PROGRESS REPORT

OFFICE OF NAVAL RESEARCH
Contract Nonr-1129(00)
Project NO 036-012
Period Covered:
November 1, 1953 to
January 31, 1954

Institute of Polymer Research
Polytechnic Institute of Brooklyn
99 Livingston Street
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February, 1954

POLYTECHNIC INSTITUTE OF BROOKLYN

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POLYTECHNIC INSTITUTE OF BROOKLYN

INTERIM REPORT

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INTRODUCTION.

In this report an account will be given of the progress made during the last quarter of the first year of research under the above contract, together with some summarizing remarks.

Recalling briefly the objects, it was planned to subject the polyvinyl butyrals and acetals used in the Wash Primer Process, as well as the parental polyvinyl acetates, to a study with respect to their molecular weights and structures, to follow their adsorption on metal and other surfaces, including an investigation of the effects of structural changes on the extent of adsorption, and finally to study the fate of the resin during reactions simulating those occurring in practical use.

It has been realized from the beginning that, on the scale permitted, such a program was far too copious to be carried through with some degree of thoroughness during the course of one year. Moreover, in a first approach like this, unforeseen difficulties would, and did, arise which create delays. Certain compromises in objectives have become unavoidable, some essential data are still missing and others will have to be improved. It is hoped that, nonetheless, the data following below in conjunction with those earlier reported will be found sufficient to provide an outline of the desired answers.

In particular, we may refer to the characterization of the polyvinyl acetates, although unfortunately solubility limitations deprived us of much of the value of the cumbersome hydrolysis and reacetylation experiments. One result of importance is the increase in molecular weight observed in every instance, if the acetals are prepared from the acetates. With results of fractionation most doubtful, because of the inevitable chemical inhomogeneity of all polyvinyl acetals, our few weight/number ratios of molecular weight averages indicate an unusually wide range of molecular sizes, probably due to associations.

Our adsorption studies have at last begun to bear fruit but still involve great experimental difficulties. It is too early to say which variables will influence adsorption, let alone adhesion, but in general our acetates and acetals seem to follow adsorption laws not very different from Langmuir isotherms. Finally, our acetals seem to be surprisingly little chemically affected by influences to which they are subject during the wash primer process, and are likely to be deposited in the form of what in first approximation might be described as Cr^{3+} complexes.

EXPERIMENTAL AND RESULTS.

I. CHARACTERIZATION OF POLYVINYL ACETALS AND ACETATES.

A. Hydrolysis and Reacetylation of Polyvinyl Acetate XYSG.

Our results on Bakelite polyvinyl acetate XYHL having been given in previous reports, XYSG was now hydrolyzed and reacetylated in the same manner. The following Table I(a) gives a comparison of the molecular weights $\overline{M}_w$ from light scattering (corrected for dissymmetry and depolarization), the radius of gyration, the second virial coefficient, and intrinsic viscosity before and after hydrolysis and reacetylation, all in MEK.

TABLE I(a)

Sample	$\overline{M}_w$	$\sqrt{\overline{R^2}}$ (Å)	$B \times 10^6$	$[\eta]$ *
PVAc-XYSG (before)	275,000	204	4.4	80.5
PVAc-XYSG (after)	280,000	357	3.7	50.7

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* Concentration in gms/ml; in the older notation of gms/100 ml. the values would be 0.805 and 0.507

The reacetylated PVAc sample passed much more slowly through sintered glass filters than before reacetylation, as was noticed before (See Progress Report August 1-October 31, 1953), indicating the presence of micro-gel particles. The drop of the second virial coefficient, too, points to a reduced solubility. The radius of gyration, R, representing a "Z"-average, is more sensitive to the presence of a few large particles than the weight average molecular weight and might be expected to appear too large under these circumstances. This in turn leads to an over correction for the dissymmetry which raises the apparent molecular weight considerably and explains why the molecular weights before and after were found to be apparently the same.

Such a behavior is quite improbable with commercial samples and, therefore, branching must be assumed. If an estimated correct dissymmetry factor were applied, the molecular weight would drop by about 100,000 and would agree with the difference in viscosity, i.e. with the changes in $[\eta]$ from 80.5 to 57.0. At the same time, such a drop in $\bar{M}_w$ is of the magnitude expected as a result of hydrolysis of branched PVAc of the type investigated. The molecular weights reported in Table I(a) are thus almost certainly too high, and estimated values of the correct order are given in Table I(b) which for comparison includes a summary of the numbers previously found. The values for B, $\bar{M}_w$, and R are from light-scattering measurement at T = 28°C, while the viscosities were measured at 25°C.

TABLE I(b)

Sample	$B \times 10^6$	$\bar{M}_w$	$\overline{R^2}$ (Å)	$[\eta]$	Solvent
PVB (XYSG)	.70	800,000	388	106.0	MEK
PVAc (XYSG)	4.4	275,000	204	80.5	"
*PVAc (XYSG)	3.7 ---	280,000** 180,000***	357** ---	50.7 ---	"
PVB (XYHL)	.32	540,000	327	64.0	"
PVAc (XYHL)	4.8	155,000	188	58.8	Benzene
*PVAc	1.6 ---	150,000** 100,000***	367** ---	40.2 ---	"

* Reacetylated; ** observed; *** estimated.

B. Polyvinyl Formals:

Our studies of the two samples designated PVF 7-70 and PVF 15-95 S of the Shawinigan Resins Corporation were continued. Previous data had been determined in ethylene chloride. However, this solvent was found unsuitable for the measurement of osmotic pressures since apparently it attacks the membranes, and leads to erratic values.

The osmotic pressures were, therefore, studied in 95/5 dioxane/water and 70/30 acetic acid/water mixtures as solvents. The membranes behave well, though in the former solvent it takes 8-10 days to reach equilibrium. In the acetic acid-water mixture, the equilibrium is reached in the course of 24 hours, but the life of the membrane is not more than twice that period. The values found are (see also Fig. 1):

TABLE II(a)

Sample		$\overline{M}_N$	$B \cdot 10^6$	$\overline{M}_W$
PVF 7-70	Dioxane 95) Water 5)	106,000	1.94	295,000
" "	Acetic Acid 70) Water 30)	130,000	1.48	---
PVF 15-95 S	Dioxane 95) Water 5)	160,000	---	---

While the osmotic molecular weights of 7-70 are approximately the same, the slopes are different, indicating that the acetic acid/water mixture is the poorer solvent of the two for this polymer. In order to obtain a weight average molecular weight of sample 7-70 in the same solvent, we determined the light scattering in 95/5 dioxane/water, and found $\overline{M}_W$ = 295,000. This high value of the weight average molecular weight relative to $\overline{M}_N$ is reminiscent of the findings with reacetylated acetates and is most likely again due to the presence of some micro-gel particles in the solution.

A table of data summarizing our results obtained thus far from the polyvinyl formals and their related polyvinyl acetates follows below.

T A B L E II(b)

Polymer	$[\eta]$	k'	$\bar{M}_w$	$\sqrt{R}$ (A)	M_N	Solvent
PVAc-V-7	40.5	---	85,000	---	---	Acetone
PVF 7-70	65.0	0.33	275,000	112	---	Eth. di-Cl.
" "	62.5	0.384	294,000	---	106,000	Diox.-H_2O
" "			---	---	130,000	Acetic-H_2O
PVAc-V-15	65.5	----	190,000	---	---	Acetone
PVF 15-95-S	91.0	0.62	340,000	157	---	Eth. di-Cl.
" "	96.0	0.684	---	---	159,000	Diox.-H_2O

II. PREPARATION OF A HIGH-MOLECULAR WEIGHT POLYVINYL ACETATE.

In view of the narrow range of molecular weights of the commercial polyvinyl acetates from which the acetals are derived, it was decided to synthesize a high molecular weight sample of polyvinyl acetate and fractionate it in order to be able to study adsorption as a function of molecular weight. To avoid the additional complication of branching, the conversion was carried to 12% only, where very little, if any, branching occurs.

Eastman Kodak inhibited vinyl acetate was freed of hydroquinone and trace inhibitors by distillation under one atmosphere of pre-purified nitrogen through a column of sixty theoretical plates.* This column was constructed, using Podbliehniak Heli-Pak random type fractionating column packing. The distilled monomer was stored in the dark at 4°C.

The vinyl acetate was then polymerized in bulk in a manner similar to that of A.R. Shultz.(1) Fifty ml. of vinyl acetate and 0.001 gr. of $\alpha - \alpha'$-azo bis-isobutyro-nitrile were added to Pyrex tubes. Each tube containing monomer and initiator was thoroughly degassed by alternate freezing in liquid N_2 and thawing under a vacuum of 10^{-5} mm. The tubes were then sealed under vacuum, placed in a cold room at 4°C. and illuminated by a medium-pressure mercury lamp from a distance of 6

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* This was calculated by using the data in the literature supplied by the manufacturer of the packing.

(1) A.R. Shultz - Private Communication.

inches for twelve hours. The lamp supplies the necessary energy to decompose the initiator.

The polymers were isolated by adding acetone to each polymerization mixture yielding an approximately 5% polymer solution. This solution was slowly added to a large excess of n-hexane (20 to 1 ratio) at 20°C. under rapid stirring. It is important during the isolation to hold the temperature at 20°C. or slightly lower in order to decrease the tendency of the precipitate to "gum", as the second-order transition of polyvinyl acetate occurs at approximately room temperature. The precipitates were rinsed with hexane and allowed to remain in hexane for 48 hours. The hexane was then decanted, the polymer dried in a vacuum oven for 12 hours at 40°C. and for 48 hours at 60°C, and designated PVAc-2. Under these conditions the percent conversion of the polymer was very close to 12%.

Viscosity and light scattering measurements were carried out with polymer PVAC-2 in methyl ethyl ketone. The following results were obtained: $[\eta]$ gms/ml. = 275; k' = .54; $\bar{M}_w$ = 993,000 (corrected for dissymmetry and depolarization); radius of gyration = 460 Å; second virial coefficient, B, = 3.8×10^{-6}.

III. ADSORPTION OF POLYMER.

A. Analytical Problems:

The problem of measuring small concentration differences of polyvinyl acetate in solution has proved to be unexpectedly difficult. Initially, we tried to use the Raleigh Interferometer to measure concentration changes of polymer in methyl ethyl ketone. However, even for the solvent itself no reproducible measurements could be obtained.

Two possibilities presented themselves; either the adsorbent, in this case the iron powder, was adding something to the solvent, or it was adsorbing something from the solvent. In order to check on the first possibility, we used another solvent, benzene, added iron powder and centrifuged. Next, we added drying agents such as $CaSO_4$, $MgSO_4$, etc. to the methyl ethyl ketone and found a decrease in refractive index after the drying. These results show that there are small amounts of water in the MEK which are adsorbed by the iron powder, giving rise to refractive index changes. However, it has been found impossible to keep the MEK dry within the required limits, since as little as .001% H_2O will change the refractive index appreciably. As for benzene, due to the fact that its refractive index is very close to that of the PVAc, we cannot detect small concentration changes of PVAc in benzene with sufficient accuracy. It follows that in order to use the Rayleigh

Interferometer we need solvents which can be obtained and held in a dry state and which must have a refractive index substantially different from the polymer. This combination is difficult to find.

Viscometry has also been tried as a means of detecting small concentration changes. After some experimentation, it was found to have several faults. First, exceedingly long flow times are needed in order to detect small changes, namely flow times of the order of fifteen to twenty minutes, consuming an inordinate amount of time. Further, although the viscosities are less sensitive than the Interferometer to amounts of H_2O adsorbed by the iron powder, an error is still introduced at very low polymer concentrations.

The principal fault, however, lies in the fact that viscosity is a function of both concentration and molecular weight. If the adsorbent fractionates the polymer, as it most likely will, the change in flow time will not only be due to changes in concentration but also to those in molecular weight distribution.(2) Similarly, some data by Jenckel(3) show that polymer degradation may take place upon shaking with a solid adsorbent, which again would lead to errors in using viscosity as a tool for measuring concentrations, especially if the

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(2) Golub, M.A., J. Polym. Sci. <u>11</u>, 583 (1953)

(3) Jenckel, Kolloid Z. <u>135</u>, 1 (1954)

experimental conditions require prolonged agitation of the mixture of polymer solution and solid adsorbent. Nevertheless, in a series of experiments reported below, viscosity was employed as the simplest method for an exploratory investigation.

The method favored at present, which is not liable to errors on account of small solvent changes, is based on the Infra Red Absorption of the carbonyl group of vinyl acetate. The instrument available is a Perkin-Elmer Recording Infra Red Spectrophotometer. The first two solvents tried, which must not contain carbonyl groups, were benzene and chloroform. Polymer solutions of known concentrations were made up and the spectra obtained in both solvents, using a 1 mm. NaCl cell, in order to see whether PVAc solutions obeyed Beer's law and thus permitted calibration.

If the law holds, i.e. if log I_0/I = a b c (log I_0/I = = absorbance or optical density; a = extinction coefficient; b = cell thickness; c = concentration of solution) a plot of optical density versus concentration should give a straight line passing through the origin. To correct for the absorbance of the solvent on account of the slight difference in cell thicknesses, spectra with solvent in both cells were first taken. The "base" line thus obtained can be seen in Figs. 2 and 3 which show typical absorbance spectra of polyvinyl acetate in benzene and chloroform. On these graphs we see two peaks, that of carbonyl at 5.75 μ in chloroform and benzene, and also a peak for the [$-CH_2-$] group, which appears at 7.3 μ in $CHCl_3$ and 8.1 μ in benzene. Tables III and IV present the analysis of these spectra, which were used to plot calibration curves, Figs. 4 and 5.

TABLE III

Polyvinyl Acetate in Benzene

Concentration	Optical density at 5.75 μ	Optical density at 8.10 μ
0.00468 gr./100 ml.	.030	.020
0.01644 gr./100 ml.	.094	.063
0.03288 gr./100 ml.	.191	.133
0.0468 gr./100 ml.	.300	.206
0.0648 gr./100 ml.	.377	.258
0.1110 gr./100 ml.	.600	.420
0.1644 gr./100 ml.	.806	.606

TABLE IV

Polyvinyl Acetate in Chloroform

Concentration	Optical density at 5.75 μ	Optical density at 7.30 μ
0.0061 gr./100 ml.	.028	.010
0.0152 gr./100 ml.	.075	.026
0.0304 gr./100 ml.	.151	.050
0.0761 gr./100 ml.	.370	.126
0.1521 gr./100 ml.	.710	.248

The latter show that Beer's law is obeyed at both peaks in both solvents. A slight deviation is noted at higher concentrations in benzene at 5.75 μ. For such concentration we can use the 8.10 μ peak for more accurate results.

With the use of these calibration curves and the optical density of an unknown solution, concentrations can easily be determined.

B. Adsorption of Polyvinyl Acetate:

Two new adsorption isotherms of polyvinyl acetate XYSG were thus obtained, one in benzene, the other in chloroform, both at 30.4°C. These results appear in Fig. 6. The results in chloroform are very interesting in that they exhibit a large increase in adsorption with concentration.

Unfortunately at the present a certain amount of caution is still advisable. It has been observed that the ratio between the -CO- and $-CH_2-$ peaks in $CHCl_3$, before and after shaking of the polymer solutions with iron powder, changes. This could possibly be due to a reaction of the $CHCl_3$ with the iron or with the -CO- group, catalyzed by iron. This possibility is under investigation. We are further going to use CCl_4 which is chemically more inert and should give rise to fewer complications of this type.

C. Adsorption of Polyvinyl Formals:

The adsorption of samples PVF 7-70 and 15-95 S on activated alumina from ethylene dichloride ($C_2H_4Cl_2$) solutions has been subject to a preliminary study.

The Formvar samples were weighed into clean bottles and dissolved in 25 mls. of solvent by shaking. To each of these bottles 5 gms. of Alcoa activated alumina were added and the bottles subjected to further moderate shaking for 16-18 hours at constant temperature, 25°C., when equilibrium was reached.

At the end of this period the solutions were removed and immediately centrifuged at 2200 r.p.m. for 30 minutes. The concentrations of the supernatant liquid were determined by measuring the flow times in a modified Ostwald viscometer at 24.8°C., and reading off a calibration curve. The data are plotted as adsorption isotherms and shown in Figs. 7 and 8.

IV. WASH PRIMER FORMATION.

In view of the complexity of the reactions leading to Wash Primer formation, any study will have to proceed stepwise under simplified conditions. As indicated in the previous report, we had decided on using a single alcohol, i.e. 95% isopropanol, as the organic phase, instead of the mixture of three alcohols and of acetone commercially employed. We further used only one-half of the usual concentration of polyvinyl butyral-resin but kept the proportions of phosphoric acid and chromium trioxide as in the recipe (100:10:4.5).

The following steps are of potential consequence:

(a) reaction of the resin with $CrO_3 \cdot H_2O$; (b) reaction of the resin with $H_3PO_4 \cdot H_2O$; (c) reaction of the resin with H_3PO_4 and CrO_3 combined; (d) reaction of the alcohol with any or all of the other reagents; (e) reaction of chromium ions, presumably Cr^{3+}, with any or all of the other constituents.

As stated in our previous report, reactions (a) and (b) appear to be relatively insignificant, reaction (c) is also apparently small or at least overshadowed by (d), the oxidation of alcohol and by the reaction of Cr^{3+} with the resin under (e) which leads to a resin-chromium precipitate.

These investigations were now continued in an effort to ascertain the nature of the polyvinyl butyral-Cr complex; in particular, information would be desirable on: the type of bond between Cr^{3+} and the resin, whether phosphate or any other constituent participates in the chromic-resin complex, and, finally, in which way the original polyvinyl butyral has been changed, if at all. To this end, a variety of experiments were carried out, with a view to separating chromium and resin, to recover the latter and check on changes in its molecular properties.

In the most successful series, solutions of resin were made up in 95/5 isopropyl alcohol/water mixtures, 10% by weight of the polymer of 85% ortho phosphoric acid and 4.5% CrO_3 in 60% aqueous solution added, and the reaction allowed to proceed for 25 to 30 minutes yielding a green suspension which slowly precipitated. Short of destructive measures, it was not possible to separate the chromium from the resin completely, or even to redissolve the complex, but redispersion occurs by employing hot, aqueous, dimethyl formamide (DMF) with the help of which one obtained a slightly cloudy, intensely green, liquid.

The best way to work this solution further consisted in repeated precipitations in excess of aqueous di-sodium Versene (ethylene diamine tetra acetic acid) solutions and dissolving again in straight DMF, as shown in the chart below. The green color of Cr was thereby partly transferred to the versene solution. The polymer, however, still stays green and repeated precipitation from DMF solution in versene solution does not remove much more chromium. This was shown by the ash contents: Once precipitated sample, 2.81%; Thrice precipitated sample, 2.51%. The following working scheme was used:

5 gms. of XYHL (Butyral) in 100 mls. of 95% isopropanol:
0.5 mls. of 85% H_3PO_4
0.225 gms. of CrO_3 in 30% solution in H_2O

50 ml.	50 ml.
precipitated in 600 mls. cold 5% NaOH; precipitate redispersed in 30 mls. of DMF and precipitated in 500 cc. of 2% solution of di-sodium Versenate; left overnight, washed and dried.* Sample designated RB 2(a), light green color, dissolved in methyl solution.	35 mls. of DMF was added and the solution heated till "dissolved"; precipitated in 500 mls. of 2% solution of di Na Versenate and left overnight, washed, redissolved in DMF and reprecipitated from Versenate, dried* at room temperature in dessicator, pale green color; designated: RB 2(b), dissolved in MEK to give clear, greenish solution.

* The drying was incomplete, since the material does not redissolve if completely dried.

To investigate the path of reduction of CrO_3, the polymer was dissolved in non-reducible solvents like pyridine, DMF and 95% dioxane-5% water. In these solvents the CrO_3 does not become reduced and the polymer remains apparently unattacked, with or without phosphoric acid. If, however, a few mls. of an alcohol are added, reduction of CrO_3 sets in immediately with subsequent formation of the chromium-polymer precipitate.

From these results it is rather clear that within the short time allowed for the Wash Primer formation, little reaction takes place between the resin, CrO_3 and H_3PO_4 and that the principal process consists in a complex formation between the resin and chromic ions which were produced in the course of oxidation of the alcohols.

In order to check on these conclusions, two further series of experiments were undertaken. In the first, CrO_3 was replaced by potassium permanganate; in the second, the viscosities and molecular weights of the recovered polymers was redetermined.

In the first series, all conditions were held the same, but a 30% aqueous solution of $KMnO_4$ was used instead of the CrO_3 solution. A brown, flocculent dispersion resulted which was subjected to the Versenate-DMF routine described above. In contrast to the result of the chromium treatment, a pure white polymer was recovered, which was also more easily soluble, and designated RB 3.

As for the characterization of the recovered polymers, the viscosities of the chromium complex were measured in methyl cellosolve and methyl ethyl ketone. The data are given in Table V, in comparison with those of the original polymer and the parent acetate.

It will be noticed that the Cr-complexes possess somewhat lower viscosities and, more strikingly, lower second viscosity coefficients, k', than those of the original polymers in the same solvents.

With respect to molecular weights, it was not possible to carry out light scattering measurements, because of the color of the solution. However, the osmotic pressure of RB 2(a) could be measured in methyl cellosolve. The membrane behaved very well and gave the result shown in Table V.

Unfortunately, the number average weight $\overline{M}_N$ from the osmotic pressure of the original polymer XYHL has not yet been determined, but only the weight average value $\overline{M}_W$.

In order, therefore, to obtain a basis of comparison the recovered polymer RB 3 was measured by light scattering, since this sample dissolves to a completely clear solution in isopropanol. The resulting viscosities and weight average molecular weights are in Table V.

It will be seen that $\overline{M}_N$ is much lower than the value of 270,000 to be expected for random distribution in the absence of degradation. We believe though that this low $\overline{M}_N$ is due to

TABLE V

Polymer	[η]	k'	$\overline{M}_N$	$\overline{M}_w$	Solvent
PVAc-XYHL	57.0	0.385	---	155,000	MEK
PVB-XYHL	64.0	0.71	---	540,000	MEK
" "	72.0	0.77	---	---	Me Cellosolve
" "	81.6	0.63	---	---	95% isopropanol
* (RB 2(a)	61.0	0.62	160,000	---	Me Cellosolve
(RB 2(b)	54.0	0.47	---	---	MEK
RB 3	91.8	0.48	---	600,000	95% isopropanol

* These two samples should be practically identical.

a small amount of low molecular weight impurities, possibly phosphate ions held by some free charges on complexed Cr^{3+}-ions. This error is absent in the light scattering data for $\overline{M}_w$ of the Manganese recovered resin RB 3. $\overline{M}_N$-osmotic values for RB 2 and XYHL are obviously desirable.

DISCUSSION.

Our study of the Wash Primer Process, in the early stages as it is, has in our opinion helped to all but settle the first points of issue: the resin stays largely unchanged, the alcohol reduces the chromic acid to chromic ion which complexes with the resin, and it ought to be this Cr - PVB complex which primarily forms the coating. These facts increase the importance of the structure of the starting resins and of the complex for our understanding of the Wash Primer process, but also leaves many important details unanswered.

It will be recalled that our hydrolysis and reacetylation experiments were undertaken because branching of the PVB is suspected to have a bearing on resin performance, and because these experiments are specially suited for the ascertaining and definition of branching in polyvinyl acetates. Our results show the presence of associated molecules, either as a consequence of incomplete reacetylation and thus incomplete solubility in ordinary solvents, or of some proper cross-linking that occurred during the polyalcohol stage. Such association makes itself particularly strongly felt in light scattering experiments, practically obliterating the effect sought. It is planned to apply sedimentation-diffusion methods which are less sensitive to the presence of micro-gel particles, and which should give a better picture of the molecular weight changes accompanying hydrolysis. All we can say now is that the magnitude of the apparent molecular weights of the reacetylated and obviously partly associated solutions falls in line with the moderate degree of branching assumed for this type of polyvinyl acetates.

If, then, the acetates drop in molecular weight by losing branches during hydrolysis, it is all the more significant that the butyrals as well as the formals have appreciably higher molecular weights than their parent acetates. In view of the general parallelism of hydrolysis-reacetylation with hydrolysis-acetal formation it is not unreasonable here, too, to assume association of hydroxyl groups or cross-linking by way of intra- and inter-molecular acetal bonds. Whatever the nature of the bonds leading to increased molecular weights, a rather tight molecular coil is indicated (for butyrals more than for formals) by a relatively small increase in viscosity on acetal-formation, by small molecular radii from light scattering, and by small virial coefficients. In view of this structure, the amount of initial branching of the polyvinyl alcohols, already reduced from that of the acetates on account of the hydrolysis, should represent only a minor contribution to the acetal structure; further, during the Wash Primer formation a reversal of the cross-linking tendency takes places and the resin molecules become more like single chains, as the drop in k' factor and in the viscosities of the resin indicates.

More light will be cast on this question by some experiments with our low conversion (unbranched), high molecular weight, sample the fractions of which will further permit a study of the influence of molecular weight. With the influence of chemical structure (type and amount of acetal groups, residual -OH groups, acetate) well documented by practical observations, all primary variables of the effects of the resin on the Wash Primer formation will be known once the factors of weight and of branching are understood.

Turning to the reaction with phosphoric and chromic acid, one would in particular like to know whether Cr^{3+} acts as an inter- or intra-molecular tanning agent; whether the compound is of the complex or of the chelate type, is inert by complete inner saturation or whether the Cr^{3+} is capable of further participation in other compounds such as phosphates, which are bound to form as soon as the pH rises, etc. The answer will decide which are the primary units to be adsorbed and to form the first film, namely resin carrying some Cr^{3+}, complexed Cr^{3+} incidentally held by the polymer as on a string, or chromic phosphate with some resin attached. Although these differences are primarily of degree, they will greatly change the nature of the adsorbed layer, as the presence of the phosphoric and chromic acids will change the nature of the metal surface, and thus the points of attachment.

Some pointers towards the answers to these questions can be found on closer inspection of our observations with the simplified Wash Primer reaction. The reaction of phosphoric acid with the resin, e.g., must be very slow, or the aldehyde liberated would lead to some chromic acid reduction which in the absence of added alcohol is not observable for several hours. Similarly, our observations render it unlikely that a large scale oxidation of the free vinylaalcohol groups takes place. This does not exclude some oxidation to aldehyde or carboxy groups which, although too few to create an observable color change, may be a contributing factor to the precipitation process initiated by the Cr^{3+}-ions.

We further observed that the chromium ions precipitating, or coprecipitating with, the resin falls into two categories, i.e., a part that can be easily removed by extraction with another chelating agent, and a smaller part which appears to be held most tenaciously. This seems to indicate two different available bond sites for Cr^{3+} on the resin; a similar indication comes from the fact itself that Cr^{3+}-ions are capable of precipitating the resin from a medium in which the chromium-free resin is soluble. This points to an involvement of the acetal group; the hydroxyl groups which do not contribute to the solubility in organic solvents and must be expected to form the other sites and to complex and hold the Cr^{3+} tenaciously. In view of the better extraction of Mn^{3+}, one should conclude that these ions are not held nearly as strongly by the -OH-groups, or are extracted more efficiently by the Versene. This difference in extraction between Mn^{3+} and Cr^{3+}, incidentally, disposes of another possibility, namely that the difficulty of extracting part of the chromium was not due to differences in sites but in accessibility.

It is of interest, that through all these operations the resin does not appear to have substantially broken down. The viscosities of the chromate treated resins are somewhat reduced, but in view of the also lowered k'-value, a certain sign of having become more flexible, the resin has presumably stayed intact as regards the primary chains, but some of the inter- and intra-molecular cross-linking which raised the molecular weight during the acetal formation, has presumably been eliminated. The metal-free resin RB 3 has thus been restored to a point where it approaches the original resin with a lowered butyral content and a more open structure, while RB 2 seems to have been somewhat degraded as well, although probably not as much as might appear from the low value of $\overline{M}_N$ which may be due to some dissociation and impurities.

In our adsorption work we met with all the problems customarily besetting this type of experimentation: difficulties of measuring small concentration differences and, if the ratio of adsorbent to solution is increased, impurities or interactions of the order of the effect under study.

One might, therefore, ask whether adsorption measurements may be expected to yield results commensurate with the investment of effort, all the more as the relation between adhesion and adsorption is far from clear-cut. The answer depends on the emphasis. While it is true that the properties of a coating or of a joint depend in addition on many other factors, adsorption is the most fundamental and generally important factor and hardest to ascertain.

Adsorption is responsible for the primary bond between the surface in question and the applied material (leading to "wetting", if the application is from a melt, paste, etc.), and on the strength and persistence of this bond in the face of cohesional thermal and mechanical disturbances depends the effectiveness of the coating or cementing operation. There is no more direct way to determine the bond strength than by adsorption isotherms which permit the calculation of bond energy as well as entropy.

In the case of configurationally so complicated molecules as high polymers, the entropy may be expected to be often the decisive factor; yet very little is known even of simpler polymers such as styrene or methyl methacrylate, let alone of complex acetals. Circuitous as adsorption measurements therefore are, they are bound to produce the results on which all further thinking has to be based. We are consequently planning to continue with our experimental studies of adsorption as function of surface and adsorbate structure, and to accompany it by a theoretical analysis.

The latter, as will be seen in the Appendices, concentrates particularly on the entropy effects. Unfortunately, a reasonably complete analysis is so complex as to lead to rather unwieldy results. Further experimental and theoretical work will have to provide the basis for simplifications which are justified and lead to more manageable equations. Up to now, our adsorption isotherms are not accurate enough to permit a decision between the several proposed laws of adsorption by studying the fit of the data with respect to such equations as Langmuir's: $1/c = K + 1/\theta$; Freundlich's: $\log \theta = K \log c$, and Frisch, Eirich and Simha: $\log K_1 + \log c =$

$$K_2 \left[\log \frac{\theta}{1 - \theta} + 2 K_3 \theta \right]$$

where c is concentration, and θ is the ratio of material adsorbed to maximum amount of material adsorbed at high concentration. In the last equation $K_2 \cdot K_3$ may be determined by considering the point when $\theta = \frac{1}{2}$.

CONCLUSIONS AND SUMMARY

The hydrolysis and reacetylation experiments for the characterization of parent polyvinyl acetates have been completed. The occurrence of some micro-gel particles in the reacetylated samples presumably due to hydrogen bonding, disturbs the molecular weight determinations and renders conclusions difficult, but the existence of moderate branching is certain.

The increase in molecular weight when polyacetals are prepared from polyvinyl acetate is also a manifestation of cross-linking reactions including acetal bridges, and leads to very broad molecular weight distributions.

The direct attack of phosphoric and chromic acids on the resin during the Wash Primer reaction is slow and leads to only minor changes in acetal content, oxidizable groups, and molecular weights, the latter changes presumably being a reversal of the cross-linking during acetal formation.

The oxidation of the low molecular weight alcohols in the Wash Primer formula by the chromic acid produces Cr^{3+}-ions which react with the resin and precipitate it, apparently forming complexes with both hydroxyl groups and acetal rings.

From these results it appears that the formation of the Wash Primer coating proceeds via adsorption of complexed and precipitated resin on metal surfaces, probably in conjunction with chromic (and zinc) phosphate, and further cross-linking and precipitation reactions during drying.

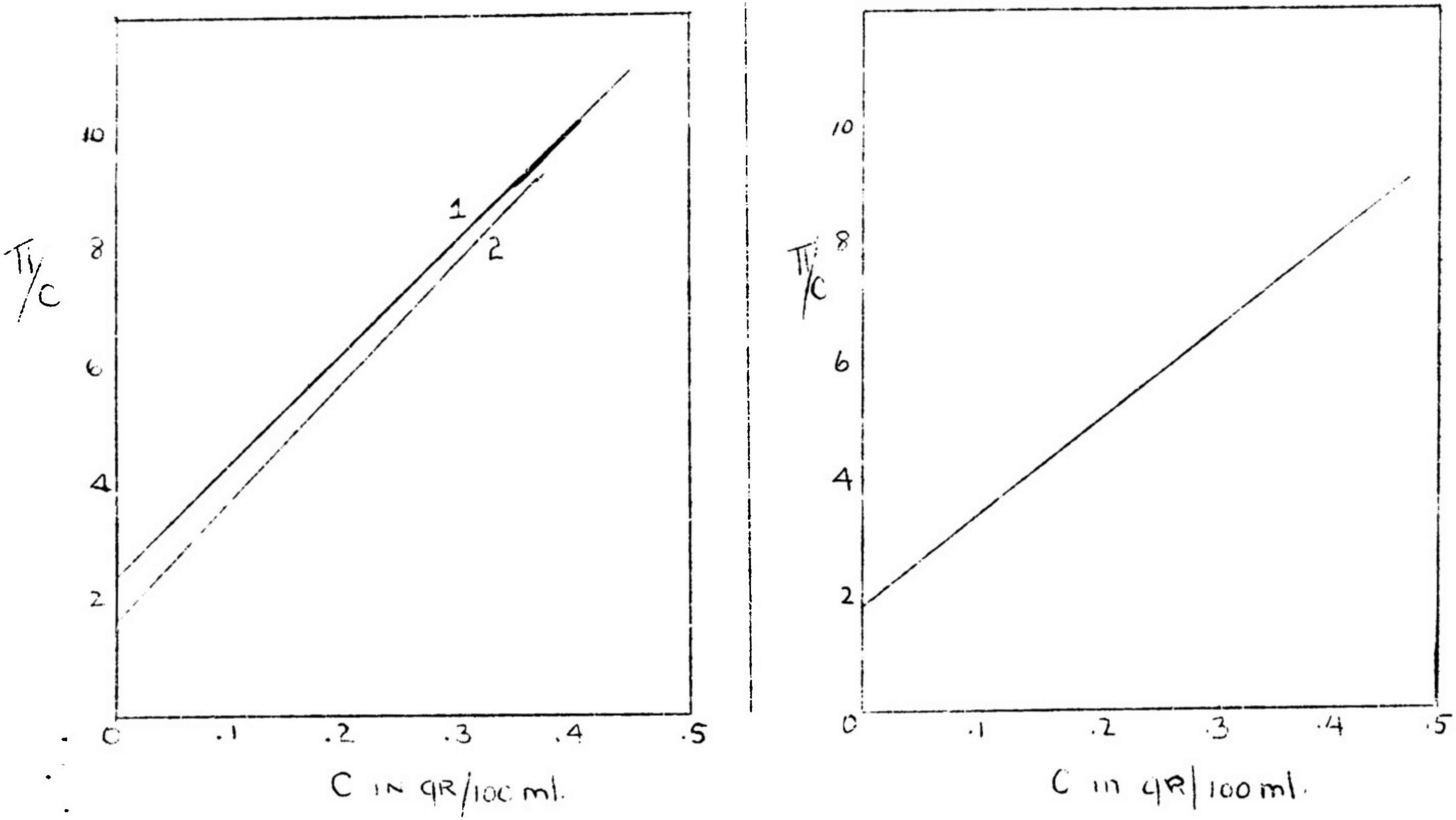
A high molecular weight polyvinyl acetate has been synthesized for systematic adsorption studies.

Refractive index, viscosity and infra red methods have been investigated for their suitability in PVAc and PV-Acetal adsorption studies.

More adsorption isotherms have been obtained for acetates and formals which do not differ greatly from Langmuir isotherms.

The mathematical analysis of the adsorption of flexible macromolecules has been continued.

FIGURE-I OSMOTIC PRESSURES OF FORMVARS



IN 95% DIUXANE/H_2O

Samples: 1 - 15-955
2 - 7-70

IN 70% ACETIC ACID

sample: 7-70

FIGURE-II

INFRA-RED SPECTRA OF PVAc IN CHLOROFORM

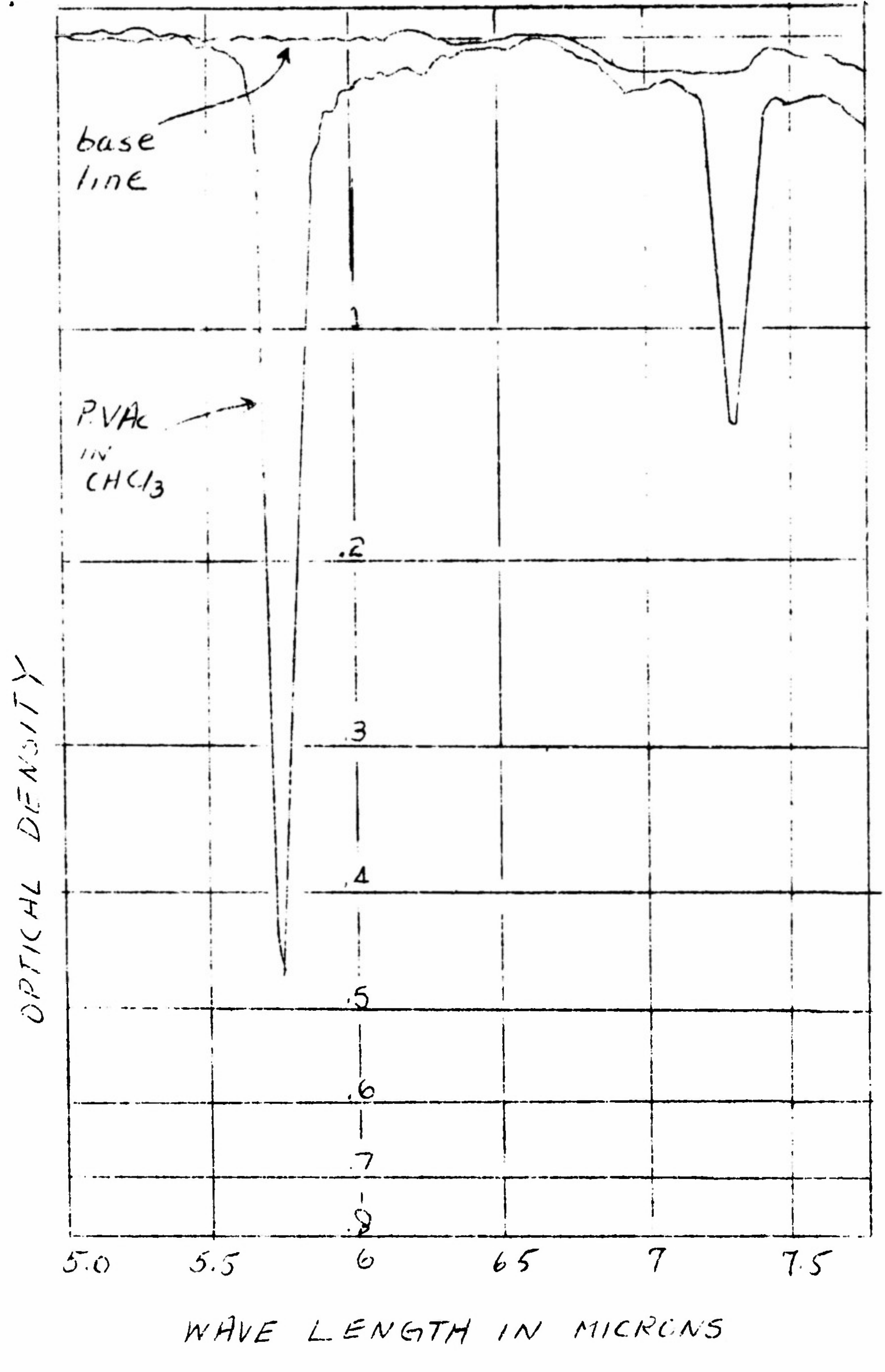
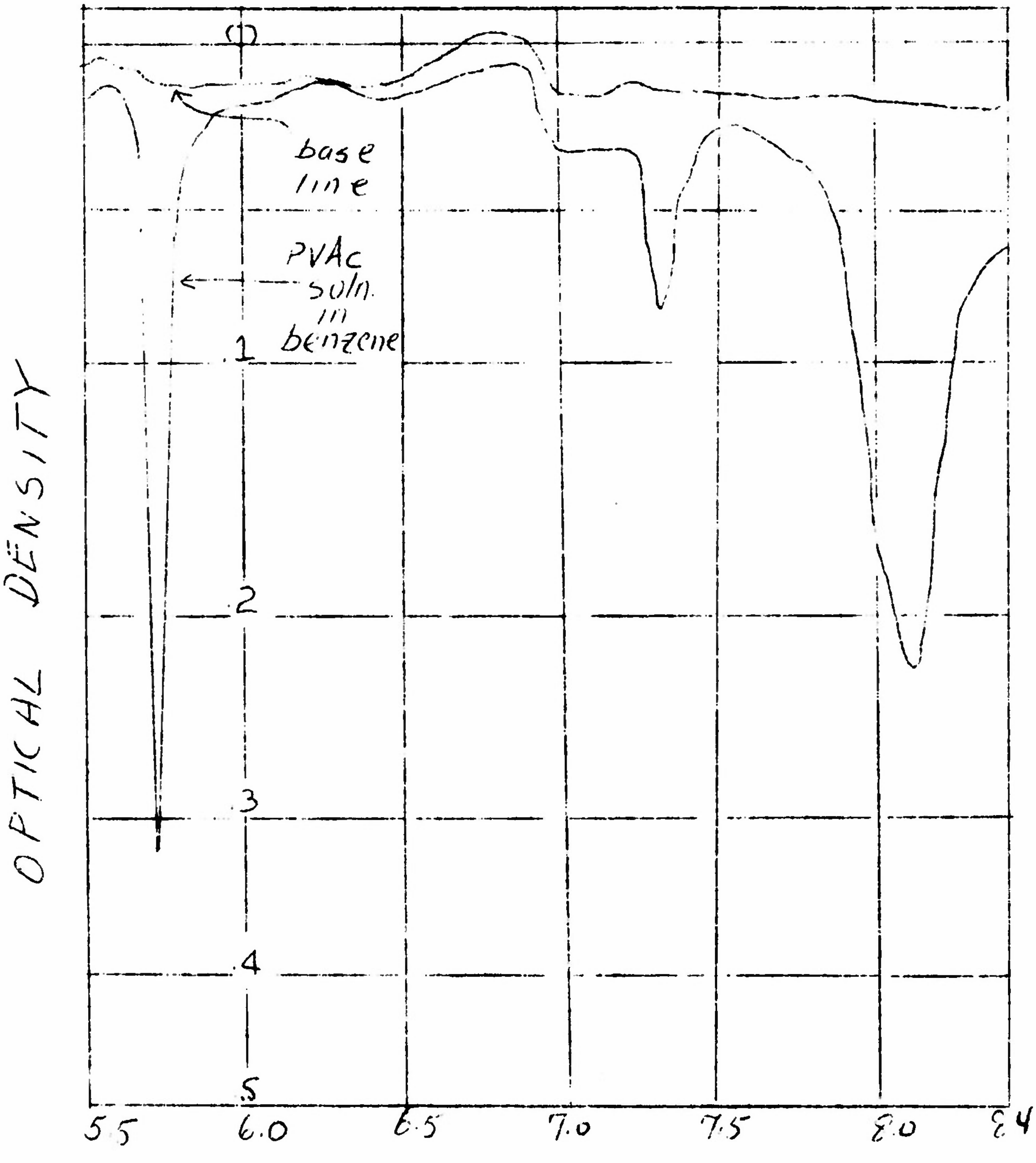


FIGURE III

INFRA-RED SPECTRA OF PVAc IN BENZENE



WAVE LENGTH IN MICRONS

FIGURE - IV CALIBRATION CURVE FOR POLYVINYL ACETATE IN BENZENE

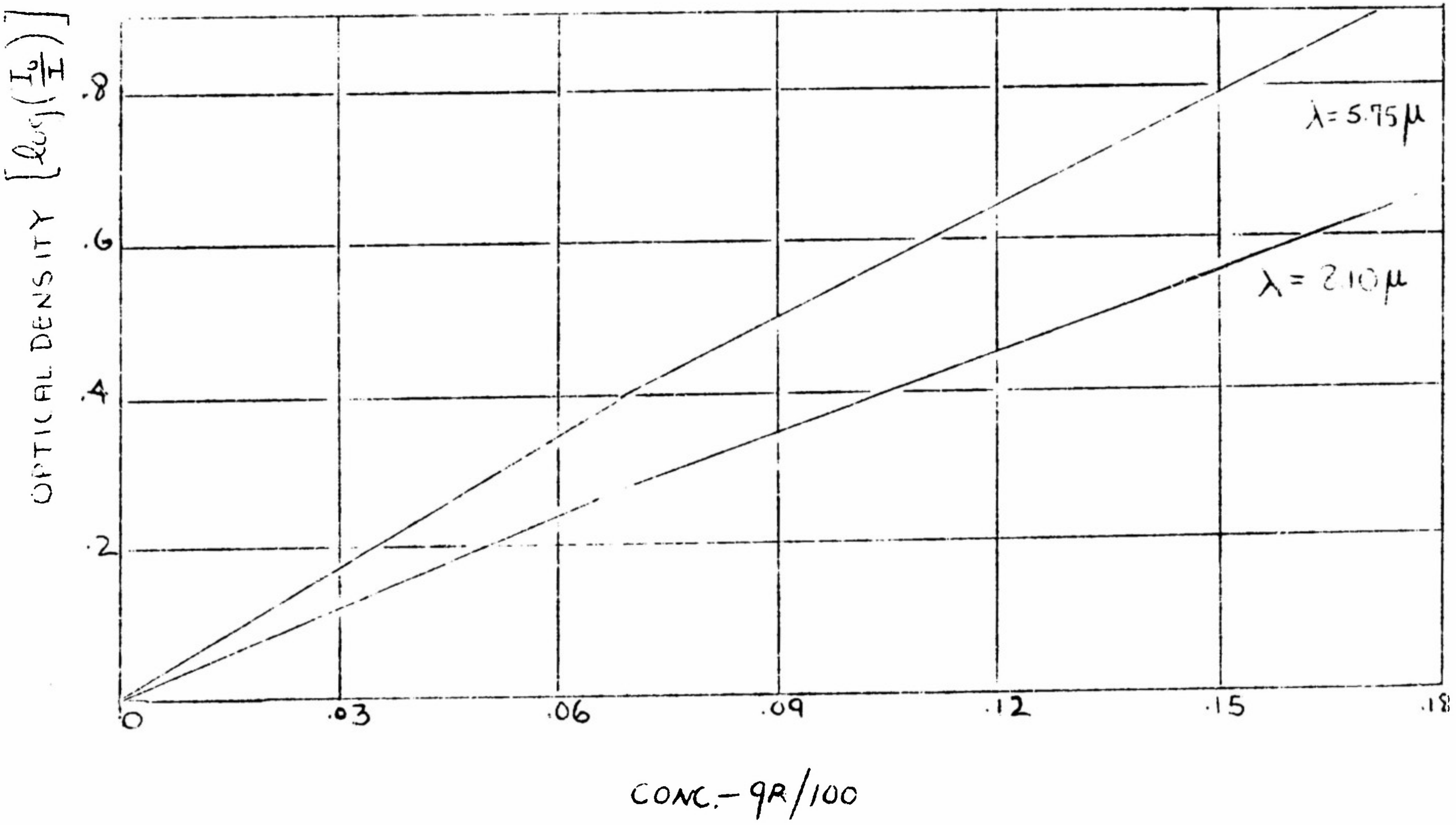


FIGURE-5 CALIBRATION CURVE FOR POLYVINYL ACETATE IN $CHCl_3$

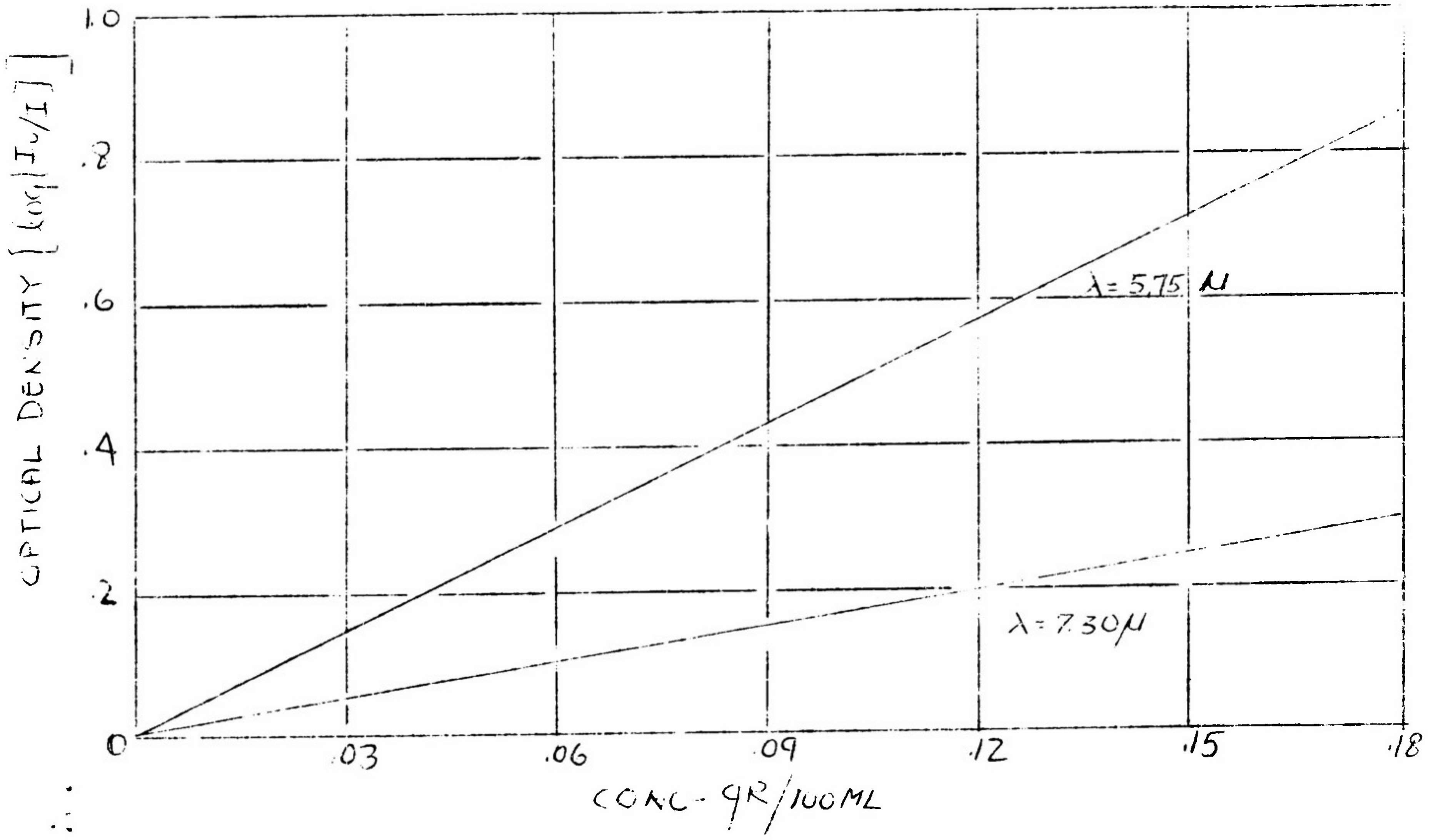
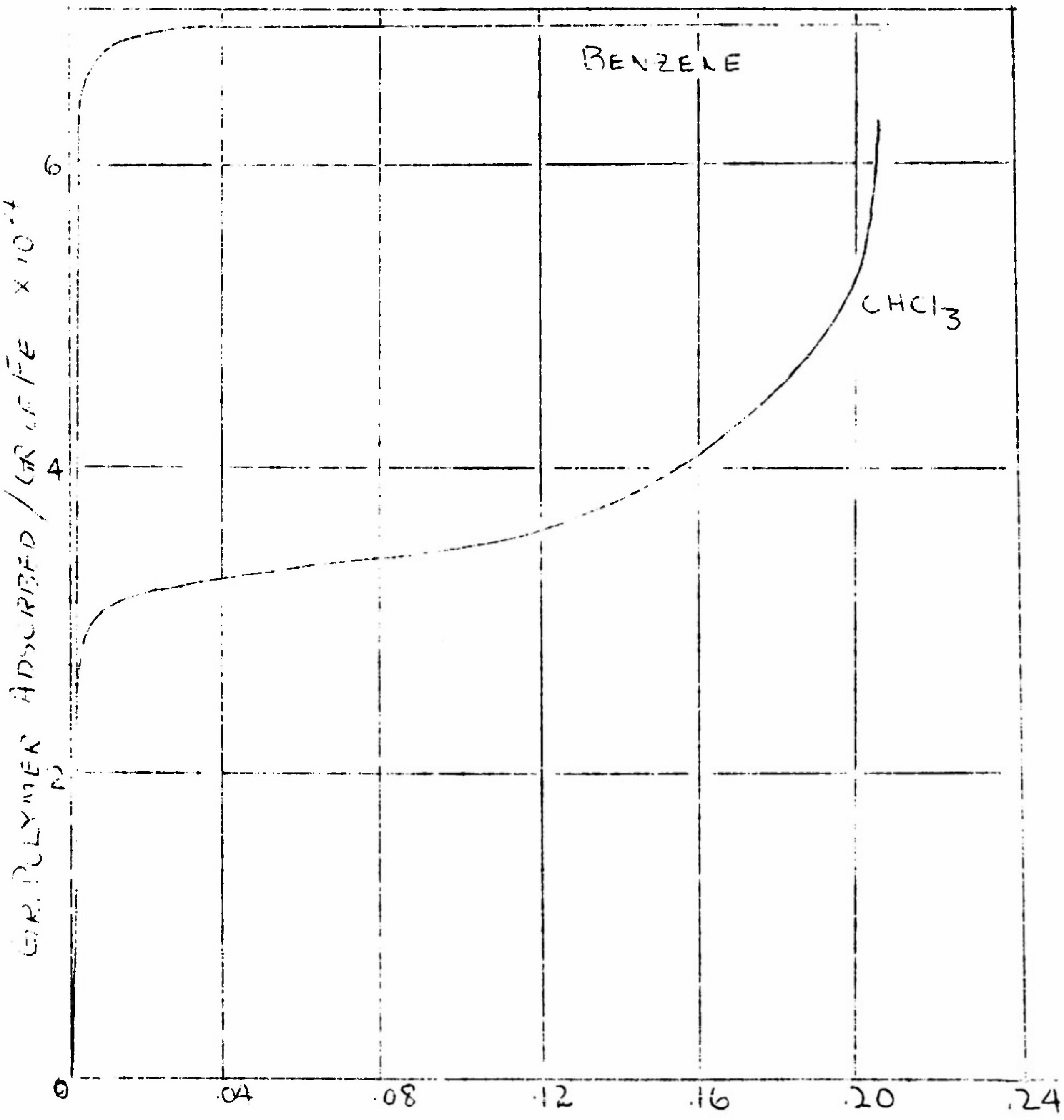


FIGURE - VI

ADSORPTION ISOTHERMS FOR PVAc - XYSG IN BENZENE AND $CHCl_3$ AT 30.4°C



EQUILIBRIUM CONC. - GR/100ML.

FIGURE-VII

ADSORPTION ISOTHERMS FOR FORMVARS IN ETHYLENE DICHLORIDE
AT 30.5°C ON ACTIVATED ALUMINA

Samples: 7-70
15-95S

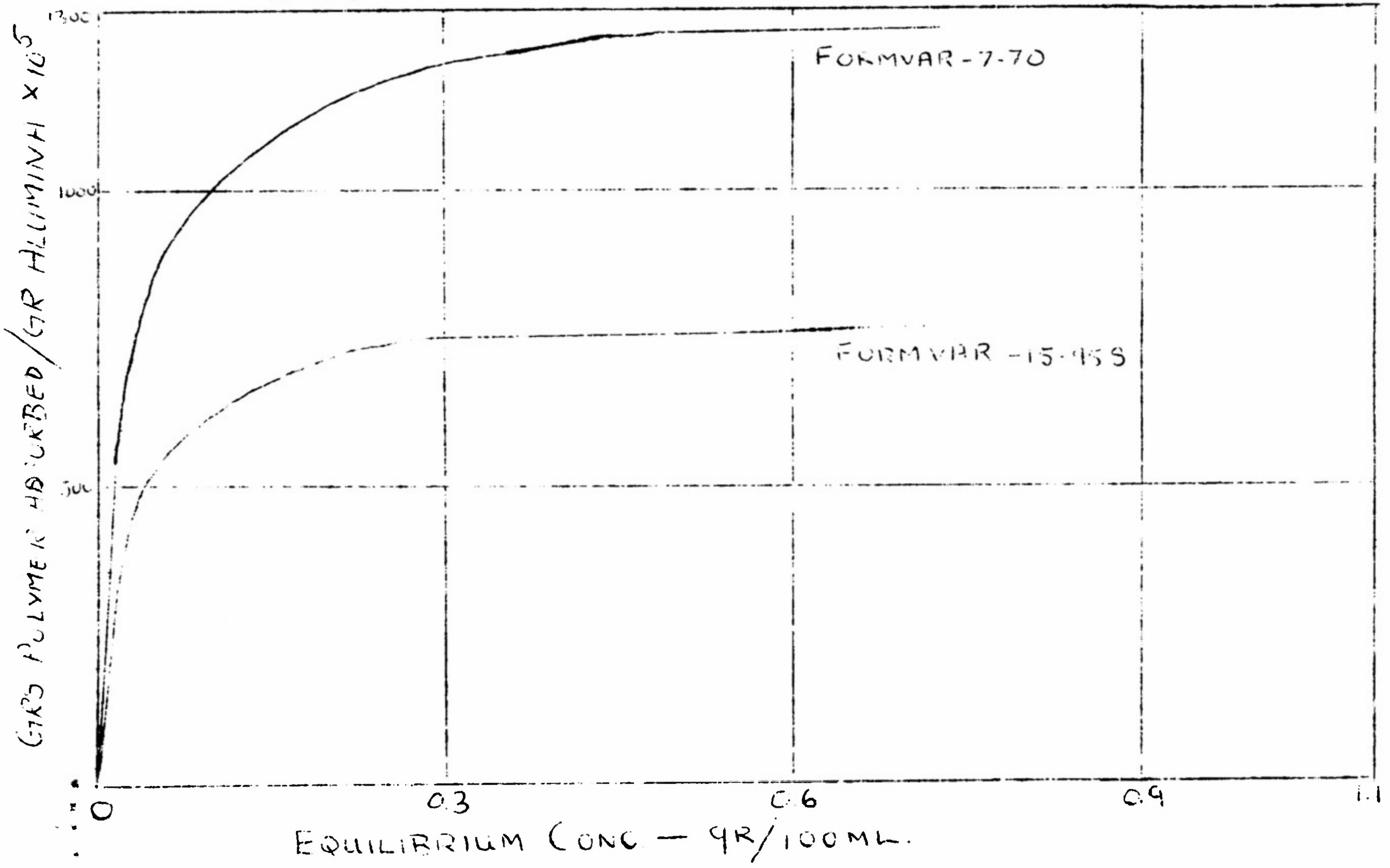


FIGURE- VIII

ADSORPTION ISOTHERMS FOR FORMVAR-7-70 IN ETHYLENE DICHLORIDE
AT 30.4°C AND 37.5°C