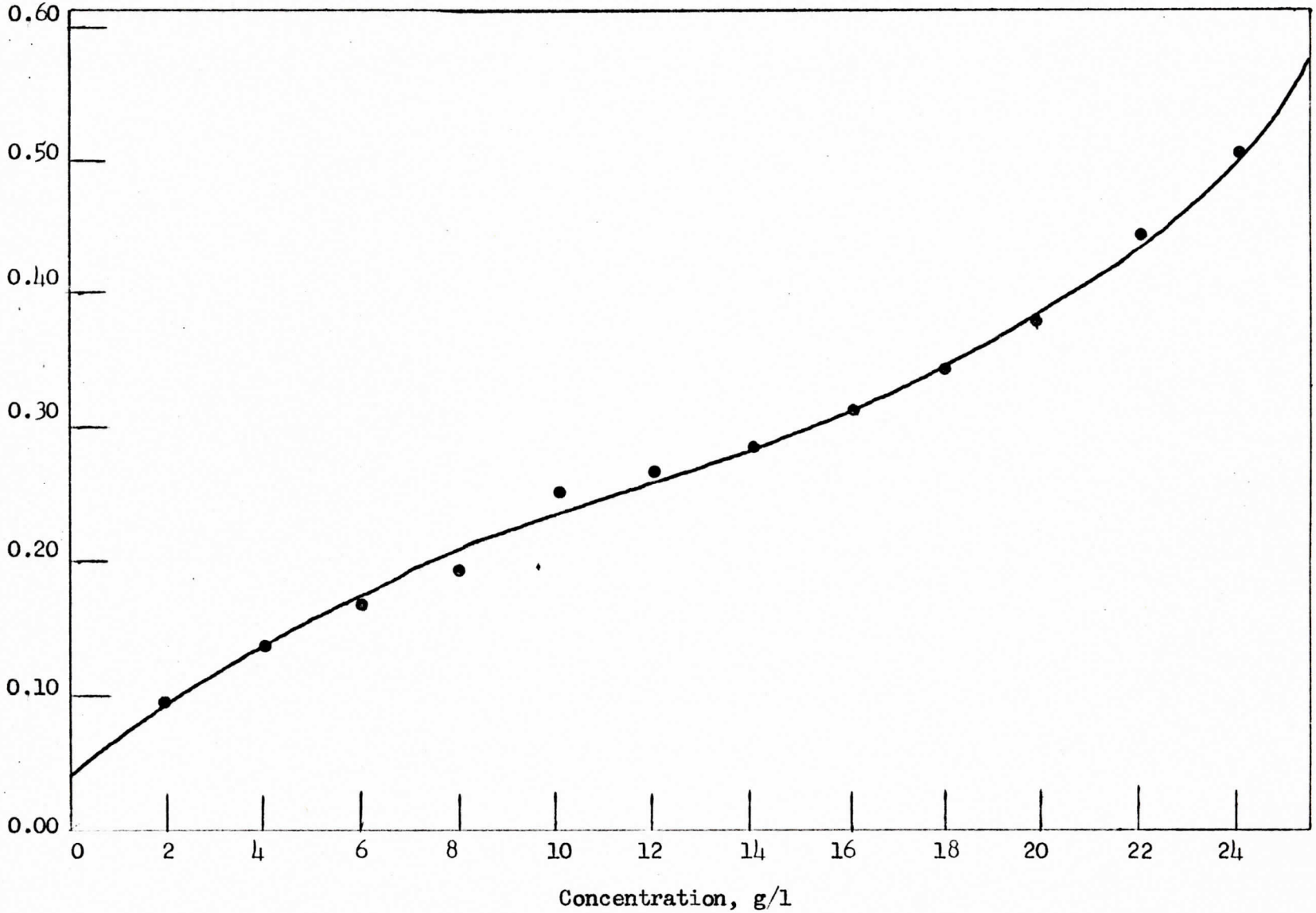


Figure 10. Grams of Iodine Sorbed Per Gram of Drawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentration at a Temperature of 30.5°C and over a Period of Thirty Minutes

TABLE XI

GRAMS OF IODINE SORBED PER GRAM OF DRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 43.7 C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
2	0.088
4	0.124
6	0.150
8	0.192
10	0.275
12	0.272
14	0.307
16	0.312
18	0.375
20	0.321
22	0.432
24	0.455

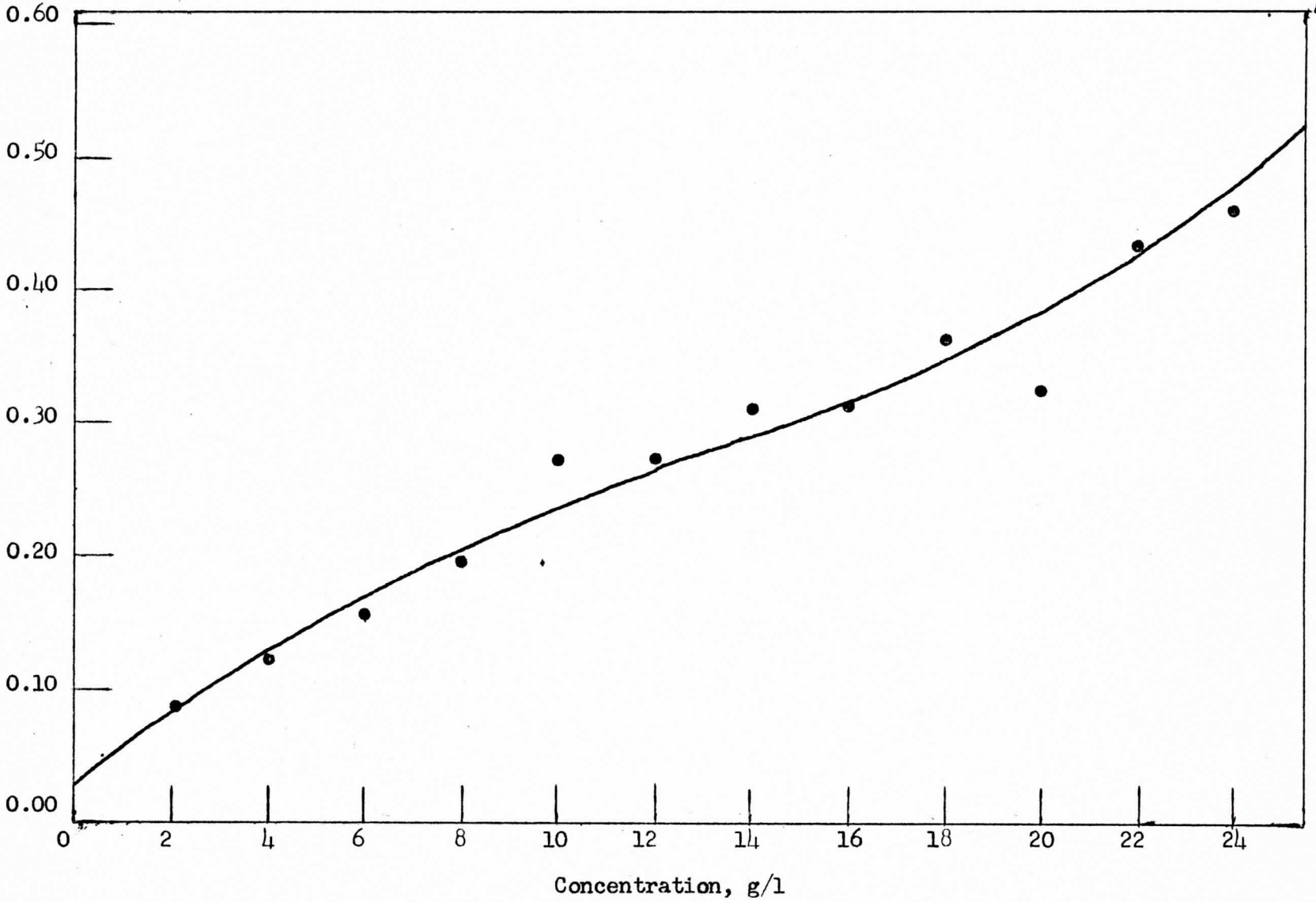


Figure 11. Grams of Iodine Sorbed Per Gram of Drawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at a Temperature of 43.7°C and over a Period of Thirty Minutes

TABLE XII

GRAMS OF IODINE SORBED PER GRAM OF DRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 58.2 C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
2	0.085
4	0.140
6	0.193
8	0.214
10	0.234
12	0.278
14	0.288
16	0.315
18	0.345
20	0.375
22	0.417
24	0.465

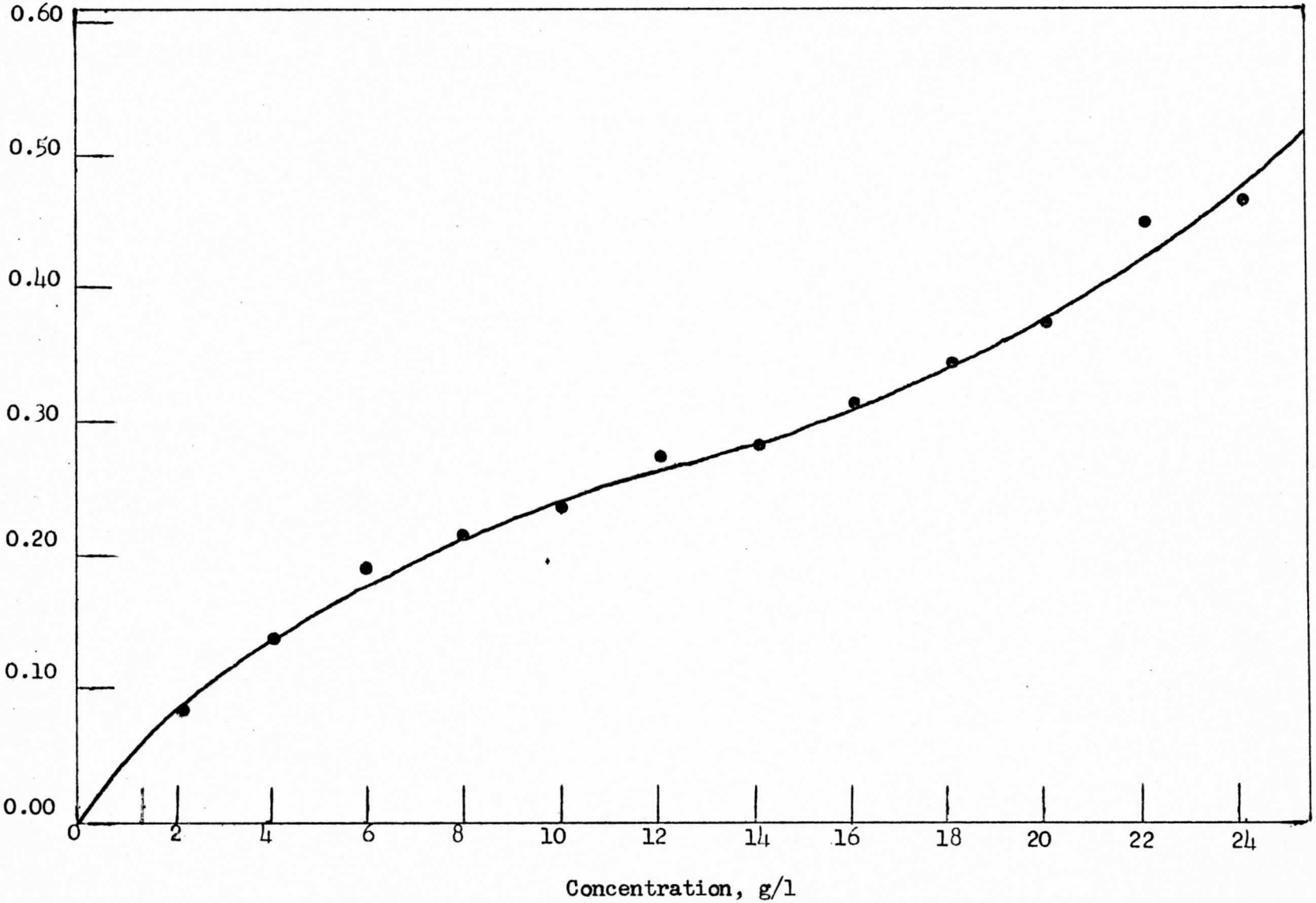


Figure 12. Grams of Iodine Sorbed Per Gram of Drawn 66 Nylon Fiber from I_2-KI Solution of Various Concentrations at a Temperature of 58.2°C and over a Period of Thirty Minutes

TABLE XIII

GRAMS OF IODINE SORBED PER GRAM OF DRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 73.0 C AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams I_2 Sorbed / Gram of Nylon
2	0.070
4	0.121
6	0.156
8	0.213
10	0.241
12	0.264
14	0.246
16	0.333
18	0.367
20	0.362
22	0.388
24	0.445

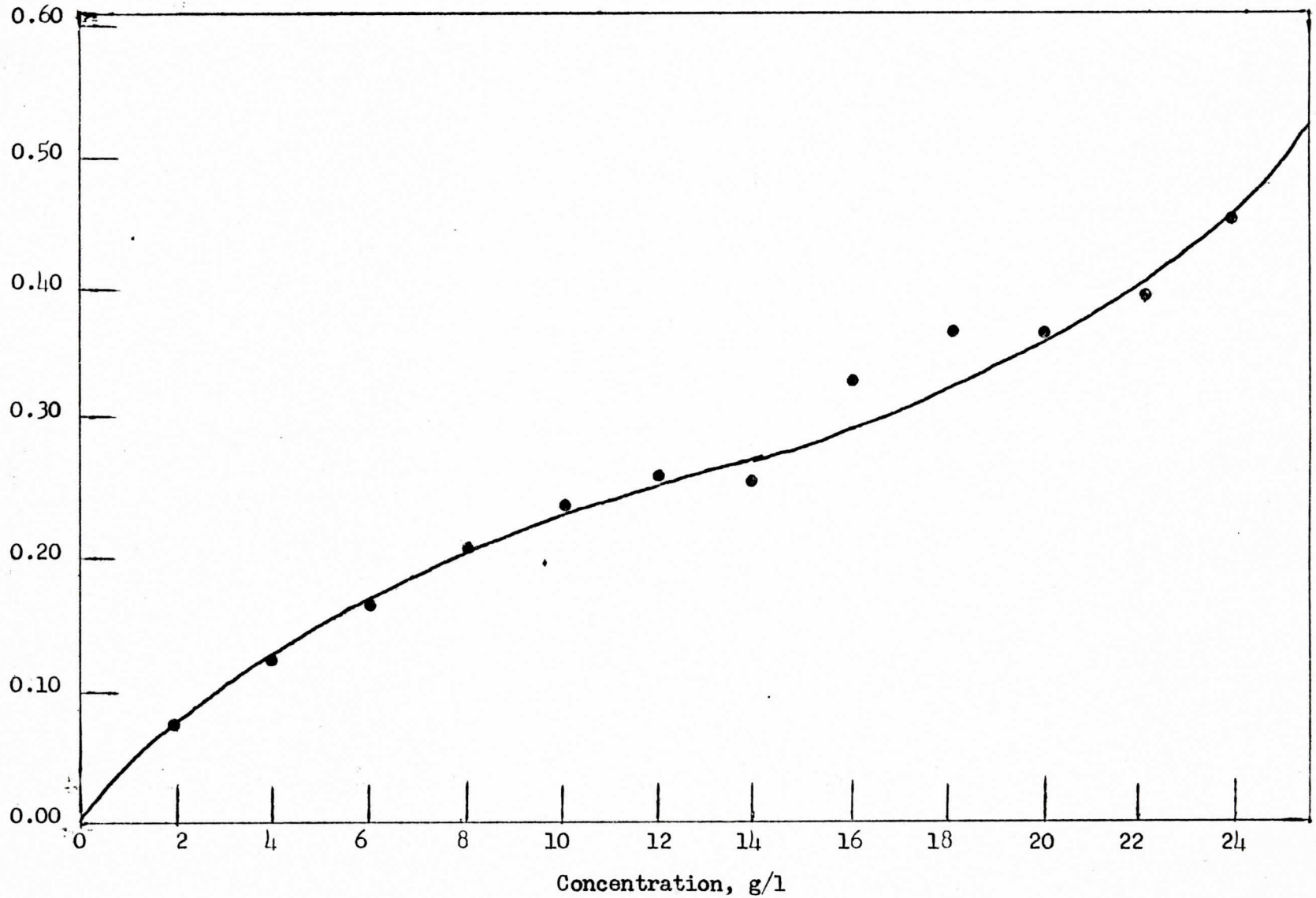


Figure 13. Grams of Iodine Sorbed Per Gram of Drawn 66 Nylon Fiber from I_2-KI Solution of Various Concentration at a Temperature of 73.0°C and over a Period of Thirty Minutes

TABLE XIV

GRAMS OF IODINE SORBED PER GRAM OF UNDRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT VARIOUS TEMPERATURES AND OVER A PERIOD OF 30 MINUTES

Concentration, g/l	Grams Sorbed at 15.0°C	Grams Sorbed at 30.5°C	Grams Sorbed at 43.7°C	Grams Sorbed at 58.2°C	Grams Sorbed at 73.0°C
2	0.062	0.095	0.088	0.085	0.070
4	0.096	0.133	0.124	0.140	0.121
6	0.133	0.165	0.150	0.193	0.156
8	0.189	0.193	0.192	0.214	0.213
10	0.233	0.258	0.275	0.234	0.241
12	0.280	0.270	0.272	0.278	0.264
14	0.290	0.282	0.307	0.288	0.246
16	0.330	0.308	0.312	0.315	0.333
18	0.407	0.341	0.375	0.345	0.367
20	0.405	0.374	0.321	0.375	0.362
22	0.413	0.445	0.432	0.417	0.388
24	0.492	0.500	0.455	0.456	0.445

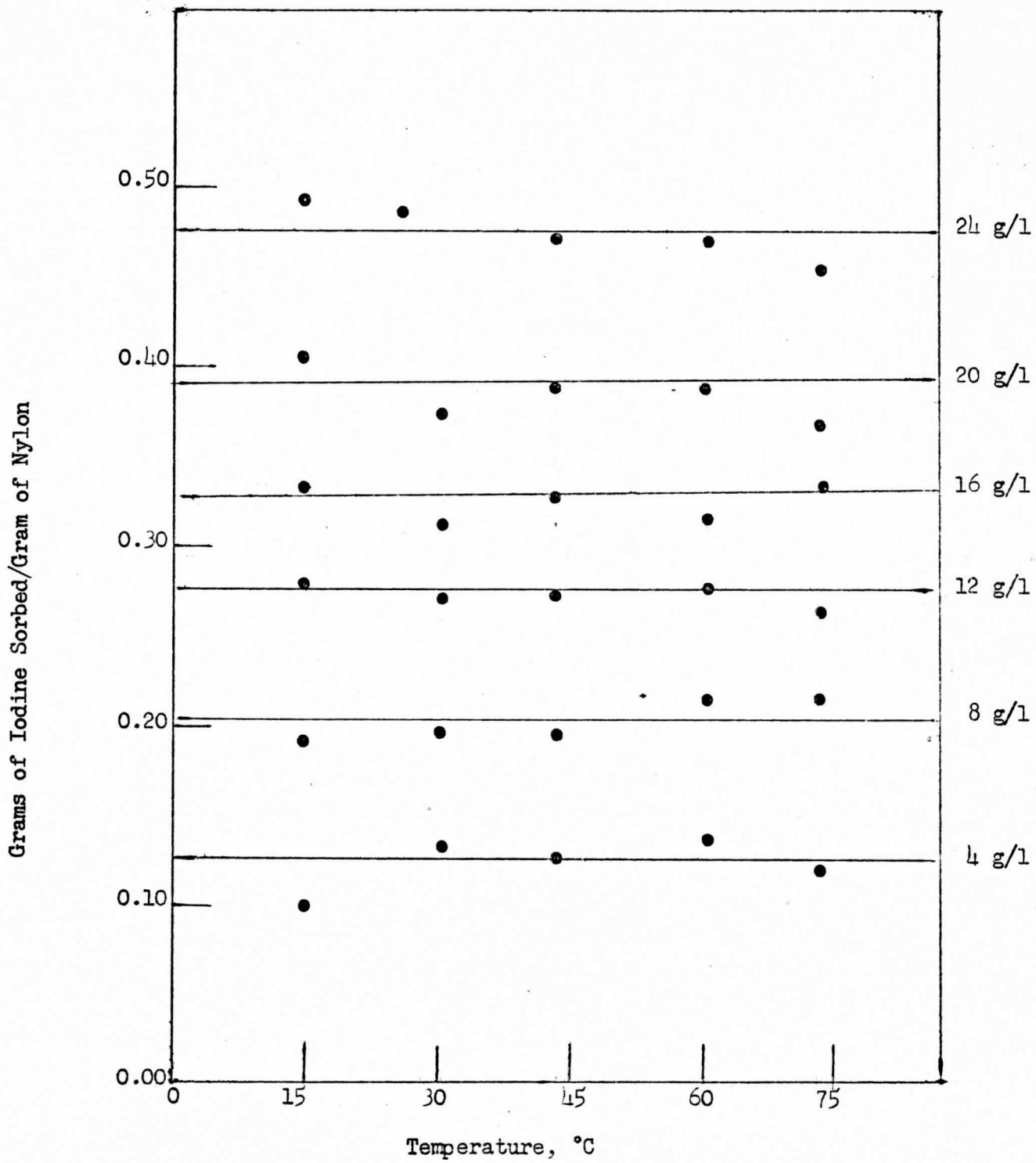


Figure 14. Grams of Iodine Sorbed Per Gram of Drawn 66 Nylon Fiber from I_2-KI Solutions of Various Concentrations at Various Temperatures and over a Period of Thirty Minutes

considerable scattering of data, the plots tend to imply that increasing the temperature does not increase appreciably the amount sorbed.

Table XV and Figure 15 depict the data obtained in the rate studies for the drawn 66 nylon fibers. Figure 15 shows that the amount sorbed increases with increasing time. A comparison of Figure 15 and Figure 7 shows that iodine is sorbed more slowly on the drawn fiber than it is on the undrawn fiber.

STRUCTURAL CHANGES OF 66 NYLON PRODUCED BY IODINE SORPTION

For the elucidation of the process or processes involved in the sorption of iodine by 66 nylon fibers, certain structural investigations were desirable. These were (1) swelling or solution of the 66 nylon in highly concentrated I_2-KI solutions at elevated temperature, (2) penetration of the iodine within the filament cross-section, and (3) changes in the molecular structure of 66 nylon as revealed by infrared absorption studies. Such studies of structure could aid materially, therefore, in deciding whether the sorption process was a simple adsorption process or a more complicated one which involved both absorption within the fiber and adsorption on the surface of the fiber.

When the cross-section of the sorbed fibers were viewed under a microscope, the cross-section had a deep coloration uniformly distributed throughout the cross-section of the filaments. This color was observed to deepen for those filaments having greater sorption of iodine.

In the experiment in which the nylon fiber was placed in the I_2-KI solution containing 445 g/l of I_2, the fibers were found to fuse together at room temperature. Further, upon heating the test tube containing the fibers in this solution to 80°C, large sections of the film broke off and dissappeared. It appears that some of the fiber dissolved in the I_2-KI

TABLE XV

GRAMS OF IODINE SORBED PER GRAM OF DRAWN 66 NYLON FIBER FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 30.5°C AND AT VARIOUS TIMES

Concentration, g/l	Time, Seconds	Grams of I_2 Sorbed / Gram of Nylon
5	10	0.011
5	30	0.012
5	60	0.021
5	90	0.030
5	120	0.039
5	150	0.040
5	180	0.050
5	240	0.063
5	300	0.080
5	360	0.069
5	420	0.082
5	480	0.094
5	540	0.092
10	10	0.011
10	30	0.026
10	60	0.042
10	90	0.063
10	120	0.072
10	150	0.090
10	180	0.111
10	240	0.108
10	300	0.137
10	360	0.146
10	420	0.151
10	480	0.192
10	540	0.206
20	10	0.026
20	30	0.066
20	60	0.112
20	90	0.160
20	120	0.181
20	150	0.216
20	180	0.242
20	240	0.307
20	300	0.315
20	360	0.310
20	420	0.305
20	480	0.292
20	540	0.320

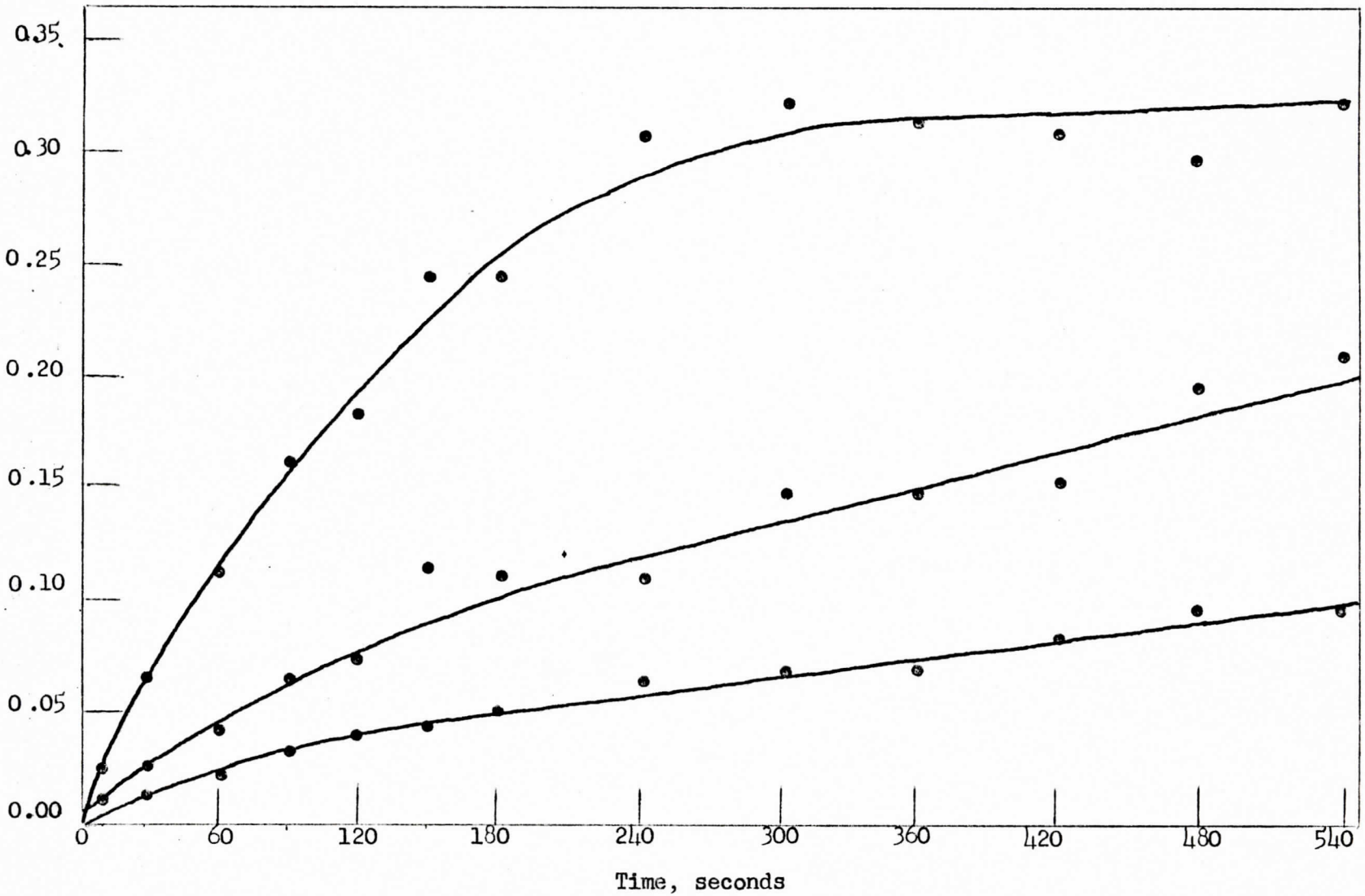


Figure 15. Grams of Iodine Sorbed Per Gram of Drawn 66 Nylon Fiber From I_2-KI Solutions of Various Concentrations at a Temperature of 30.5°C and at Various Times

solution at this temperature.

Figures 16, 17, and 18 are reproductions of the infrared absorption spectra in the range from 600 cm^{-1} to 4000 cm^{-1} for untreated, mildly iodine treated, and heavily iodine treated 66 nylon film. In Tables XVI, XVII, and XVIII the absorption peaks and the relative intensities are given for the three films.

A comparison of the absorption peaks with respect to both wavenumber and relative intensities of the untreated and iodine treated films show drastic changes in the spectra as a result of the iodine treatment. Certain of the absorption bands have disappeared, changed in relative intensities, and shifted their wavenumber values. All of these observations represent very strong evidence for a change in the molecular structure as a result of the sorption. It is indicative that an absorption process is involved.

Of particular importance is the 3290 cm^{-1} absorption band. This is the hydrogen bonded N-H stretching frequency in 66 nylon. This absorption shifted its position to 3320 cm^{-1} for the mildly treated film. Also, on heavier treatment the band shifted to an even higher value, 3335 cm^{-1}. This observation is in reasonably good agreement with the work of Arimato (4), who found that a more drastic iodine treatment than used in this study resulted in a shift of this absorption from 3290 cm^{-1} to 3350 cm^{-1}.

TABLE XVI

WAVENUMBER, CM^{-1} AND RELATIVE INTENSITIES OF INFRARED ABSORPTION BANDS FOR UNTREATED 66 NYLON FILMS

Wavenumber, cm^{-1}	Relative Intensity
690	23
730	40
795	83
905	78
935	45
999	85
1005	84
1040	79
1060	79
1140	46
1200	19
1230	42
1280	12
1375	20
1415	13
1440	28
1470	13
1480	,9
1540	0 broad
1645	0 "
1740	77
2860	10
2940	2
3080	35
3290	0

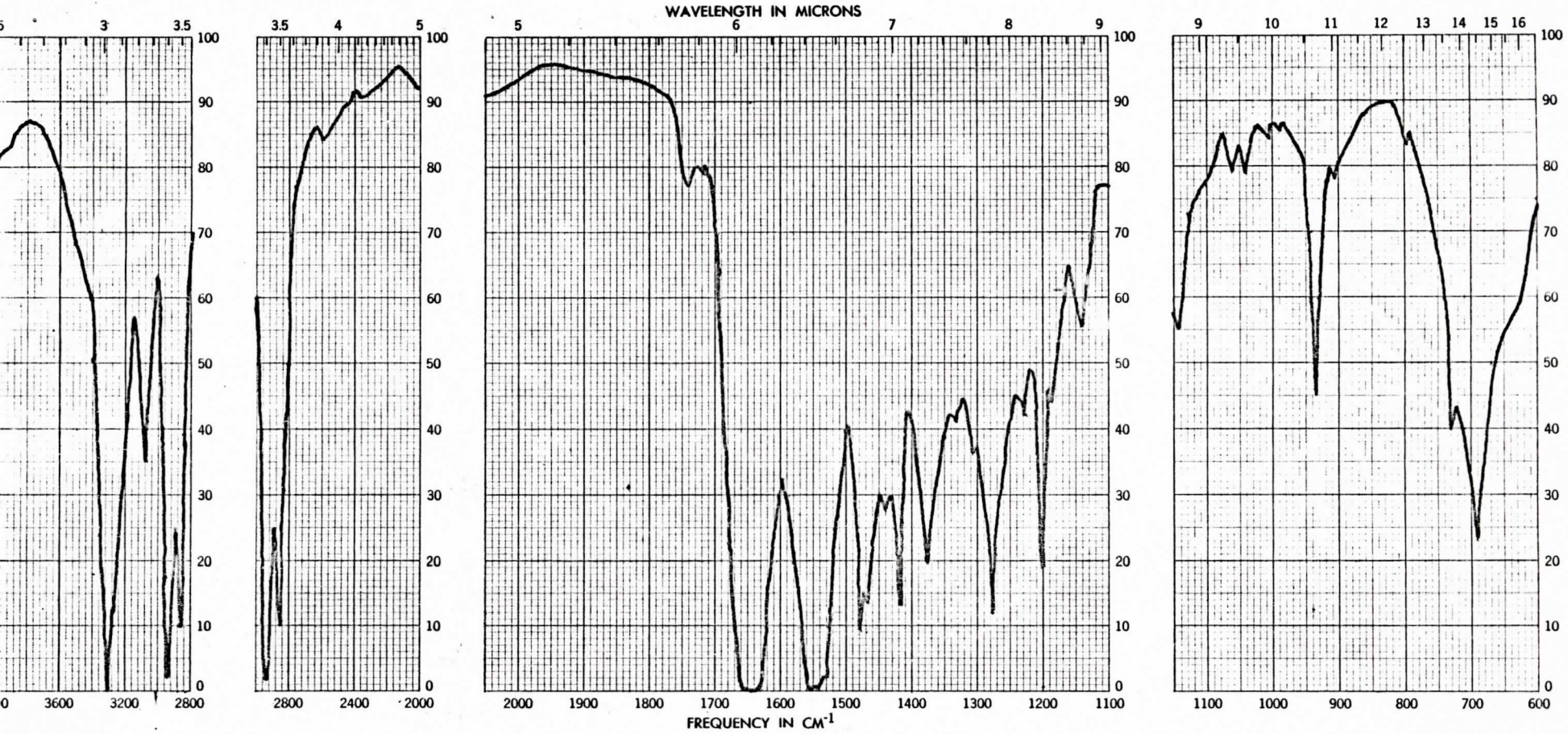


Figure 16. Infrared Spectra of Untreated 66 Nylon Film

TABLE XVII

WAVENUMBER, CM^{-1} AND RELATIVE INTENSITIES OF INFRARED ABSORPTION BANDS FOR MILDLY TREATED 66 NYLON FILM

Wavenumber, cm^{-1}	Relative Intensity
690	27
730	47
795	85
910	82
935	52
1045	72
1070	72
1150	60
1185	46
1210	22
1285	13
1380	23
1420	16
1450	28
1470	17
1480	13
1540	0 broad
1645	0 "
1755	79
2880	11
2960	2
3100	45
3320	1

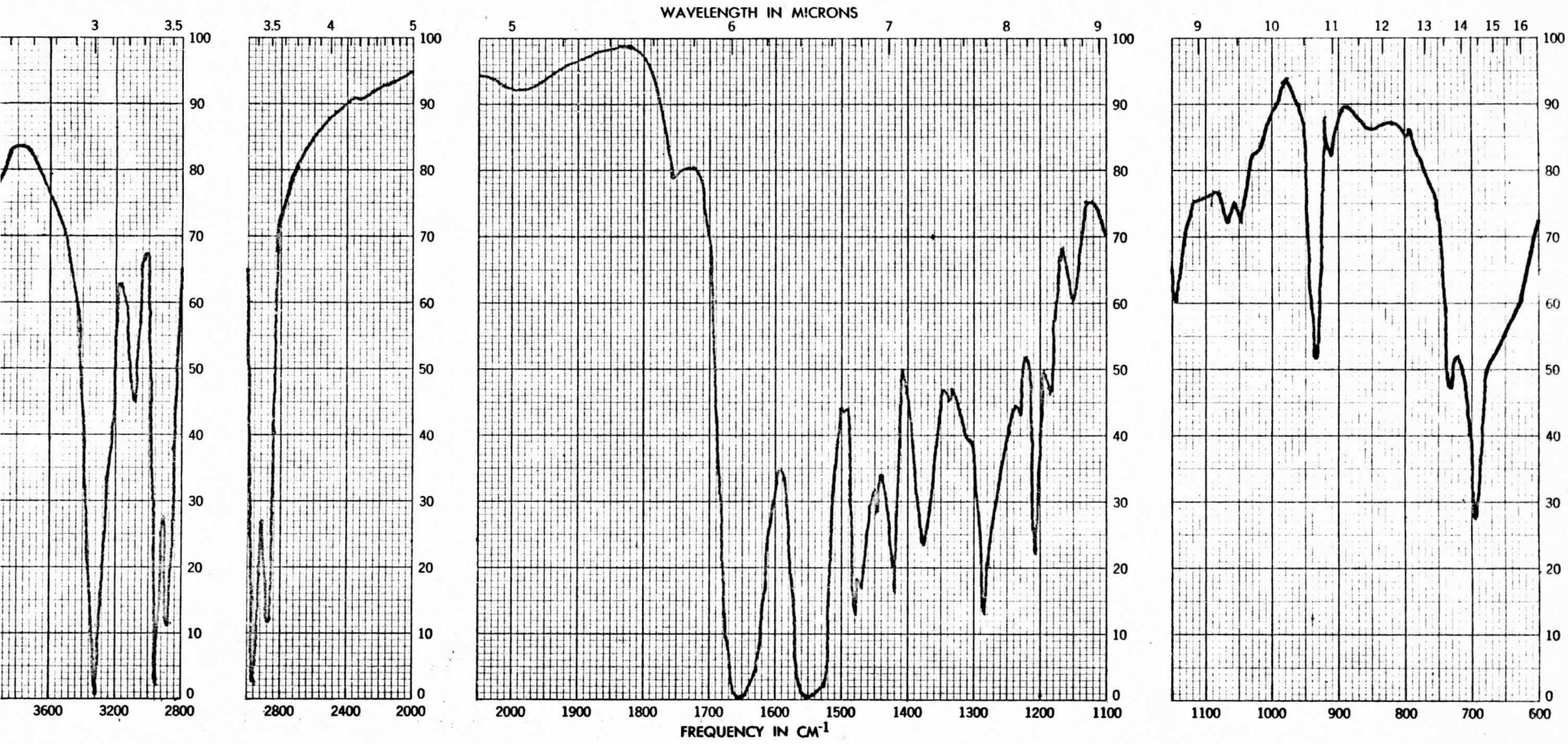


Figure 17. Infrared Spectra of Mildly Treated 66 Nylon Film

TABLE XVIII

WAVENUMBER, CM^{-1} AND RELATIVE INTENSITIES OF INFRARED ABSORPTION BANDS FOR HEAVILY TREATED 66 NYLON FILM

Wavenumber, cm^{-1}	Relative Intensities
690	29
730	40
800	88
910	90
950	55
990	92
1040	75
1060	77
1100	82
1210	33
1280	18
1340	60
1380	28
1440	23
1470	15
2880	30
2960	10
3080	98
3360	13

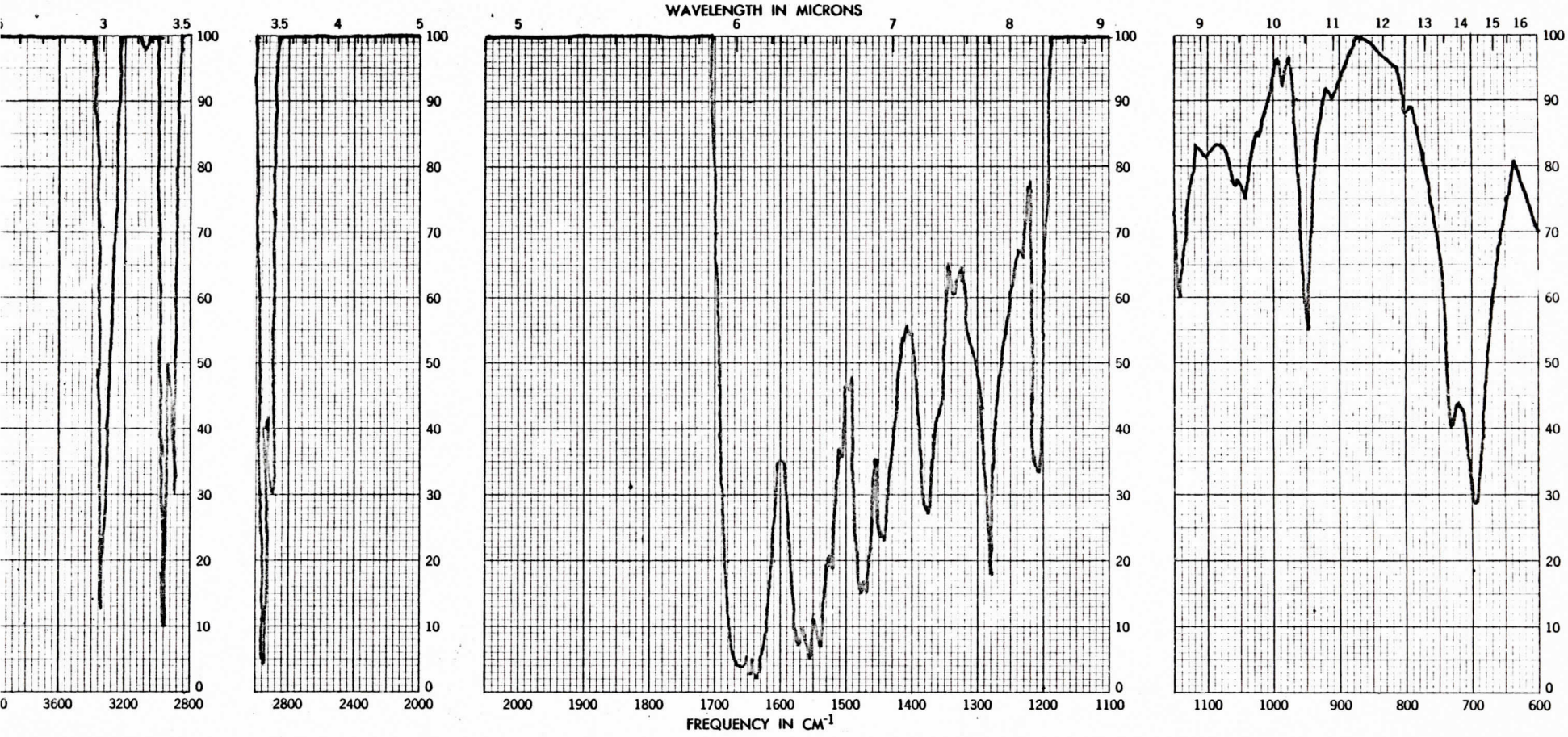


Figure 18. Infrared Spectra of Heavily Treated 66 Nylon Film

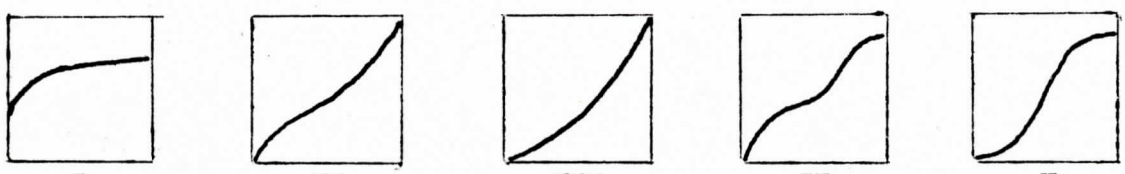
CHAPTER V

DISCUSSION OF RESULTS

The study of the sorption process with respect to concentration shows that for a given temperature and time of sorption, the amount of iodine sorbed per gram of 66 nylon fiber increases with concentration in an approximately sigmoidal slope manner.

At first consideration, we might assume that the sorption process is truly an adsorption process. In adsorption, two types of adsorption may be considered--physical adsorption and chemisorption. Physical adsorption involves attraction of adsorbate to adsorbent by van der Waals attractions. Chemisorption, on the other hand, involves the attraction of adsorbate to adsorbent by forces of a chemical nature.

Five different adsorption isotherms have been distinguished and are shown below (11).



Type I corresponds to the formation of a monolayer of adsorbate on the adsorbent surface. Types II and III correspond to several physically adsorbed layers. Types IV and V correspond to adsorption of adsorbate in small pores and capillaries existing in the adsorbent.

It is tempting to explain the curves obtained in this study, on the

assumption of pure adsorption by curves II and III and/or curves IV and V.

An inspection of the sorption isotherms obtained show the greatest similarity to types II and III. Types IV and V with a leveling off of the amount of iodine adsorbed is not shown for any of the curves. There are certain differences in the experimental curves from types II and III. Some of them, especially at higher temperatures appear to be very nearly linear relationships. This would seem to imply that the sorption process is not simply a purely chemisorption type of adsorption. It becomes necessary to inquire into the possibility of an absorption process also being involved.

The uniform penetration of iodine throughout the filament cross-section, the partial dissolving of the fiber in I_2-KI solution of high concentration, and the drastic changes in the infrared absorption spectrum of 66 nylon films treated with iodine give strong evidence that an absorption process is involved in the sorption of iodine by 66 nylon.

The observation made that no appreciable quantity of iodine is sorbed by 66 nylon from I_2-CCl_4 solution is strong evidence that the I_3^- ion-dipole is involved in the sorption process with 66 nylon fibers.

Finally, the comparision of the rates of sorption by undrawn and drawn nylon fibers are of considerable interest. The rate of sorption of the drawn nylon was slower than that of the undrawn nylon. However, crystallinities as determined from density measurements gave crystallinities of undrawn and drawn nylon of approximately 40% (19). They were not significantly different.

If it is assumed that an affine deformation is involved in the stretching process, then the surface for adsorption should be roughly 1.9 times as great for the drawn fiber. On the basis of a truly adsorption process, a greater amount of adsorption would be expected for the drawn fiber.

From the crystallinity values, the decreased sorption rate for the

drawn fiber is not a function of crystallinity.

It seems, therefore, that the most tenable explanation for the decreased rate is that the chain alignment due to stretching has made regions in the fiber less accessible for interaction with the I_3^- ion-dipole. These results strongly suggest that the major type of sorption involved is predominantly an absorption process. The mechanism of this process appears to involve a weakening or disruption of the intermolecular hydrogen bonding and the formation of some sort of iodine bridge with the carbonyl oxygen of the 66 nylon polymer chain.

The known swelling and dissolving behavior of 66 nylon in phenol, formic acid and other highly polar solvents would be expected to follow a similar type of mechanism, i.e., the disruption of intermolecular hydrogen bonds by a predominantly absorption process.

CHAPTER VI

CONCLUSIONS

The following conclusions may be drawn from this investigation.

(1) The amount of iodine sorbed by both drawn and undrawn fibers is dependent upon concentration. As concentration is increased, the amount of iodine sorbed per unit mass of nylon increases.

(2) For the conditions in the experiment, it is seen that maximum sorption of iodine is reached in about 15 minutes. Also the rate of sorption is faster for the undrawn nylon as compared to drawn nylon.

(3) When conditions are drastic enough, fusion of the filaments and partial solution of the nylon will take place in I_2-KI solution.

(4) The intermolecular forces of hydrogen bonding are weakened as a result of iodine sorption. This is seen by a shift in the hydrogen bonding N-H stretching frequency.

(5) The type of sorption of iodine by 66 nylon fibers is mainly absorption. Also the process of sorption involves the I_3^- ion.

CHAPTER VII

SUGGESTIONS FOR FUTURE WORK

In an article by Ford and Warwicker (10), it is stated that 11 nylon and 6·10 nylon were unstained when treated with a 20% solution of iodine in saturated potassium iodide. Fibers of 66 and 6 nylon were stained black after immersion for one minute.

The crystal structure of 66 nylon and 6·10 nylon were reported in an article by Bunn and Garner (5) as being similar. The intermolecular forces acting in both nylons is that of hydrogen bonding. If the latter statement is true, then it seems strange that 6·10 nylon will not sorb iodine, whereas 66 nylon will.

A suggestion for future work is to study the sorption of iodine on 6·10 nylon. If Ford and Warwickers' statement is true, it would be of interest to know why it is true.

A second suggestion is obtained from the work of Arimato (4). Iodine is sorbed on 6 nylon which is in an α structure. On desorption of the iodine it was found that the nylon now has an γ structure. It would be of interest to study the sorption of iodine on the α structure and compare it to the sorption on the γ structure.

BIBLIOGRAPHY

(1) Arimato, H., Kobunski Kagaku, 19, 101 (1962); cit., C. A., 57, 16844c (1962).

(2) Arimato, H., Kobunski Kagaku, 19, 205 (1962); cit., C. A., 58, 4686h (1963).

(3) Arimato, H., Kobunski Kagaku, 19, 461 (1962); cit., C. A., 60, 1852h (1964).

(4) Arimato, H., J. Polymer Sci., 2, 2283 (1964).

(5) Bunn, C. W. and Garner, E. V., Proc. Roy. Soc., A189, 39 (1947).

(6) Cannepin, A. and Rayon, J., Bull. Inst. Textile France, 89, 33 (1960); cit., C. A., 55, 2112d (1961).

(7) Chappel, F. P., Arlpin, M. F., Gasden, R. G., and Tranter, T. C., J. Appl. Chem., 14, 12 (1964).

(8) Conant, J. B. and Blatt, A. H., "The Chemistry of Organic Compounds," 5th ed., The MacMillan Company, New York, 1963.

(9) Elliott, A., Ambrose, E. J., and Temple, R. B., J. Chem. Phys., 16, 877 (1948).

(10) Ford, J. E. and Warwicker, J. O., J. Textile Inst., 51, T80 (1960).

(11) Glasstone, S. and Lewis, D., "Elements of Physical Chemistry," 2nd ed., D. Van Nostrand Company, Inc., Princeton, New Jersey, 1962.

(12) Holmes, D. R., Bunn, C. W., and Smith, D. J., J. Polymer Sci., 17, 159 (1955).

(13) Kimura, T., Kobunski Kagaku, 15, 288 (1958); cit., C. A., 54, 8139c, (1960).

(14) Little, K., British Journal of Applied Physics, 10, 225 (1958).

(15) Tetyushkina, V. D., Pakshver, A. B., and Fralar, S. S., Colloid Journal (U.S.S.R.), 57, 1955.

(16) Mysels, K. J., "Introduction to Colloid Chemistry," 1st ed., Interscience Publishers, New York, 1964.

(17) O'Driscoll, K. F., "The Nature and Chemistry of High Polymers," 1st ed., Reinhold Publishing Corporation, New York, 1964.

(18) Pierce, W. C., Sawyer, D. T., and Haenisch, E. L., "Quantitative Analysis," 4th ed., John Wiley and Sons, Inc., New York, 1958.

(19) Starkweather, H. W. and Maynikan, R. E., J. Polymer Sci., 22, 363 (1956).

(20) Stratmann, M., Z. ges Textile Ind., 60, 450 (1958); cit., C. A., 52, 17723a (1958).

(21) Thompson, H. W. and Torkington, P., Trans. Faraday Soc., 41, 246 (1945).

(22) Veda, S. and Kimura, T., Kobunski Kagaku, 15, 243 (1958); cit. C. A., 54, 5155i (1960).

(23) Yoshida, M. and Endo, M., Kogys, Kagaku Zasshi, 59, 1074 (1956); cit. C. A., 52, 10687c (1958).