INTERIM REPORT

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SUMMARY

Two polyvinyl acetate samples of the Shawinigan Corporation of weight average molecular weights of 85,000 and 190,000 respectively possessing a wide molecular weight distribution but, presumably, a low degree of branching were found to have increased their molecular weights by factors of 2-3 when converted into formals. Osmotic and, in fact, all measurements in ethylene dichloride as solvent present great and as yet unexplained difficulties.

Two polyvinyl acetates of similar molecular weights and of low degree of branching as proven by their hydrolysis and re-acetylation, were supplied by the Bakelite Co. and show an increase in viscosity on butyral formation which, too, has to be interpreted as a sign of molecular weight increase. Here, too, solvent systems more suitable for precise measurements in solution will have to be found, especially as there are indications that the cross-linking process indicated by the molecular weight increase leads to the formation of some microgel particles.

The theory of adsorption of macromolecules with special consideration of their flexibility has been further worked on. Adsorption measurements of formals and butyrals on iron powder of uniform size were started. The first curves obtained show a very steep initial increase in adsorption with polymer concentration followed by a rather flat rise.

FUTURE WORK

The results described above stand in need of consid-
erable broadening.   If received in time, two more acetates
and butyrals will be characterized.   The measurements on
all samples are to be extended to more solvents.   Efforts to
obtain satisfactory osmotic data are to be continued.   Some
sedimentation work and studies of the dissymetry of light
scattering is under way so that a decision can be made as
regards the existence of microgel particles.

The reaction of characterized acetates with phosphoric
acid and chromate in organic solvents is under study and this
work will be continued.   The oxidized products will be re-
characterized to establish the changes brought about by the
oxidation process.   Special attention will be paid to vis-
cosity changes, molecular weight, occurrence of carboxylic
or peroxidic groups, and the fate of the acetal ring.

The adsorption studies of oxidized and non-oxidized
acetals will be continued and compared with that of other
types of high polymers.

August, 1953

POLYTECHNIC INSTITUTE OF BROOKLYN

INTERIM REPORT

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INTRODUCTION.

In our first Progress Report we described instrumentation work aiming at the characterization of the polyvinyl acetates (PVAc), polyvinyl alcohols (PVA) and their acetals with a view to elucidating the part played by the polymer structure on the binder efficiency, as explained in our proposal. We reported on some experimental difficulties and on some data on polyvinyl formals (PVF) supplied by the Shawinigan Resins Corporation. Since then we have received polyvinyl acetate samples from this Company which correspond closely to certain of these formals, as well as acetates and butyrals (PVB) from the Bakelite Company. Moreover, we studied more closely the experimental difficulties surrounding our investigation. In fact it appears that they have been underestimated; this is not entirely surprising since no thorough investigation of polyvinyl acetals seems ever to have been undertaken and since an accumulation of three types of groups of various polarity and reactivity on one polymer must tend to complicate solution behavior. In the following we will report on the more important results and observations so far obtained and

on our efforts concerning the implementation of other parts
of our program.

EXPERIMENTAL AND RESULTS.

a. Polyvinyl formal.

The measurements of intrinsic viscosities, $[\eta]$*,
and viscosity interaction constants, k', have been continued
(cf. previous report). The data on the Shawinigan polyvinyl
acetates were obtained from acetone solutions at 25°C, and
are reproduced in Fig. 1a. In addition, weight average
molecular weights were obtained from light scattering (Fig.1b).

The relationship $HC/\gamma = \frac{1}{M} + 2BC + \ldots$ is used
to calculate the weight average molecular weight $\bar{M}_W$. In
this equation c is the concentration in gms/ml, γ is the
excess scattering of solution above the solvent at 90° angle
to the direction of the incident beam,
$H = 32\pi^2 n_0^2 / 3N \lambda^4 (dn/dc)^2$ where n_0 is the refractive
index of the solvent, N is Avogrado's number, λ is the wave-
length of the incident light, and dn/dc the slope of the plot
of refractive index versus concentration for the polymer solu-
tion. A plot of HC/γ vs. c extrapolated to c = o is
usually linear for uncharged molecules and yields the weight
average molecular weight, M_W. The dissymmetry of the

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* According to an international proposal, the term "Limiting
Viscosity Number" is the new name given to the quantity
called "Intrinsic Viscosity".

scattering envelope is surprisingly high, indicating either
a stiffening of the polymer coil or the presence of some
heavily scattering, microgel type, particles. The relevant
data are collected in Table I, together with earlier data on
the formals in ethylene dichloride.

T A B L E I

Viscosities and Light Scattering Molecular Weights of two
Polyvinyl acetates in acetone, and of the derived Formals
in ethylene dichloride.

Polymer	Designa-tion	% OAC*	% OH*	[η]	k'	M_W
PVAc	V7	100	---	0.405	0.29	85,000(±10,000)
PVF	7-70	40-45	4.7	0.65	0.33	275,000(±20,000)
PVAc	V15	100	---	0.655	0.37	190,000(±20,000)
PVF	15-95 S	9-13	7-9	0.91	0.62	340,000(±30,000)**

* Data kindly supplied by the Shawinigan Resins Corporation,
Springfield, Mass.

** In the previous report the value was misprinted as 34,000

A considerable amount of time has been spent in our
attempts to obtain number average molecular weights for the
formals from osmostic pressure measurements. However, all
efforts to obtain membranes with no or small diffusion of the
polymer were so far without success. It does not seem to be
possible to condition cellulose membranes in ethylene dichloride

so that the membranes remain sufficiently tight. All osmotic experiments were suffering from diffusion, were poorly reproducible, and yielded molecular weights which were obviously too high.

It was then attempted to tighten the membranes by a technique which had proved successful in other cases. It had been found that high molecular polyvinyl pyrrolidone (PVP) often plugged cellulose membranes on standing. Since PVP is readily soluble in ethylene dichloride, the possibility of a similar action was explored. However, no improvement was found as regards PVF diffusion, and even the osmotic pressures of PVP in ethylene dichloride using pretreated membranes were found to be faulty. It is possible that there is some attack by the solvent on the membrane which increases the pore size, probably by deswelling the texture. Work will be continued by investigating the use of non-cellulose membranes. It should be remembered, however, that ethylene dichloride seems to be a tricky solvent for PVF altogether, since even the light scattering experiments were beset with greater difficulties, than normal, as concerns refractive index determinations, filtration, and general reproducibility. The action of other solvents will be looked into.
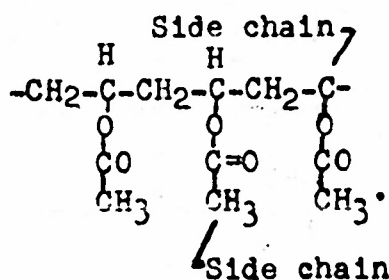
b. Polyvinyl butyral.

We received from the Bakelite Company two samples of polyvinyl butyrals, designated XYSG and XYHL, and two polyvinyl

acetates akin to those used in making these butyrals. The
viscosities of the butyrals were measured at 25°C. in methyl
ethyl ketone and are shown below; light-scattering molecular
weights are being determined.

	$[\eta]$	k'
PVB - XYSG	1.06	.66
PVB - XYHL	.64	.71

Concerning the important question of branching in
polyvinyl acetals, the most direct way to estimate branching
in the parent polyvinyl acetate is based on its hydrolysis
and reactylation of the polyvinyl acetate. This possibility
springs from the fact that the branched vinyl acetate polymer
has most of the side chains attached to the methyl of the
acetyl group, and only a relative few to the carbons on the
main chain.

```
                     Side chain
         H       H          
    -CH2-C-CH2-C-CH2-C-
         O       O       O
         CO      C=O      CO
         CH3     CH3      CH3
                  
                  Side chain
```

Upon hydrolysis and reacetylation, the branches on the acetyl
are removed from the polymer molecule. This usually lowers

molecular weight of the polymer but, if the side chains are
linked in a ring in the same molecule, hydrolysis and reacetyla-
tion will not change the degree of polymerization. Similarly,
the measurement of change in molecular weight is not suited for
an estimate of the extent of branching which stems from tertiary
carbons of the polymer chain. These are not hydrolyzable and
not detected by the above procedure. No satisfactory method
for the determination of such branches exists, though some
information can be obtained from η-M plots for high molecular
weights, or from gel point determinations on further polymeri-
zation.

Inasmuch as the parent acetates are never exhaustively
hydrolyzed, so that some branches may still exist on the
remaining acetyl groups, the molecular weights of acetals too
may change on thorough hydrolysis, beyond the effect caused by
splitting off aldehyde. Apart from this, branching of the
acetals will have to be determined, as in the case of other
polymers, by comparison of molecular diameters and viscosities
of a series of molecular weights.

Since a knowledge of the degree of hydrolyzable
branching of the parent acetates remains valuable for the
interpretation of the degree of molecular weight change on
acetal formation, and of the probability of branches on remain-
ing acetyl groups, the polyvinyl acetate samples XYSG and XYHL
were hydrolyzed and reacetylated according to a procedure given

(1)
by Wheeler and co-workers described below.

Two volumes of 5% methanolic solution of the resin were added over a period of 2 hours to 1 volume of a vigorously stirred 1% methanolic KOH solution at room temperature. The agitation was continued for an additional 4 hours. It is essential that the PVA obtained in this step be finely divided. The PVA was then filtered and repeatedly washed with methyl acetate. The drained, but not dry, resin was disprsed in an acetylating solution in the approximate proportions of 40 ml. of solution for each gram of polymer. The acetylating solution comprised 1 volume of pyridine, 5 volumes acetic acid and 15 volumes acetic anhydride. The dispersion was agitated at room temperature for 24 hours longer than required for the resin to dissolve (4-8 days depending upon the state of subdivision of the resin). The solution was dissolved in 2 volumes of benzene and the acetylating solvents removed by repeated extraction with water. The resin was recovered by the boil-out procedure, dried and redissolved in the acetylating solution. After agitating for 2 days at room temperature it was recovered as before, except for 2 additional boil-outs.

The viscosity data on these reacetylated polyvinyl acetates was obtained in two solvent systems, 95% methanol-5% water, and benzene. The results are given in Table II, together with light scattering measurements also carried out in 95% methanol and in benzene.

Viscosities of original and reacetylated Polyvinyl acetates.

Solution	$[\eta]$	k'	M_w	dn/dc
PVAc - XYSG - in 95% methanol	.67	.45	---	.1211
PVAc - XYSG - reacetylated in 95% methanol	.54	.36	---	"
PVAc - XYHL - in 95% methanol	.43	.39	---	"
PVAc - XYHL - reacetylated in 95% methanol	.38	.32	---	"
PVAc - XYSG - in benzene	.935	.19	133,000	.0542
PVAc - XYSG - reacetylated in benzene	---	---	---	"
PVAc - XYHL - in benzene	.588	.24	47,500	"
PVAc - XYHL - reacetylated in benzene	.402	.34	---	"

The data from the reacetylated XYSG, XYHL in 95% methanol show that the plot of HC/γ vs. c is not linear at low concentration but tends to curve upward, see Fig. 2.   The reasons for this anomaly are not clear; it may be due to residual emulsifying agent, or to polymer aggregation. Whatever the reason, it is certain that here too the solvent system

used is not well suited for molecular weight determinations, and the data were not evaluated.

In benzene the refractive index increment of vinyl acetate is very low (.0542). As the amount of light scattered is proportional to the square of the refractive index increment, the total amount of scattering is low, and the molecular weight determination somewhat inaccurate. The data are given in Table II. Measurements in a more suitable solvent are being conducted.

Adsorption Measurements.

As mentioned briefly in the first report, some measurements of adsorption of polymer from solution were conducted. The polymers used for these experiments were polyvinyl butyral and polyvinyl formal. The adsorbent chosen for these first experiments was an iron powder prepared by Antara Chemicals Division of the General Dyestuff Corporation. This seemed to be a particularly suitable material, because our problem is centered on the adhesion of the acetals to iron and steel. This iron powder is produced by heating iron pentacarbonyl. The particles are almost perfect spheres of extremely pure iron, but with the inevitable oxide surface.

The iron sample used by us is the "SF" type, has a chemical analysis of 98.2-98.8 % iron, 0.50-0.70 % carbon, 0.10-0.13 % oxygen, and 0.55-0.75 % nitrogen. The average

particle size is 3 microns in diameter; less than 5% of the particles are greater than 5 microns and less than 5% of the particles are greater than 1.5 microns in diameter. Some more experiments were conducted using activated carbon and activated alumina.

At the outset of the experiments, it was planned to determine the adsorption of polymer from solution on to solid particles by the measurement of the change in the refractive indices of the polymer solutions. The Rayleigh interferometer which is sensitive to 10^{-6} refractive index units was used for this purpose. In a polymer solvent system with sufficiently high refractive index increment, small changes in concentration could be easily detected.

The polymer solution was shaken up for periods of the order of 12 hours with adsorbents, separated by centrifuging and purified through ultra fine filters; the change in refractive indices was then measured.

About 30 sets of experiments were conducted with the pure solvents alone and some more with solvent-polymer systems. The solvents were pretreated by careful fractional distillation and extraction with the adsorbents, before being used, and the adsorbent was also washed with the solvent.

The measurements obtained were not reproducible, for the pure solvent itself on treatment with the adsorbents showed erratic deviations in refractive indices. It was therefore

decided to try the change in viscosity of a polymer with con-
centration as the analytical method for detecting the adsorp-
tion.   After some initial difficulties reproducible results
were obtained in the case of polyvinyl butyral XYSG from
methyl ethyl ketone on the iron powder mentioned above. Fig.3
shows the dependence of the amount of adsorption on time for a
solution of .265 gm/100 ml concentration.   Fig. 4 shows an
isotherm obtained with the XYSG sample.   The measurements
were made at room temperature (29 $\pm$ 1°C.).

In order to obtain a fuller understanding of the
process of adsorption of polymers from solution on to solid
substrates, it was necessary to further develop the theory of
adsorption of polymer molecules.   Some work of this character
has already been published by us[2] and in addition an investi-
gation proceeding from a different point of view has been
undertaken.   A report on this is to be presented shortly.[3]

The essential part of this new analysis consists in
the construction of a partition function for the adsorbed
layer, and partial differentiation with respect to certain of
the variables.   The calculations are based on the lattice
model of polymer solutions.

From this procedure, two equations can be obtained.
The first relates the fraction of the surface covered by
polymer molecules adsorbed at i points with the fraction of
molecules adsorbed at i points.   The second equation relates

-11-

the fraction of surface covered by polymer molecules at $\underline{1}$
points with the activity of these molecules. The combination
of these equations yields the expression for the isotherm.
The form of the isotherm has certain similarities with the
Langmuir equation, but is considerably more complicated. The
course of the curve in Fig. 4 gives an experimental indication
of an adsorption curve which is at first steeper and then
flatter than a corresponding adsorption curve of low molecular
materials. Further comparison of the present theories[2,3] with
experiment, and extension of the theoretical work so that the
model of the adsorbed polymer is more nearly in accord with
our ideas of the form of a real polymer chain, constitutes the
next steps in this phase of our work.

DISCUSSION.

The molecular weights of the starting Gelvas
(Shawinigan PVAc) appear to be somewhat high compared with
accepted viscosity conversation figures but the discrepancies
are not beyond the range of possible variations. They ray be
caused, e.g., by a small amount of large and highly branched
molecules.

More striking is the increase in molecular weight on
converting the PVAc's into the formals. This is somewhat
unexpected and indicates that the loss of branching was more
than outweighed by aldehyde cross-linkings between molecules.

The larger k'-values, too, are in accord with denser structures. For, if there is on the average at least one half intermolecular bond per molecule, as the weight changes indicate, an appreciably larger number of intramolecular bonds may be expected, which would tend to reduce the volume of the coils. Both inter and intramolecular bonds are certainly in part at the root of the observed solution anomalies; others will spring from the very active solvent ethylene dichloride necessary to dissolve internally netted coils. This possibility will have to be kept in mind when the adhesion properties will be investigated, particularly with a view to the possible differences in the reaction towards the preceding oxidation.

The polyvinyl butyrals also exhibit strikingly high k'-values and the viscosity numbers are also higher than those of the corresponding acetates, although the comparison is not perfect on account of the different solvents. Pending confirmation it appears, therefore, as if the butyrals too had been cross-linked when they were formed from the acetates. The latter were certainly very little branched, as shown by the modest drop in viscosity on hydrolysis and reacetylation, but what amounts in effect to branching has been reintroduced by the intermolecular links formed by the condensing butyraldehyde molecules. This branching, as that caused in the formals, is of a rather special type, namely on the average two long branches stemming from a short, schematically shown

like below:
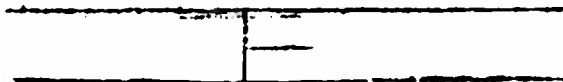
with the possibility of more such links formed within the same molecular pair.   Again, the "ladder" structure of such tied molecules may well be found of consequence in the subsequent oxidation or,if this structure survives, in the adsorption on metal oxide surfaces.

Concerning the adsorption measurements, the majority of the rather extensive difficulties in the path of every adsorption study seem to have been overcome.   The first experimental data exhibit a behavior which is rather different from what would be expected if the classical Langmuir isotherm were followed, and more in line with a recent study of the adsorption of high polymers.   The continuation of our own theoretical analyses, taking into account the flexibility of linear macromolecules, tries to express this case of adsorption in general, and of polyvinyl acetates and acetals in particular.

REFERENCES

1. Wheeler, Lann and Crozier, J. Polym. Sci. 9 (195)

2. Simha, Frisch and Eirich, J. Phys. Chem. (1953)

3. R. Ullman, "A Theory of Polymer Adsorption" - Presented at the September meeting of the American Chemical Society

4. E. Jenckel and B. Rumbach, Z. Elektrochem. 55, 612 (1951)

FIGURE 1A - VISCOSITY OF POLYVINYL ACETATE IN ACETONE AT 25.0°C.
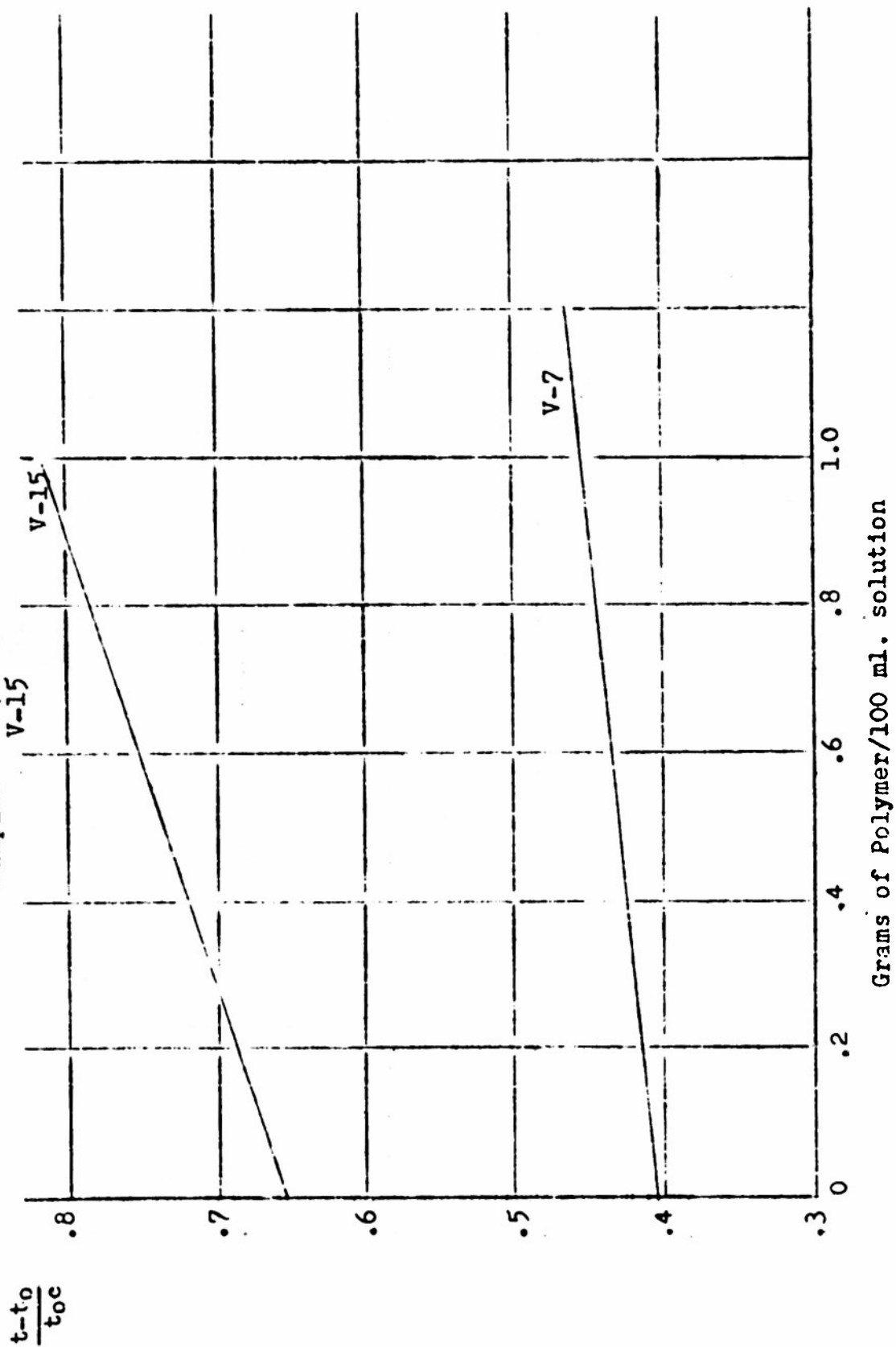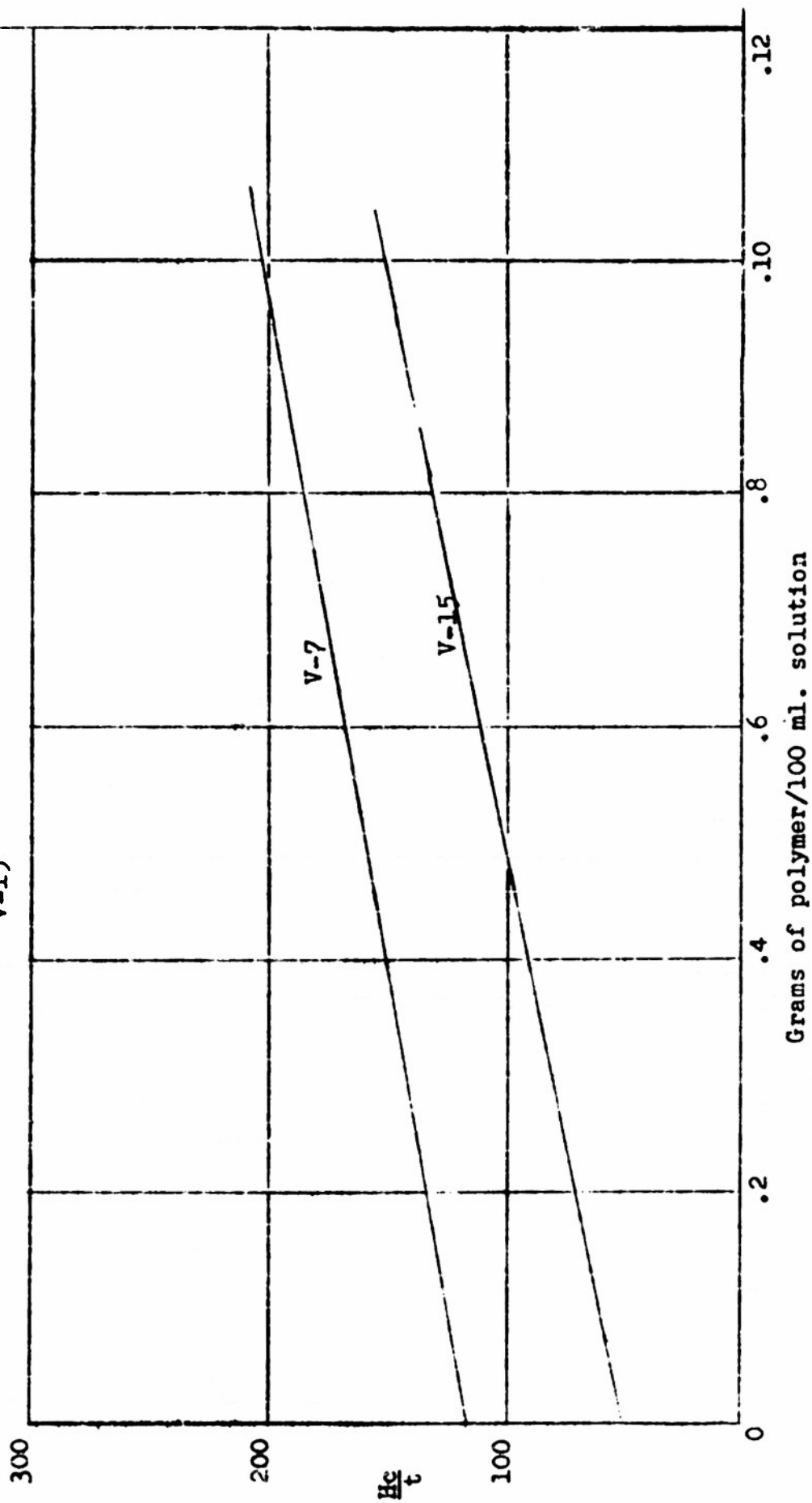
Samples: V-7
          V-15

$\dfrac{t-t_0}{t_{oc}}$

Grams of Polymer/100 ml. solution

FIGURE 1B. LIGHT SCATTERING OF POLYVINYL ACETATE IN ACETONE

Samples: V-7
         V-15

FIGURE 2. LIGHT SCATTERING OF POLYVINYL ACETATE IN 95% METHANOL.

Samples: XYSG
XYSG (reac.)
XYHL
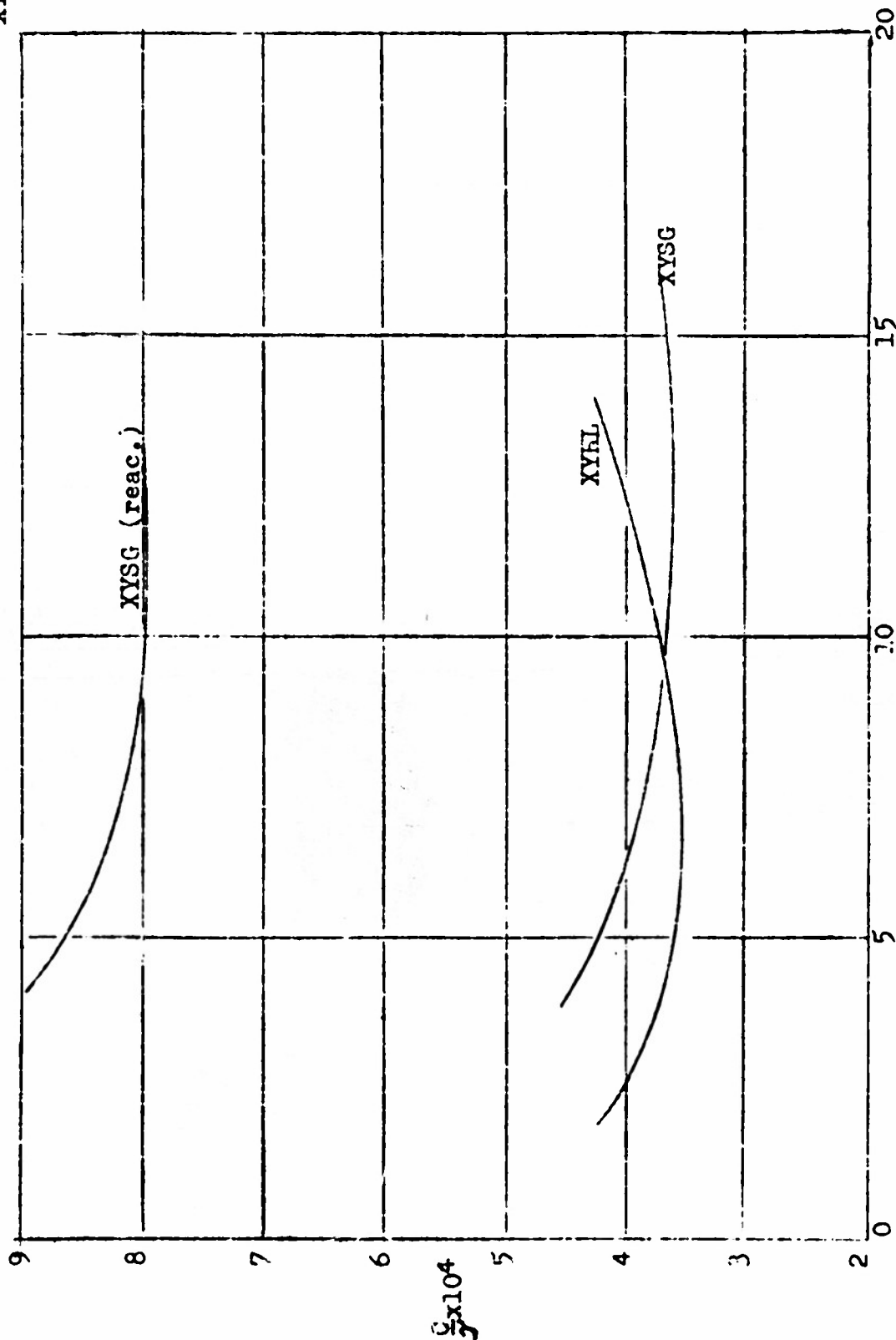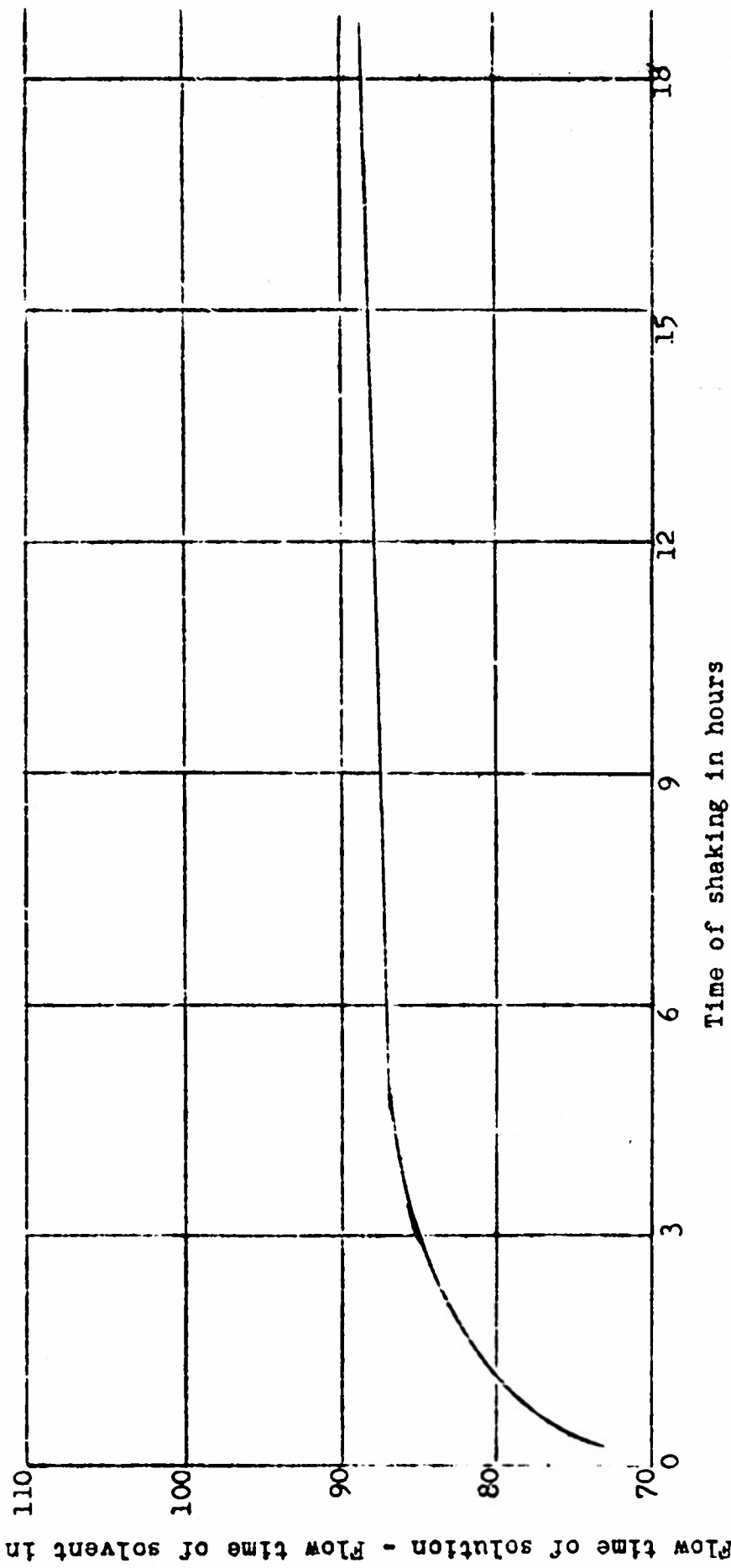
FIGURE 3.

TIME OF SHAKING VS. AMOUNT OF POLYMER ADSORBED.

FIGURE 4.

ADSORPTION ISOTHERM FOR POLYVINYL BUTYRAL (XYSG)

AT $29 \pm 1°C$.

Equilibrium concentration for solution (gr.polymer/
100 ml. solution)