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The Sorption of Water-Soluble Cellulose
Ethers by Cellulose

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THE SORPTION OF WATER-SOLUBLE CELLULOSE
ETHERS BY CELLULOSE

A thesis submitted by

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INTRODUCTION

Paper is modified in a variety of ways to meet consumer demands. For simplicity, these modifications may be roughly grouped into (1) coatings, (2) fillers, (3) saturants, and (4) additives. Coatings adhere to the sheet surface, fillers are mechanically entangled in the paper web, and saturants are imbibed by the sheet. Additives are materials which are introduced in small amounts at some point in the wet-end system and depend on sorption for retention rather than on the above-mentioned mechanisms. Additives may be further identified according to the point at which they are introduced--i.e., beater and headbox additives--and are represented by such substances as mannogalactan gums, starch, wood hemicelluloses, and water-soluble methylcellulose, together with wet strength and other resins.

The use of additives in papermaking is attracting increased interest in the industry, not only for certain specialty papers, such as those with wet strength, but also for the purpose of decreasing the power requirements in the hydrating of pulps and permitting an increased use of shorter-fibered or poorer quality pulps in furnishes. Mannogalactan gums and methylcellulose are pulp deflocculators and, therefore, contribute to more uniform formation on the paper machine. Additives may increase the ultimate strength properties of a given furnish and, consequently, widen market horizons for a particular product.

Additives are introduced in the wet-end system of the paper machine in amounts approximating several per cent of the fiber present.

Since pulp consistencies vary from 5% in the beater to 0.5-1.0% in the headbox, the absolute concentration of additive is very low. In order to be effective, an additive must be picked up from this dilute solution in sufficient amounts so that resulting modification of the fiber surface can stabilize pulp suspensions, thus resulting in better formation, increased fiber-to-fiber bonding, and improved strength properties. Fundamental studies on additive retention have not been extensive. This is particularly true of polysaccharide additives. Additional information on the manner of additive sorption by pulps and the factors which influence this sorption should result in more effective utilization of these new papermaking raw materials.

Water-soluble cellulose ethers were chosen for the present investigation because they have shown great promise as beater additives and because they readily disperse in water to form clear viscous solutions. In addition, cellulose ethers are relatively resistant to biological attack, thus obviating extraordinary precautions.

HISTORICAL REVIEW

Water-soluble cellulose ethers are made commercially by
steeping purified wood or cotton cellulose in 50% sodium hydroxide and
treating with methyl or ethyl chloride under pressure at elevated
temperatures (1 - 3). The properties of the product depend on (a) the
nature of the etherifying radical and the degree of substitution
(D.S.), (b) the degree of polymerization (D.P.), and (c) the uni-
formity of etherification. The D.P. is controlled largely by aging
the alkali cellulose formed in the steeping operation. Methylcellulose
of D.S. 0.7-2.6 and ethylcellulose of D.S. 0.8-1.3 are soluble in
cold water for certain ranges of D.P. Cellulose ethers are insoluble
in hot water and precipitate from solution on heating (3, 4). Gela-
tion is accompanied by a slight volume increase in the system (5).
Methylcellulose and gelatin hydrosols form coacervates when mixed (6).
Methylcellulose in solution positively adsorbs weakly hydrated anions
and negatively adsorbs highly hydrated anions in the order of the
lyotropic series. The effect of salts on methylcellulose solubility
also follows this series; highly hydrated anions are more effective
in decreasing the solubility (4, 7, 8). Methylcellulose is said to
have no zeta-potential in solution (9). Polybasic acids, phenols,
tannins, aldehydes, and certain albumen precipitants will precipitate
methylcellulose from solution (2, 10, 11). Sonnerskog (12) studied
the gelation of water-soluble ethylcellulose and hydroxyethylcellulose
and postulated an aggregate formation for solutions of the former
ether. Hydroxyethylcellulose solutions do not show such aggregates.
Solutions of methylcellulose ordinarily do not ferment or mildew (2, 3).

Methylcellulose has been fractionated from water solution using a salting-out technique (13). Signer and Tavel (14) investigated these fractions by ultracentrifuge sedimentation equilibrium. The molecular dimensions of methylcellulose in solution were determined from the weight-average molecular weight [using the formula of Burgers (15)] and experimentally determined reduced viscosity and partial specific volume. The results were checked using a molecular length of D.P. times the length of a glucose residue (5.15 A.). Good agreement was found for the values calculated by the two methods. The diameter of a methylcellulose molecule was found to be 7-9 A., indicating a long, thread-like molecule of one methylated cellulose chain. Worden (16) reports the experiments of Katz and Samuel, who found the thickness of methylcellulose molecules on water to be 4.1-4.3 A. as measured with a film balance. These findings coincide with those of Signer and Tavel, if orientation of the glucose ring at the water surface is considered. Staudinger and Reinecke (17) and Staudinger and Schulz (18) determined the viscosity and osmotic pressure molecular weights of methylcellulose in water, m-cresol, acetic acid, and chloroform. The Staudinger K_m constant was found to be 11×10^{-4} for a methylcellulose with 22-32% methoxyl content in water solution.

Water-soluble methylcellulose has been proposed as an adhesive for paper coatings (19) and as a greaseproof coating (20). A number of writers have referred to the use of water-soluble methylcellulose as an additive and have reported improvement in strength properties of treated pulps (21 - 26). A review of beater additives

in general is given by Jayne, et al (27), which includes the
utilization of methylcellulose. Erspamer (28) and Broadbent and
Harrison (29) have reported that methylcellulose is a pulp de-
flocculator and dispersing agent. Dixeon (30) concluded that
fiber-to-fiber bonding was a function of the hydrophilic nature of
the pulp surface. He also found that methylcellulose was particularly
effective in imparting a more hydrophilic character to pulps.

Because the retention of beater additives must involve some
type of sorption by the pulp, recent investigations on the adhesion
of high polymers to cellulose are of interest. Mark (31) reviewed
adhesion to cellulose in general and mentioned four possible types of
bonds. (A) Mechanical bonds in which the adhering surfaces approach
to within 100-200 A. Such bonds are possible because electron-
micrography has shown inhomogeneities in cellulose fiber surfaces
which are as much as 300 A. deep. The mechanical bond is very weak.
(B) Polar bonds, in which attraction occurs between polar groups.
These groups approach to within 4-5 A. and the bond energy is 2-4
kilocalories per mole. (C) Hydrogen bonds occurring between fluor-
ine, oxygen, or nitrogen atoms, in which the atoms are separated by
2.5-2.8 A. and the bond energy is 5-8 kilocalories per mole.
(D) Covalent bonds (chemical) in which the constituent groups are
1.5-2.0 A. apart and the bond energy is 50 kilocalories or more per
mole. McLaren (32) found that polymer adhesion to cellulose from hot
melts was a function of the tack temperature and the ratio of the square
of the polymer dipole moment to the dielectric constant. This agreed
with the data of Moll and Ostwald, who showed that polymers dissolve in

solvents which fall within certain limits of this ratio. A lower tack temperature results in a lower viscosity and more ready adaptability to the cellulose interface. Hofrichter and McLaren (33) varied the carboxyl content of a vinyl chloride-vinyl acetate copolymer by adjusting the content of maleic acid. They found that adhesion to cellulose varied with the carboxyl content according to a Freundlich adsorption isotherm. Adhesion increased with increasing temperature; the heat of adhesion was determined to be 12,500 cal./mole (endothermic). The hypothesis was advanced that adhesion is a resultant of an exothermic sorption process and an endothermic fluidity or cohesion process. The heat of adhesion is the sum of the heats associated with their processes and is endothermic or exothermic according to the relative magnitude of the two quantities. Since adhesion is endothermic, the heat of fluidity is greater than the heat of sorption. The heat of fluidity was experimentally determined from the tack temperature at varying carboxyl contents and the heat of sorption was calculated to be 17,500 cal./mole (exothermic). McLaren and Seiler (34) studied the influence of molecular weight on adhesion and found that above a certain minimum, the molecular weight did not influence the adhesion of polymers to cellulose or aluminum foil. They also found that increasing humidity improves adhesion of polar polymers because of a plasticization effect. McLaren and Hofrichter (35) and McLaren (36) have reviewed the above experimental work in a general way.

Although some investigations have been carried out on the retention of certain wet-strength resins and polyelectrolyte cellulose derivatives (carboxymethylcellulose) by cellulose, the case of

greatest interest in the present study is the sorption of essentially
neutral, highly hydrated, straight-chain polysaccharides from water solu-
tion. Data on such systems are not plentiful. The selective sorption
of the amylose (straight-chain) fraction of starch by cotton or filter
paper was used by Tanret (37) for quantitatively separating this frac-
tion from the amylopectin (branched-chain) fraction. Samec (38) used
cotton wadding for sorbing amylose from four 0.1% starch sols contain-
ing decreasing amounts of amylose. The cotton sorbed 1.7% of its
weight in the sol consisting mainly of amylose, and 0.3% in the sol
which was largely amylopectin. Pacsu and Mullen (39) found that cotton
removed the amylose from a 1% starch paste and that the cotton plus
adsorbate could be washed free of amylopectin. Hot water decomposes
the adsorption complex and the amylose can be recovered. Kerr and
Severson (40) confirmed these results and found that cotton sorbed
1% of its weight from a 0.33% solution of crystalline amylose. The
retention was determined by washing the cotton with cold distilled
water and drying. The dry cotton placed in iodine solution turned
blue but did not affect the iodine solution itself, indicating an
irreversible sorption.

Obermanns (41) measured the retention of wood hemicelluloses
by sulfite, alpha, and rag pulps in connection with an investigation of
hemicelluloses as beater additives. Xylan prepared from a 6% sodium
hydroxide extraction of soda pulp was added to rag pulp and increased
the pentosan content from 0.7% to 6.5% at 500 S.-R. freeness and 18%
at 100 S.-R. freeness. The amount of xylan added was not specified.
Beta-cellulose (acid-precipitable fraction of the 6% caustic extract

from sulfite pulp) was added to sulfite and alpha pulps in amounts vary-
ing from zero to 18% (based on the pulp). These data are reproduced in
Table I with calculated values of the equilibrium concentration and the
sorption. The pulp consistency was 1.42%. When sorption is plotted
against equilibrium concentration, an almost straight-line relationship
exists for both pulps. Since the estimation of the beta- plus gamma-
cellulose in the above pulps was made on handsheets, it follows that the
retention of the beta-cellulose is practically irreversible in that,
suspending the pulp in water, did not result in removal of the hemi-
celluloses.

TABLE I

SORPTION OF BETA-CELLULOSE BEATEN
WITH PULP TO 350 S.-R. FREENESS

(Computed from the Data of Obermanns)

Beta-Cellulose Added, %	Equilibrium Concentration, g./100 ml.	Beta- Plus Gamma-Cellulose in the Sheet, %	Sorption g./g. Pulp X 10^2
Sulfite Pulp			
0.0	0	17.78	0
3.16	0.041	18.08	0.31
18.5	0.227	20.0	2.27
Alpha Pulp			
0.0	0	7.98	0
2.6	0.020	9.15	1.17
10.16	0.098	11.14	3.24

March (42) extracted aspen wood chlorite holocellulose with
varying concentrations of potassium hydroxide and then returned these
hemicelluloses to their respective holocellulose residues. Although

the retention data given are complicated by a constantly varying

substrate (i.e., different holocellulose residues), it may be calculated

that xylan retentions varied from 0.2 to 7.0% on the pulp for additions

of 4 to 110% xylan. For the only data which are comparative, retention

plotted against equilibrium concentration showed a curve suggestive

of a typical Freundlich adsorption isotherm. This was for hemicelluloses

extracted with 10% potassium hydroxide. These hemicelluloses might be

expected to possess the longest chain-lengths of the alkali-extractable

materials.

Data on the retention of methylcellulose (25) by pulps obtained

by analysis of the methoxyl content of dried handsheets are of immediate

interest to the present study. The data show an increasing retention

with increasing concentration of methylcellulose in the beater liquid,

but definite conclusions as to the type of curve resulting from an

equilibrium concentration-sorption plot cannot be drawn. Some of the

data plot as a curve concave to the concentration axis and some as a

curve convex (Freundlich type) to this axis. One reason for this

ambiguity may be the factor of time which will be shown to be very im-

portant in such researches. Retention of methylcellulose increased

slightly with degree of beating but it is questionable whether an

effect actually existed. There was no conclusive effect of molecular

weight on retention but the data were somewhat contradictory, probably

for reasons previously mentioned. Rosin size had no effect on the

retention of methylcellulose. By heating the methylcellulose with the

stock above the gel point (at which more concentrated solutions of

methylcellulose set to a firm gel) greater retentions could be obtained, probably because of the adherence of precipitated discrete particles of methylcellulose to the fibers. However, strength properties were decreased in comparison with untreated pulp, in spite of increased retention of additive. The fact that the handsheets in this investigation contained methylcellulose indicates at least a partially irreversible retention, since the bulk concentration of the additive surrounding the fiber must have been very greatly reduced in making the sheets. This equilibrium concentration was below 0.1% in all cases studied. The reduction of the fiber consistency from 1.7% in the beater to 0.02-0.04% in the handsheet mold would reduce the concentration of methylcellulose about 60-fold.

It is reasonable to expect that the sorption of additives must involve either a process in which diffusion is the paramount mechanism or one in which true surface adsorption occurs. A combination of these processes may also be involved. The literature on diffusion and adsorption is extensive, but the reader is referred particularly to experimental work in the field of dyeing of cotton and regenerated cellulose for pertinent information on diffusion (43). Williams and Cady cover the fundamentals of diffusion (44). An excellent review of experimental techniques is given by Geddes (45). The book by Mantell (46) covers the theory of adsorption and contains key literature references. Textbooks on physical and colloid chemistry also deal in part with adsorption (47, 48).

PRESENTATION OF THE PROBLEM

The primary purpose of the present study was to investigate some of the principal variables which could conceivably affect the retention of water-soluble methyl- and ethylcelluloses by papermaking pulps. Because adsorption has been shown to be a function of concentration, particular emphasis was to be placed on this variable. Of hardly less importance, however, was time, temperature, additive molecular weight, and the effect of other elements of the papermaking furnish, such as rosin and alum.

Since existing analytical techniques for estimating the retention of cellulose ethers were inadequate, methods of analysis suitable for measuring a very dilute concentration of additive in the pulp-additive-water system had to be developed.

On the basis of the results obtained in the investigation of the variables mentioned above, possible mechanisms for sorption were to be hypothesized and discussed.

EXPERIMENTAL PROCEDURES

RAW MATERIALS

Data on the properties of the additive raw materials used
are tabulated in Tables II and III. The methylcellulose was obtained
in four different grades and was a white, fibrous product made by the
Dow Chemical Company of Midland, Michigan, which kindly furnished some
of the analytical data. Clear solutions of methylcellulose were made
by soaking the material for 0.5 hour in half the required water for
dilution at near the boiling temperature. After this soak, water was
added to nearly the mark on the volumetric flask. The suspension was
cooled below 10° C. until the methylcellulose was completely in solution;
the solution was diluted to the mark after bringing the flask and con-
tents to room temperature. Solutions of required concentration (based
on ovendry weights) were made by volumetric dilution at room tempera-
ture from 0.5% stock solutions. Stock solutions were stored at room
temperature.

The ethylcellulose was an experimental sample furnished by
the Dow Chemical Company. Solutions of the ethylcellulose were made
in a manner similar to that used for the methylcellulose, except that
the stock solution was filtered to remove insoluble material before
diluting to obtain lower concentrations. The actual concentration of
the stock solution was obtained by evaporating and oven drying 25-ml.
aliquots. The ethylcellulose was 68.5% water soluble.

TABLE II

PROPERTIES OF ADDITIVE RAW MATERIALS

Grade (Viscosity 2% Solution, 20° C.), cp.	Alkoxyl, %	Ash (NaCl+Na$_2$CO$_3$), %	Arrhenius Viscosity Constant[1] $\underline{K}$	Intrinsic Viscosity, η[2]	Viscosity Molecular Weight[3]	Monomer Weight	Degree of Polymerization	Degree of Substitution
Methylcellulose (Dow Methocel)								
25	32.6	0.09	0.84	1.85	31,000	190	160	2.00
100	30.7	0.15	1.38	3.20	53,000	188	280	1.86
400	31.5	0.07	2.12	5.05	84,000	189	445	1.92
4000	30.8	0.03	3.34	7.55	126,000	188	670	1.87
Ethylcellulose								
74	33.7	0.09	0.55	1.30	24,000	205	117	1.53

1. In equation $\log \eta_r = \underline{K}c$ where η_r = relative viscosity, $\underline{c}$ = concentration grams/100 ml.

2. Defined by Kraemer as $(\eta_{sp}/\underline{c})$ $\underline{c} \to 0$ where η_{sp} = specific viscosity and $\underline{c}$ = concentration grams/100 ml.

3. From Staudinger equation $(\eta) = \underline{KM}$, where $\underline{M}$ = molecular weight and $\underline{K}$ = Staudinger constant; $\underline{K}$ is 6.0 x 10-5 for methylcellulose where concentration is expressed in grams/100 ml.

TABLE III

VISCOSITY DATA ON METHYLCELLULOSE

Grade Methocel	Methylcellulose Concentration, g./100 ml.	Relative Viscosity, ηr	Reduced Viscosity, η_{sp}/c	Arrhenius k	Av.
400	0.0100	1.052	5.22	2.20	2.20
	0.0200	1.108	5.36	2.22	
	0.0300	1.164	5.48	2.20	
	0.0500	1.286	5.73	2.18	
	0.0150	1.077	5.14	2.15	2.12
	0.0300	1.158	5.28	2.12	
	0.0500	1.278	5.57	2.13	
	0.1000	1.616	6.16	2.08	
	0.0150	1.078	5.20	2.19	2.11
	0.0300	1.154	5.13	2.08	
	0.0500	1.274	5.48	2.11	
	0.1000	1.610	6.10	2.07	
In 0.00045 molar alum	0.0300	1.154	—	2.09	2.09
	0.1000	1.610	—	2.09	
In 0.005 molar alum	0.0150	1.073	—	2.04	2.07
	0.0300	1.153	—	2.07	
	0.0500	1.274	—	2.10	
In 0.05 molar alum	0.0296	1.146	—	2.03	2.03
	0.0493	1.258	—	2.02	
	0.0985	1.584	—	2.03	
In 0.02 g./ 100 ml. rosin	0.0498	1.256	—	1.99	1.99
25	0.0500	1.099	1.98	0.823	0.829
	0.0400	1.078	1.95	0.816	
	0.1000	1.208	2.08	0.822	
	0.1000	1.216	2.16	0.850	
	0.1500	1.336	2.24	0.839	
	0.2000	1.463	2.31	0.825	
100	0.0150	1.049	3.28	1.39	1.38
	0.0500	1.172	3.44	1.38	
	0.1000	1.366	3.66	1.36	
4000	0.0150	1.122	8.13	3.34	3.34
	0.0500	1.474	9.49	3.37	
	0.1000	2.141	11.41	3.31	
Ethylcellulose	0.0103	1.010	0.975	0.422	0.551
	0.0342	1.045	1.31	0.557	
	0.0684	1.090	1.32	0.547	

Note: Consult "Analytical Procedures" for viscometric methods.

Data from the literature on the molecular weights of water-soluble methylcellulose are summarized in Table IV. From these data the Staudinger K_m constant may be found to be 11×10^{-4}. (Concentration is in gram monomer weights per liter.) Certain objections to the use of the Staudinger equation (Table II) for computing molecular weights have arisen, and a modification of this equation is that proposed by Mark and discussed by Ewart (49) where $(\eta) = K M^a$ (a = constant). The constant a has a theoretical basis and has been found to vary from 0.5 to 1.0. The above equation may be written $\log (\eta) = c + a \log M$, and a plot of $\log (\eta)$ vs. $\log M$ should yield a straight line of slope a and intercept c. A plot of the data in Table IV gives an excellent straight line and a value of 0.94 for a. Since the value of a is so nearly unity, the Staudinger equation as originally proposed was used in the present investigation for computing molecular weights from viscosity data.

As has been repeatedly pointed out in the literature, weight average and number average molecular weights are equal only for mono-disperse systems (sharp molecular weight fractions). Since only the ultracentrifuge data in Table IV were obtained on fractions, an objection to the use of the osmotic pressure data for calibrating the viscosity method might legitimately be raised. The justification for such a calibration must lie in the fact that methylation tends to degrade cellulose severely and such degradation shifts the molecular weight distribution toward lower molecular weight species and, at the same time, makes the distribution more uniform (50). Thus the material used in obtaining the values in Table IV was probably fairly uniform, even though unfractionated.

TABLE IV

MOLECULAR WEIGHTS OF METHYLCELLULOSES
IN WATER SOLUTION

MeO, %	MeO Groups Per Monomer	Monomer Molecular Weight	Molecular Weight	Polymer DP	Intrinsic Viscosity	Source
22.5	1.31	180	77,000	425	5.00	(1)
24.0	1.41	182	67,000	370	3.97	Osmotic
24.7	1.46	183	42,000	230	2.90	Pressure
24.9	1.47	184	52,000	280	3.48	
26.3	1.56	185	47,000	255	2.84	
27.0	1.60	186	108,000	580	5.78	
31.6	1.93	189	45,500	240	2.67	
22.5	1.31	180	82,000	456	5.00	(2)
25.3	1.50	183	79,000	432	4.37	Osmotic
24.6	1.45	182	49,000	269	3.08	Pressure
23.4	1.37	181	46,000	254	2.37	
22.6	1.32	180	14,100	79	0.81	(3)
28.8	1.71	187	24,300	130	1.49	Equilibrium
31.7	1.93	189	38,100	202	2.23	Ultracentrifuge
34.6	2.14	191	90,000	418	5.06	

(1) Staudinger, H., and Reinecke, F., Ann. 535:95(1938)
(2) Staudinger, H., and Schulz, G. U., Ber. 68:2320(1938)
(3) Signer, R., and Tavel, P. V., Helv. Chim. Acta 21:535(1938)
    Signer, R., and Liechti, J., Helv. Chim. Acta 21:530(1938)

The pulps used for the sorption experiments consisted of cotton

linters from the Hercules Powder Company; western hemlock bleached

sulfite from the Pulp Division, Weyerhaeuser Timber Company; western

hemlock unbleached sulfite from Puget Sound Pulp and Timber Company;

and jack pine bleached and unbleached kraft from Nekoosa-Edwards Paper

Company. These pulps were beaten in a Valley Laboratory beater according to Institute method 403 except that 2000-4000-cc. samples were taken at the beaten intervals selected. The linters and sulfite pulps were beaten with a 5500-gram and the kraft pulps with a 6500-gram bed-plate load. The cotton linters and the bleached pulps were extracted with distilled water at room temperature until the filtrate pH was 6.5-7.0. The unbleached pulps were extracted at 60-80° C. for two 1-hour periods; the final unbleached sulfite extract pH was 6.5-7.0. The unbleached kraft was given an additional wash in 0.01 N sulfuric acid and was again extracted at room temperature until the final extract pH lay between 6.0-7.0. The cotton linter samples used in the rate experiments were extracted with water in a Soxhlet extractor for four weeks for the 655 S.-R. pulp and five days for the unbeaten pulp.

After filtration, the extracted pulp pads were pulled into small pieces, thoroughly mixed, and stored in 32-ounce wide-mouth, screw-cap bottles below 10° C. Moisture contents were taken at frequent intervals by random sampling from the stock bottle and all duplicate samples agreed within 0.4%, although the precision was frequently much better. Consistencies varied between 16 and 30% and did not change appreciably over a period of many months. Since the maximum deviation from the mean, for moisture samples, was about 0.2%, it may be concluded that the actual weights of the one-gram pulp samples (ovendry basis) taken for sorption runs agreed within 1.5%.

Pulp consistencies are listed in Table V.

TABLE V

PULP BEATING DATA AND CONSISTENCIES

| Pulp	Time Beating, min.	Freeness, cc. S.-R.	Consistency (ovendry pulp), %
Cotton linters	0	880	21.9
	50	795	22.6
	67	635	19.3
	89	470	21.2
	98	335	22.6
Bleached sulfite	0	885	26.1
	29	770	22.1
	43	570	19.3
	59	300	16.8
Bleached kraft	0	850	21.0
	15	775	19.9
	23	580	17.5
	29	325	16.4
Bleached kraft (rewashed)	0	850	20.6
	15	775	—
	23	850	16.9
	29	325	19.3
Unbleached sulfite	0	855	29.8
	20	795	—
	36	630	22.3
Unbleached kraft	0	870	24.6
	25	815	—
	39	695	—
	48	610	20.2

DEVELOPMENT OF ANALYTICAL TECHNIQUES

The sorption* or retention of any sorbate by a sorbent may
be determined by one of two basic methods. The first is to measure
the sorbed substance directly on the sorbent, or to strip the sorbate
from the sorbent before analysis. This allows use of the so-called
"infinite bath," in which the bulk concentration of the sorbate is main-
tained essentially constant during sorption. The other method is to
measure the change in concentration of the sorbate in the solvent. The
change in concentration multiplied by the volume of the solvent gives
the quantity taken up by the sorbent. Analytically speaking, the first
method is the better since it measures directly the quantity desired.
In addition, it permits sorption determinations at a constant concen-
tration of sorbate. However, the problem of removal of mechanically
held liquor from the sorbent is a difficult one. The sorbate in the
mechanically held liquor will be analyzed as sorbed when actually it
is not. The sorbent cannot be washed with solvent if the sorption is
reversible, since sorbate will be removed. The second method measures
a difference and consequently must be very sensitive. It also tends
to be inaccurate if this difference is small—i.e., when there is very
little sorption.

Use of Anthrone

A colorimetric test which appears to meet the specification

*This general term, first introduced by J. W. McBain, is used to
avoid premature commitment as to the mechanism of retention—i.e.,
whether adsorption or absorption.

of sensitivity for measuring sorption by concentration difference is
that of anthrone. Anthrone is a reduction product of anthraquinone
and is formed by heating the latter under reflux in the presence of
granulated tin and a mixture of acetic and hydrochloric acids (51, 52).
The compound may now be obtained commercially in reasonably pure
form (53).

Anthraquinone   Anthrone
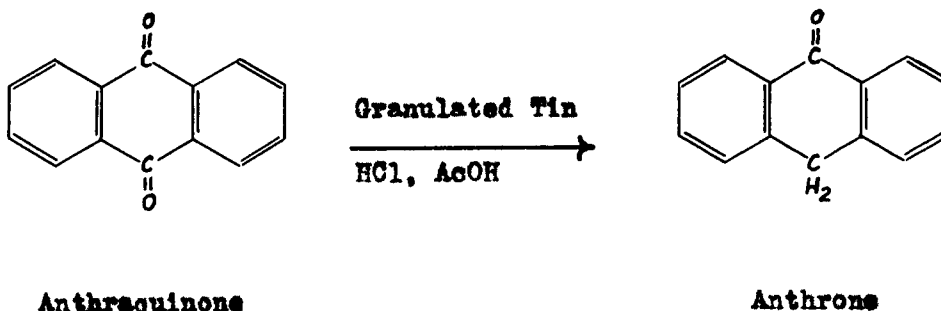
Anthrone was initially used as a test for glycerol (a red
color is formed) in paper (51). In 1946, Dreywood (54) proposed
anthrone as a sensitive test for carbohydrates. A positive blue-green
color was given by a group of 18 carbohydrates, including starch and
cellulose, a hexose, a pentose, some natural gums, cellulose ethers,
and cellulose esters. In essence, the anthrone test comprises the
mixing of one volume of carbohydrate solution with two volumes of
anthrone reagent (prepared by dissolving anthrone in concentrated sul-
furic acid to give a 0.2% solution).

In 1948, Morris (55) confirmed the claims of Dreywood and
used the reagent for the quantitative colorimetric determination of
glucose, maltose, fructose, α-methyl glucoside, galactose, and lactose
with a filter photometer. Beer's law was obeyed at 620 mmu. Morse (55)
used anthrone for the measurement of sucrose (concentrations of 10 to

25 p.p.m.) in beet sugar waste liquors. Sattler and Zerban (52) continued the work on the specificity of the test and hypothesized that the anthrone color was due to the formation of furfural-type compounds in the strong sulfuric acid. Viles and Silverman (53) applied anthrone to the analysis of starch and cellulose in cotton lint from air samples in textile mills.

Morris (55) swirled the anthrone reagent and carbohydrate solution in the test tube to effect mixing, whereas Morse (56) shook the test (like a clinical thermometer) or used a glass stirrer after forming two layers of reagent and solution. Viles and Silverman (53) preferred a rapid mixing as reagent was added. It was found in the present investigation that neither a glass stirrer nor vertical shaking yields precise results. A pouring technique, however, was found to give a precision in duplicate determinations of ± 0.5% transmittance from the mean. This technique consists of cautiously adding the reagent to the solution in order to form a double layer. The two layers are then poured rapidly into a clean test tube and poured back into the original one. Shaking the test tube with an oscillarotary motion of the forearm for 15 seconds also gave results identical with those of the pouring technique. The latter method was adopted, however, because of its extreme simplicity.

With increasing age anthrone reagent gives a weaker color for a given concentration and, consequently, must be calibrated frequently and, preferably, at the time samples are examined. It was hoped, at first, that a simple correlation between transmittance (for a given concentration) and age of reagent would be possible, but
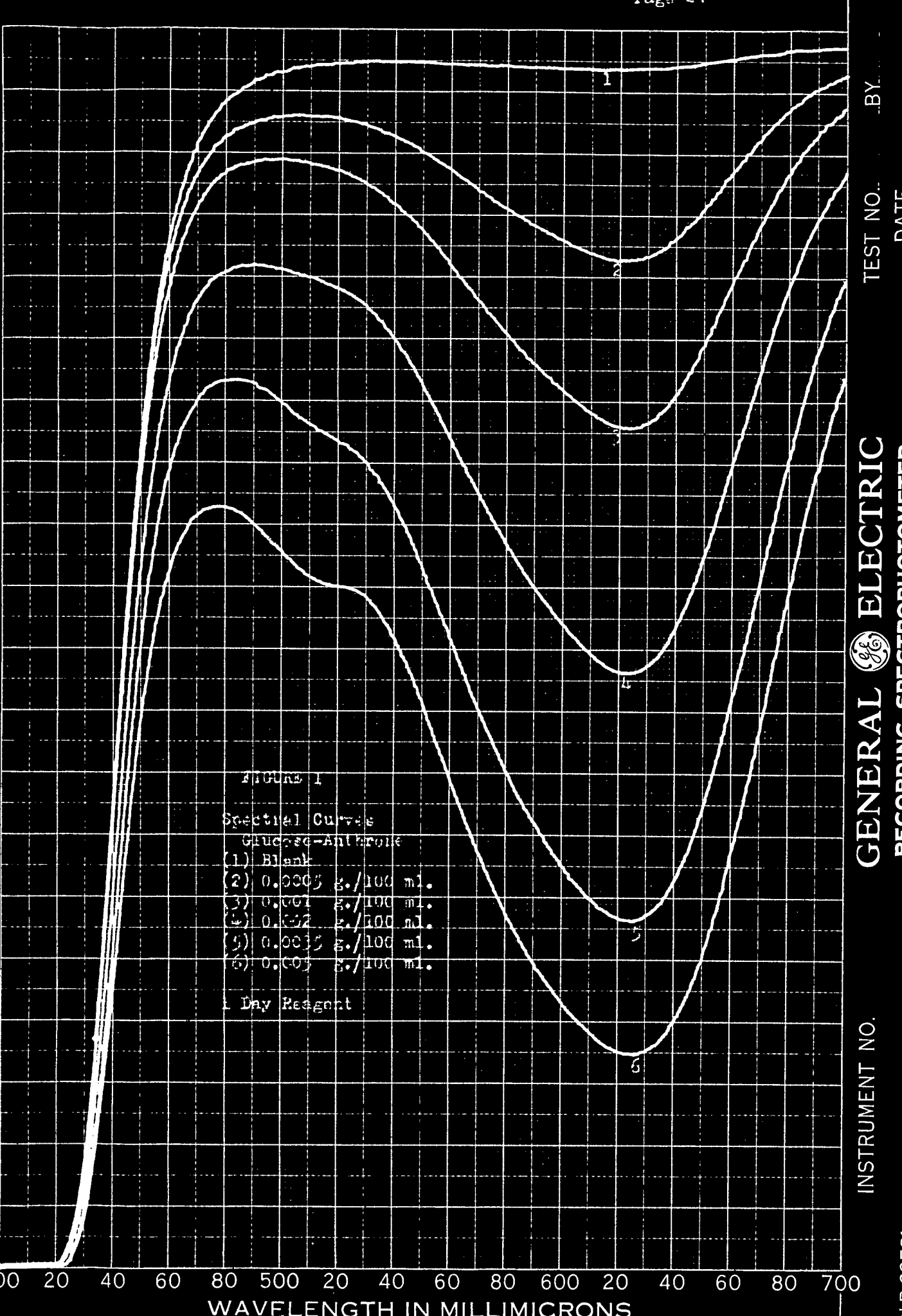
extensive data indicate that different batches of reagent vary
erratically with age and only a crude correlation is possible. Such
a correlation might suffice for rough analyses but for accurate work
it cannot be recommended. Viles and Silverman (53) also found that the
reagent behaved erratically with age and suggested that the reagent be
allowed to age at least 4 hours before use since inconsistencies
occurred otherwise. This was confirmed in the present study and it
was found that the transmittance for a given concentration passed
through a minimum for one day old reagent.

Spectral transmittance curves for the anthrone color complex
were run on the General Electric recording spectrophotometer for the
hexoses, oligohexoses, polyanhydrohexoses, pentoses, and derivatives
listed in Table VI. Four of these curves may be found in Figures 1-4.
The curves provide almost quantitative proof of the theory of Sattler
and Zerban that hydroxymethylfurfural formed from hexoses in acid
solution is responsible for the anthrone color. Except for minor
deviations, the spectral curve of hydroxymethylfurfural is identical
with those obtained for the hexoses. The optimum wavelength for
spectrophotometric analysis for all the hexose-type carbohydrates
studied was found to be 625 mmu, in agreement with the findings of
Viles and Silverman for cellulose and starch.

TABLE VI

ANTHRONE EXTINCTION COEFFICIENTS
OF CARBOHYDRATES

Carbohydrate	Specific Extinction Coefficient, $\frac{100 \text{ ml.}}{g. \times cm.}$	Gram Equivalent Weight	Equivalent Extinction Coefficient, $\frac{100 \text{ ml.}}{\text{Equivalents} \times cm.}$
		625 mм	
Glucose	151	180	27,200
Cellobiose	158	171	27,000
Maltose hydrate	153	180	27,500
Fructose	146	180	26,300
Sucrose	157	171	26,900
Tetramethylglucose	114	236	26,900
Methylcellulose (31.5% MeO)	131	189	24,800
Ethylcellulose (33.7% EtO)	101	205	20,700
Galactose	81.4	180	14,650
Mannose	70.4	180	12,680
Locust bean gum	72.4	162	11,730
Lactose hydrate	120	180	21,600
Hydroxymethylfurfural	2748	126	347,000
		580 mм	
Arabinose	8.2-15.4	---	---
Xylose	15.6-33.3	---	---
Furfural	55.0-103.2	---	---

Note: Tests were made with 10 ml. 0.2% anthrone in concentrated sulfuric acid added to 5 ml. carbohydrate solution in 25-mm. test tubes mixed by pouring once into a clean test tube and pouring back. Reagent was 1-3 days old for hexose-type carbohydrates and derivatives (except 9 days old for ethylcellulose); 5 days old for pentose and derivatives.

FIGURE 1

Spectral Curves
  Glucose-Anthrone
(1) Blank
(2) 0.0005 g./100 ml.
(3) 0.001 g./100 ml.
(4) 0.002 g./100 ml.
(5) 0.0035 g./100 ml.
(6) 0.005 g./100 ml.

1 Day Reagent

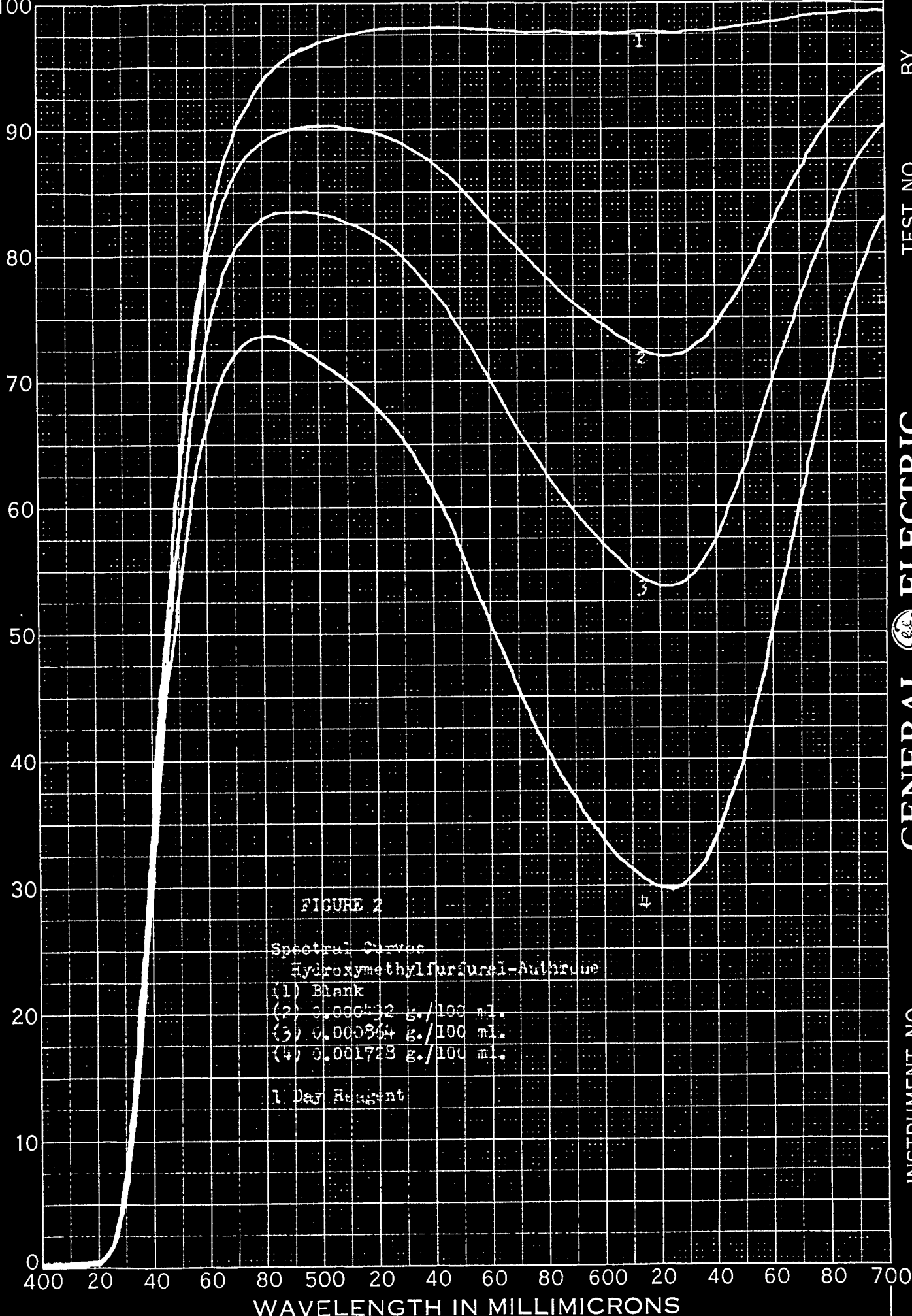WAVELENGTH IN MILLIMICRONS

FIGURE 2

Spectral Curves
Hydroxymethylfurfural-Anthrone
(1) Blank
(2) 0.000432 g./100 ml.
(3) 0.000864 g./100 ml.
(4) 0.001728 g./100 ml.

1 Day Reagent

FIGURE 3

Spectral Curves
Xylose-Anthrone
(1) Blank
(2) .0050 g./100 ml.
(3) .0100 g./100 ml.
(4) .0200 g./100 ml.

5 Day Reagent

WAVELENGTH IN MILLIMICRONS

20 40 60 80 500 20 40 60 80 600 20 40 60 80 700

FIGURE 4

Spectral Curves
Furfural-Anthrone
(1) Blank
(2) .0010 g./100 ml.
(3) .0025 g./100 ml.
(4) .0040 g./100 ml.

5 Day Reagent

REFLECTANCE
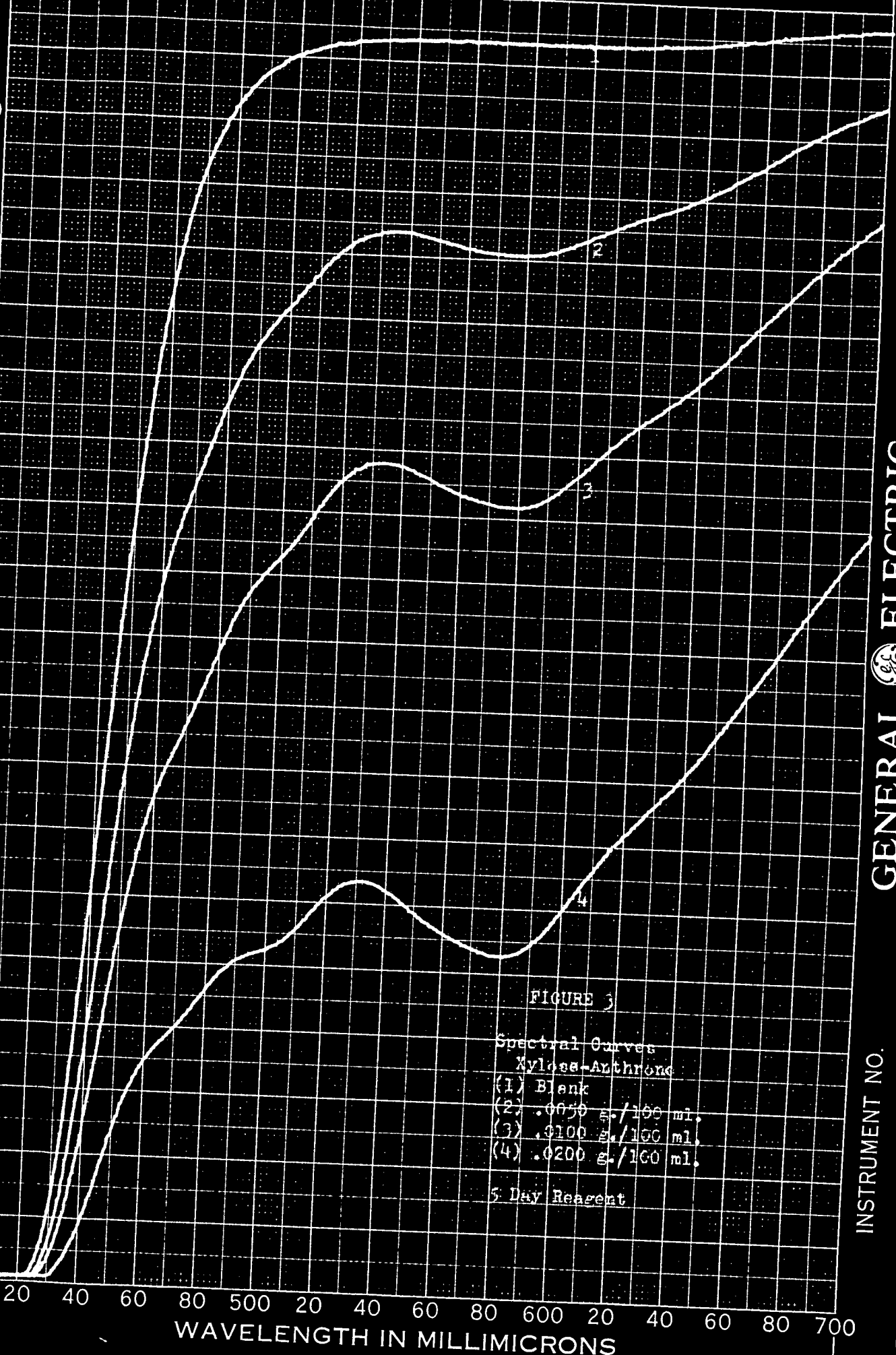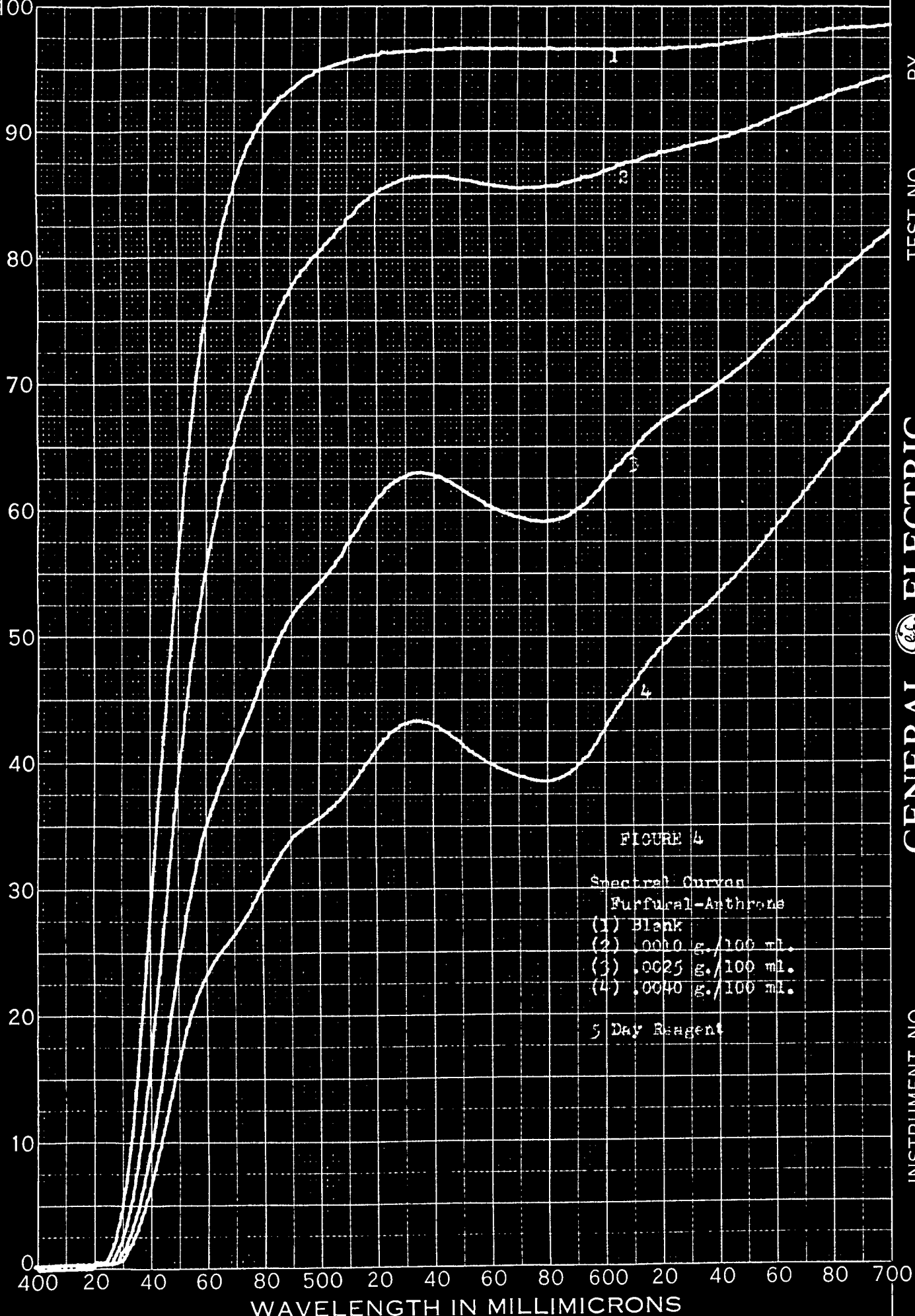TRANSMITTANCE (PERCENT)

WAVELENGTH IN MILLIMICRONS

GENERAL ⊕ ELECTRIC
RECORDING SPECTROPHOTOMETER

TEST NO.
DATE
BY
INSTRUMENT NO.

The present work confirmed the formation of a blue-green color for the hexoses and pentoses, but it was found that the pentose color was not stable and changed very rapidly to a brownish-red or amber color. The spectral transmittance curve for the amber pentose color is quite different from that for the blue-green hexose color. Furfural also showed the initial formation of a blue-green color, followed by the rapid shift to amber. The spectral curve of the amber furfural color was very similar to those for arabinose and xylose. This is further evidence in support of the hypothesis that furfural-type compounds are precursors of the anthrone color. The blue-green to amber color shift of the pentoses immediately suggests anthrone as a qualitative test for differentiating hexoses and pentoses.

The methylpentoses (fucose and rhamnose) give the stable blue-green hexose color, but furoic acid and furfural alcohol give the transient blue-green color, followed by the stable amber pentose color. It was previously noted that glycerol gives a red color with anthrone. This is apparently due to the formation of acrolein from glycerol in the strong hot acid present, since acrolein alone gives a red color. Formaldehyde and propionaldehyde also give a red color. Mixing of the red aldehyde color with the blue-green hexose color produces a color similar to the amber pentose color. An arabogalactan isolated from western larch gave the blue-green hexose color which changed to reddish-green on standing, indicating a mixture of the hexose and pentose colors. These qualitative observations are presented as a matter of interest, since it would be unwise to postulate a reaction mechanism between

furfural-type compounds and anthrone in the strong hot sulfuric acid
(78.5% at about 90° C.) of the reaction zone.

As mentioned previously, the optimum wavelength (maximum
absorption) was 625 mmu for the hexoses and anhydrohexoses, but Beer's
law was also obeyed at 530 mmu. Unfortunately, Beer's law was not
obeyed for any wavelength for the amber pentose color, which decreases
the usefulness of the test for these sugars. Perhaps a careful calibra-
tion of the reagent with a pentose would permit quantitative measurements.

Included in Table VI are the specific extinction coefficients,
equivalent weights, and equivalent extinction coefficients for the
carbohydrates studied. It will be noted that the equivalent extinction
coefficients for all hexose-type carbohydrates yielding glucose and/or
fructose on hydrolysis are approximately equal, with the exception of
methyl- and ethylcellulose. Apparently there is some steric effect
(perhaps the hydration layer) which decreases the rate of conversion
of methyl- and ethylcelluloses to furfural-type compounds, resulting
in a weaker color. The influence of ether groups, as such, is negligi-
ble as can be seen from the data for tetramethylglucose. The evidence
for steric hindrance is supported by the highly hydrated nature of the
water-soluble cellulose ethers, plus the fact that the color for
ethylcellulose is weaker than that for methylcellulose; this indicates
a greater hydration layer with ethoxyl groups which is verified by
the higher ethylcellulose gel point. The possibility that beta-
glucoside linkages are sufficiently more resistant to hydrolysis to
decrease the rate of conversion to furfural-type compounds in comparison

with alpha-linkages might be considered, but this is ruled out as
the sole explanation because the coefficients of methyl- and ethyl-
cellulose are not equal. All grades of methylcellulose tested
(25, 100, 400, 4000 cp.) gave identical extinction coefficients.
This agrees with the previous data and with those of Morris in that
the chain length of the molecule does not influence the depth of color.

Galactose and mannose have much lower extinction coefficients
(i.e., a weaker color for a given concentration) than glucose- or
fructose-containing sugars. Locust bean gum is a polymannogalactan
containing a ratio of approximately 75:20 anhydromannose to anhydro-
galactose. The extinction coefficient for the gum is seen to fall a
proportional distance between those for mannose and galactose. In
like manner, lactose hydrate consists of equal amounts of galactose
residues. The lactose extinction coefficient lies very nearly half
way between those of its components. The foregoing data are in ex-
cellent agreement with those of Morris (55). The difference in extinc-
tion coefficients of galactose and mannose and the glucose-fructose
hexoses suggests a method for measuring the former sugars in mixtures
with the latter. Preliminary work with the method of differential
extinction, however, has not been especially successful with mixtures
of glucose and mannose.

Separation of Cellulose from Additive

Since any hexose or polyanhydrohexose will give a blue-
green color with anthrone, it is necessary to separate completely such a

carbohydrate additive from cellulose in making retention measurements

on pulps with anthrone. Cellulose in water breaks down upon heating

or handling into small fragments and debris, which presumably have a

distribution from supercolloidal down through colloidal size, although

evidence has been presented which indicates that fibrils of beaten

papermaking fibers attain a minimum diameter of 200 to 300 A. (58).

It is this cellulosic debris which has given rise to the idea

that cellulose may be "soluble" in water. Strachan (59) obtained a

solubility value of 21 p.p.m. for cellulose in water by extracting

bleached spruce sulfite pulp at 15-18° C. (20 grams of pulp in 800 ml.

of water) after thorough removal of water-soluble impurities from the

pulp. Unfortunately, no details are given of the filtration technique

used for separating the cellulose from the water. The evaporated fil-

trate showed a reducing power but Strachan admitted this may have re-

sulted from hydrolysis during evaporation of the aqueous solution.

It has been found during the present investigation, however,

that the concentration of cellulose in a water extract of well-beaten

cotton linters may be reduced to as little as 0.5 p.p.m. of cellulose

(equivalent to glucose as analyzed with anthrone) in water using only

a Corning medium fritted glass filter and discarding the first portions

of the filtrate. Various techniques, using filtration through fritted

glass, and Celite pads and centrifugation, indicated that "soluble"

cellulose in the filtrate or centrifugate is largely a function of the

method of separating the liquid and solid phases. Centrifuging alone,

for example, was found to give a solubility of 1 p.p.m. of unbeaten

cotton linters in water. (The above extractions were all performed at 1% consistency of pulp.)

In addition to these experiments, viscosity determinations on the supernatant liquid from a variety of settled pulp-water suspensions (0.5% consistency) showed practically no viscosity increase over that of water. (These pulps were previously extracted with hot water to remove water-soluble impurities.) In another experiment on beaten cotton linters, an obviously turbid suspension showed no viscosity increase over water alone. Since lyophobic colloidal systems show only a slight viscosity increase with increasing concentration in contrast to lyophilic systems which exhibit a great viscosity increase, it must be concluded that cellulose is not appreciably soluble in a molecular sense but displays some of the properties of a lyophobic colloid in suspension.

Centrifugation. Centrifugation and filtration appeared to be the simplest and most feasible methods of separating cellulosic debris from polysaccharide solutions. A centrifuge having a centripetal acceleration varying from 1.07 to 2.25 x 10^6 cm./sec.^{2} over a path of 6 cm. (centrifuge of 14-20 cm. radius, 3200 r.p.m.), failed to separate cellulose quantitatively from water or polysaccharide supernatant liquor in 15 minutes. Application of Stoke's law and substitution of 1.5 x 10^6 cm./sec.^{2} for the acceleration indicates that particles equivalent to a sphere of about 0.4 mu diameter would be separated. This, of course, can only be an estimate of the size of cellulose fines centrifuged out, since the netlike webs which characterize this

material would show a greater resistance to motion than a sphere of equal volume. The general technique was to allow 0.5% consistency pulp in distilled water to settle at least overnight and to pipet the supernatant liquor for experimentation. Twenty-five ml. of supernatant liquor or mixtures with methylcellulose were placed in a centrifuge tube with 0.1 gram glass wool to prevent disturbance of centrifuged particles. Exhaustive experiments indicated no sorption of methylcellulose by glass wool. Five-ml. samples were carefully pipetted for analysis.

Typical data are presented in Table VII. The concentrations given were determined with the anthrone technique and are equivalent to methylcellulose. To test the separation of cellulosic fines, standard methylcellulose solutions were mixed in equal volume with supernatant liquor from settled pulp-water suspensions. The supernatant cellulose present was apparently too small to sorb appreciable amounts of methylcellulose. (This assumption was checked using cotton linters and the viscometric analytical method to be described later.) The maximum sorption on the fines was found to be 10% of their weight, which may be neglected.

The equivalent concentration in the settled supernatant liquor of unextracted pulp-water suspensions is somewhat variable, as may be seen from the table. This concentration is, of course, dependent to some extent on the type of pulp and time of settling, and increases with degree of beating as expected. The centrifugate concentration also increases with beating. Further evidence that sorption by the cellulose fines is negligible is found in the good agreement between the centrate

TABLE VII

CENTRIFUGATE AND SUPERNATANT LIQUOR
CONCENTRATIONS AS DETERMINED WITH ANTHRONE

| Pulp | Unextracted Pulp | | | | Extracted Pulp | |
| | Settled Water Suspension | | Settled MC-Supernatant Liquor Mixture | | Settled Water Suspension | |
	Supernatant Concentration, g./100 ml.	Centrifugate Concentration, g./100 ml.	MC Concentration in Mixture, g./100 ml.	Centrifugate Concentration, g./100 ml.	Supernatant Concentration, g./100 ml.	Centrifugate Concentration, g./100 ml.
Cotton linters unbeaten	--	0.00012*	--	--	--	--
	--	0.00036*	--	--	--	--
Cotton linters, 470 S.-R.	0.00555	--	--	--	--	--
Bleached sulfite, 770 S.-R.	0.00168	0.00066	0.00100	0.00135	--	--
		--	0.00500	0.00548	--	--
Bleached sulfite, 570 S.-R.	0.00233	0.00060	--	--	0.00018	0.00006
Bleached sulfite, 300 S.-R.	--	0.00150	0.00250	0.00318	--	--
Bleached kraft, 580 S.-R.	--	0.00075	--	--	--	0.00041
Unbleached sulfite, 630 S.-R.	--	--	--	--	--	0.00025

*One per cent consistency.

Unextracted pulp was extracted with water at room temperature only prior to experimentation. Extracted pulp was extracted batchwise for three one-hour periods in boiling water.

MC = methylcellulose.

concentrations of the supernatant liquor and the methylcellulose-
supernatant liquor mixtures. For example, the cellulose concentration
of the 770 S.-R. bleached sulfite pulp was 0.00066 gram/100 ml. in
the supernatant liquor. In the mixture, the cellulose concentration was
0.00070 gram/100 ml. (dilution taken into account).

In the case of pulps extracted with boiling water, a con-
siderably better separation of the cellulose fines appears to have been
achieved and was almost quantitative for the centrifuged bleached sul-
fite. This better separation makes the extracted pulps attractive for
experimental work. However, the unknown effect of boiling on fiber
properties raises a possible objection, since it is known that boiling
physically dehydrates the fibers. The question of whether this same
separation of fines could be achieved in the presence of methylcellulose
must also be raised. Since methylcellulose should have a stabilizing
and deflocculating effect on the cellulose fines according to the work
of Erspamer (28) it would be expected that the same degree of separation
could not be attained. For the present study no pulps were extracted
at the boil and, as indicated in Table VII, centrifugation alone is not
a satisfactory method of analysis.

Fritted Glass Filtration. Two considerations manifest them-
selves in the development of a filtration technique. First, the cellu-
lose fines must be separated from the gum solution; second, the gum
molecules must not be removed by ultrafiltration. A brief review of
some of the experimental work in this connection will suffice to bring
out the salient findings. Cotton linter pulp was used.

As filtering medium, fritted glass filters developed by the Corning Glass Company were used. The experiments to be described may be classified as follows: (A) Experiments in which settled supernatant liquor from pulp-additive suspensions was forced through fritted filters, discarding the first portions of the filtrate in order to obtain a "plugged" filter for filtration of analytical samples; (B) experiments in which standard additive solutions were filtered through these "plugged" filters; (C) experiments in which mixtures of supernatant liquid from pulp-water suspensions and standard additive solutions were filtered through a "plugged" filter; and (D) experiments in which supernatant liquid from pulp-water suspensions was treated as in (A).

In general, the fritted glass filters used were 10 mm. in diameter and were employed as filter sticks. The "medium" porosity filter consisted of Corning tube-type microfilter funnels with the tube chipped down flush with the fritted disk, leaving the stem and the disk. Suction was applied to the stem. The "fine" porosity filters consisted of Corning straight tube sealing stock with a fritted disk in the middle. One end of the tube was cut flush with the fritted disk and discarded, leaving the other tube end terminating in the disk. Suction was applied to the open tube end. For all of the experiments, 0.5% consistency pulp (1 gram in 200 ml. of liquid) was used. For the additive experiments, 1 gram of pulp was added to 200 ml. of 0.005 gram/100 ml. of methylcellulose.

A summary of the important results from the fritted glass filtration experiments is presented below.

1. In type (A) experiments, the concentration of filtrates

from medium filters came to a constant value after 20-25 ml. had been discarded. The viscosity analytical method checked the results on one of these experiments. Initial portions of the filtrate showed higher concentrations than the constant values obtained, which is to be expected since it may be supposed that plugging of a filter results in increasing filtering efficiency. The concentration of the filtrates from the fine filters came to a constant value after 5-10 ml. of filtrate had been discarded. However, initial portions of the filtrate showed concentrations which were slightly below the constant values obtained. This is difficult to explain. An adsorption by the filter system is unlikely since glass wool showed no sorptive capacity for methylcellulose. The filters were dry so that dilution is eliminated. Perhaps initial increments of the liquor solute became mechanically trapped in the fritted disk. Methylcellulose molecules dispersed in water have lengths which would render them readily visible under an ordinary microscope provided the molecular diameters were larger. This fact makes the mechanical trapping hypothesis more plausible. A serious objection to fritted glass filtration became apparent, however, as experimentation progressed. The filtration times for each 5-ml. increment of filtrate increased progressively with plugging, so that the increment for analysis required 20 minutes to filter in the case of well beaten pulps.

2. In type (B) experiments, standard solutions filtered through plugged medium filters were recovered nearly quantitatively. The slight loss noted may well have resulted from dilution by liquor of lower concentration left in the plugged filter. The fine filters

definitely removed methylcellulose by ultrafiltration, since standard solutions could not be recovered without a readily measurable (although not appreciable) loss in concentration. For most purposes this effect could probably be ignored. There was some indication that formation of pulp pads on the face of the fritted filters also increased ultrafiltration. Accordingly, filtrations were performed on settled pulps to avoid filter cake formation.

3. In type (C) experiments, in which standard methylcellulose solutions in mixtures with supernatant cellulose fines from pulp-water suspensions were filtered through plugged filters, it was found that the standard solutions were recovered quantitatively in the filtrate for both medium and fine filters, indicating no passage of cellulose fines or ultrafiltration by the filter. Only one experiment of this type was run for the fine filters; thus these findings are by no means conclusive.

4. In a type (D) experiment, a medium filter almost quantitatively removed the cellulose from the supernatant liquid of a pulp-water suspension after discarding 30 ml. of filtrate.

In summary, it may be stated that medium fritted glass filters will quantitatively remove cellulosic debris from settled pulp-methylcellulose supernatant liquors without ultrafiltration of the additive by first "plugging" the filter with 20-25 ml. of liquor. Fine filters, on the other hand, appear to remove additive from solution as well as pulp fines. An objection to both types of filters is the excessive filtration times required.

Filtration with Filter Aids. In an attempt to speed up the filtration technique, filter aids, such as analytical grade Celite (Johns-Manville diatomaceous earth) and acid-washed asbestos were considered. Exploratory experiments indicated that both Celite and asbestos sorbed methylcellulose in appreciable quantities. Table VIII gives the preliminary data obtained with the filter aids in the form of a 2-5 mm. pad made from slurries on Corning coarse tube-type microfilters. Standard methylcellulose solutions of 0.005 gram/100 ml. were filtered through these pads, as well as equal volume mixtures of standard solution and supernatant cellulose liquor mixtures. Filtration increments of 6 ml. were used, except for the standard solution through asbestos, for which 25-ml. increments were employed. Each increment was analyzed with anthrone. The Celite mixture was centrifuged 30 minutes before filtration.

It is apparent from Table VIII that sorption of methylcellulose is occurring, since the second and third increments (where dilution by the wet filter pads is not possible) still do not equal the standard solution concentration. In the case of Celite, however, the fifth increment yielded the standard solution concentration, and the cellulose fines in the mixture were quantitatively removed. Some ultrafiltration appears to have occurred in the case of the asbestos, although the evidence is not conclusive. Asbestos also quantitatively removes cellulose fines.

Experiments were undertaken to determine the extent of sorption of methylcellulose by Celite and asbestos. The Celite sorbed

TABLE VIII

FILTRATION OF METHYLCELLULOSE WITH CELITE AND ASBESTOS

6-ml. Increment	Asbestos		Celite	
	Standard Solution* Filtrate Concentration, g./100 ml.	Mixture** Filtrate Concentration, g./100 ml.	Standard Solution* Filtrate Concentration, g./100 ml.	Mixture** Filtrate Concentration, g./100 ml.
1	0.00018	0.00023	0.00163	---
2	0.00272	0.00186	---	0.00226
3	0.00443	0.00218	0.00490	0.00240
4	0.00486	0.00230	0.00485	0.00245
5	---	0.00233	0.00500	---

* 0.005 gram/100 ml. methylcellulose

** Equal volumes of 300 Schopper-Riegler bleached sulfite supernatant fines and 0.005 g./100 ml. methylcellulose

very slightly less of the 25-cp. than the 400-cp. Methocel. This sorption amounted to approximately 0.3% on the sorbent weight. The asbestos also retained less of the 25-cp. material and the sorption was about 0.1% on the weight of asbestos.

Since asbestos filter pads exhibited an early tendency to plug, resulting in lengthy filtration times, the use of asbestos was discontinued and Celite tentatively adopted. The data in Table VIII seemed to encourage the use of Celite, since it seemed necessary to discard only 10-15 ml. of filtrate before sampling.

It was soon discovered that the analytical results on bleached sulfite pulp systems seemed to check those obtained by the viscometric method only for dilute concentrations of methylcellulose above 0.003 gram/100 ml. This was readily traced to a lack of saturation of the pulp pad with the dilute methylcellulose in the 10-15 ml. of discarded filtrate, inasmuch as the pulp pad contained 65-80 mg. of Celite. Accordingly, the practice was adopted of making the Celite slurries for filter pads in 0.010 gram/100 ml. methylcellulose instead of distilled water. This treatment assured saturation of the Celite and eliminated the trouble mentioned.

The results of tests on the refined Celite filtration technique are reported in Table IX. The data of the table indicate that standard methylcellulose solutions can be recovered practically quantitatively in filtering through saturated Celite filters and that discarding 10 ml. of filtrate is sufficient to wash the filter pad thoroughly. The filtrate concentration data for supernatant fines alone, using (in all but one case) unsaturated Celite filter pads, show a removal of fines comparable with that obtained by centrifugation of extracted pulps. However, the methylcellulose solutions in the mixtures were almost quantitatively recovered.

There is some indication that the sorbed methylcellulose in the Celite filter pad contributes to its filtration efficiency with respect to cellulose fines, since a greater concentration of cellulose debris passed the unsaturated filters than the saturated ones, even after allowing for the dilution of fines in the mixture.

TABLE IX

FILTRATION WITH SATURATED CELITE

Increment	Standard Solutions Standard Soln. 0.001 g./100 ml. Filtrate Concentration, g./100 ml.	Standard Soln. 0.005 g./100 ml. Filtrate Concentration, g./100 ml.	Pulp	Supernatant Fines Filtrate Concentration, g./100 ml.	Mixtures Equal Volume 0.002 g./100 ml. and Supernatant Fines Filtrate Concentration, g./100 ml.	Equal Volume 0.010 g./100 ml. and Supernatant Fines Filtrate Concentration, g./100 ml.
1	0.00112	0.00492	Cotton linters, 335 S.-R.	0.00013		
2	0.00102	0.00492	Bl. sulfite, 770 S.-R.	0.00019*	0.00100	0.00505
3	0.00095	0.00492				
4	0.00090	0.00492	Bl. sulfite, 570 S.-R.	0.00035*	0.00091	0.00513
5	0.00110			0.00028*		
6	0.00088			0.00009*		
7	0.00097					
8	0.00100					

*Unsaturated Celite filter pads.

Note: For saturated filters, 10-12 ml. of filtrate were discarded before sampling. All samples were centrifuged 15 minutes before filtration except in the case of the cotton linters.

Celite filtration is convenient and rapid and, from all available evidence, appears to meet the primary requirements of separating cellulosic debris without removing methylcellulose from solutions. Therefore, this technique was adopted for use with anthrone in sorption analysis. However, data obtained with techniques in use before adoption of Celite filtration will also be reported.

Viscometry

In a solution of a given high polymer in a given good solvent, the viscosity exhibited is a function of the molecular weight distribution of the polymer and its concentration. The above statement is true provided the range of concentration is low enough that viscometric anomalies resulting from failure to obey Poiseuille's law do not occur. For a given molecular weight distribution, viscosity is a function of concentration. Viscosity, therefore, is a possible means of measuring the concentration of polysaccharide additives after sorption on cellulose. The requirements for such a method are that materials leached from the cellulose contribute nothing to the viscosity (or can be corrected for) and that sorption does not alter the molecular weight distribution of the sorbate. Another way of stating this latter requirement is to say that the molecular weight distribution in the solid phase must be the same as that of the liquid phase. These requirements appear to be largely met in working with papermaking pulps, although the evidence against a selective sorption of a given molecular weight is by no means conclusive.

Of the many empirical equations which have been proposed for quantitatively relating viscosity and concentration (60), the earliest and simplest is that of Arrhenius (61) log η_r = kc, where η_r = relative viscosity, c = concentration of solute in appropriate units, and k = a constant. In a capillary viscometer, such as that used in the present study, the relative viscosity is η_r = $td/t_o d_o$, where t and t_o are, respectively, solution and solvent efflux times, and d and d_o are densities. For the usual case with dilute solutions, in which $d \cong d_o$, the relative viscosity is simply the ratio of solution to solvent efflux times.

In studying the viscometric analytical method, it was discovered that the water extract of cotton linter pulps had practically no viscosity. However, it was soon learned that sulfite and kraft pulps had an appreciable "residual" viscosity which remained after extraction with distilled water at room temperature. This residual viscosity was apparently not the result of inorganic impurities, since the pH of the extracts was 6.5-7.0. The residual viscosity could be greatly reduced by batch extracting pulp samples for 2 one-hour periods at 60-80° C. and practically eliminated with 3 one-hour extractions in boiling water. Table X contains the viscosity data on the various pulps studied. The "residual" viscosity was determined by rotating pulps at 0.5% consistency in distilled water for 3 to 5 days at room temperature and analyzing the settled liquor or its concentrate according to the viscometric analytical scheme. In addition to the effect of extraction in boiling water, the information in Table X indicates that

TABLE X

RESIDUAL VISCOSITY OF PULPS

	Before Extraction		After Extraction	
	Relative Viscosity Supernatant Liquor	Relative Viscosity Centrifugate	Relative Viscosity Supernatant Liquor	Relative Viscosity Centrifugate
Cotton Linters				
795 S.-R.	1.008	1.006	--	--
470 S.-R.	1.002	--	--	--
335 S.-R.	1.002	1.001	--	--
Western Hemlock Bleached Sulfite				
Unbeaten	1.042	--	--	--
770 S.-R.	1.029	--	--	--
570 S.-R.	1.031	--	1.002	1.001
300 S.-R.	1.044	--	--	--
Jack Pine Bleached Kraft				
Unbeaten	--	1.018	--	--
775 S.-R.	1.027	1.027	--	--
	--	1.036	--	--
	--	1.033	--	--
580 S.-R.	--	1.024	--	--
325 S.-R.	--	1.032	--	--
Jack Pine Bleached Kraft*				
Unbeaten	1.012	--	--	--
580 S.-R.	1.015	1.015	1.003	1.003
325 S.-R.	1.005	--	--	--
Western Hemlock Unbleached Sulfite**				
Unbeaten	1.001	--	--	--
630 S.-R.	1.006	1.003	1.002	1.000
Jack Pine Unbleached Kraft**				
Unbeaten	1.005	--	--	--
610 S.-R.	1.004	1.001	1.001	1.001

*Re-extracted with cold water.
**Pulp extracted for two 1-hour periods at 60-80° C. instead of with cold water only.

centrifuging has only a minor effect on the residual viscosity and for pulps extracted with boiling water it can be practically ignored.

The pulp residual viscosity is apparently due to water-soluble polysaccharides which leach out of the pulp, but was too large to be explained by the carbohydrate concentration as determined with anthrone (Table VII). It was therefore attributed to soluble pentosans of considerable chain length which would affect the polyhexose anthrone color very little (Table VI) and would not be accounted for in the analysis. This view is supported by the substantial amount of hexose carbohydrate found in the extracted bleached kraft and unbleached sulfite centrifugates, although the residual viscosity was practically zero. The analytical result was probably the result of suspended cellulose, the pentosans having been removed in the extraction.

Although boiling water-extracted pulps would be preferable in applying the viscometric analytical technique, unextracted pulps were used in order to obtain data comparable with those obtained with the anthrone analyses. This necessitates a correction for the residual viscosity when sorption samples are analyzed. A modified form of the Arrhenius equation is applicable to such computations. It may be shown that the relative viscosity of two solutes dissolved in a given volume of liquid may be obtained from the relationship:

$$\log \eta_{rm} = \log \eta_{r1} + \log \eta_{r2}$$

where η_{rm} = relative viscosity of the mixture

η_{r1} = relative viscosity component 1

η_{r2} = relative viscosity component 2

or more specifically

$$\log\ \eta_{rmc} = \log\ \eta_{rm} - \log\ \eta_{rp}$$

where η_{rmc} = relative viscosity of the methylcellulose

η_{rm} = viscosity of the mixture

η_{rp} = residual relative viscosity of the pulp

Bacterial Degradation

Although cellulose ethers are resistant to bacterial degradation, spoilage may result if sufficient protein is also present to sustain certain specific microorganisms (3). The results of bacterial degradation, if limited to chain scission (hydrolysis), would not affect the analyses with anthrone but would, of course, result in an erroneous viscometric analysis. Complete fermentation of the cellulose ether would invalidate both analytical methods.

Methylcellulose solutions up to 0.1% concentration were stored for many months without any measurable reduction in viscosity. As a further check on possible bacterial action on the cellulose ethers used, viscosities were run on mixtures of methylcellulose solutions and on the filtrate from a suspension of 325-cc. S.-R. bleached kraft pulp which had soured slightly (as determined olfactorily). Over a period of 96 hours, the viscosity of two such mixtures increased slightly, apparently because of plugging of the viscometer capillary by agglomerated bacteria. Small particles could be seen in suspension after this time. After filtration, part of the liquor from one of these experiments was used to inoculate other samples of methylcellulose and the viscosities were determined. In two experiments, the viscosities were constant over

a period of 15 days. It may be concluded from these experiments that bacterial degradation of cellulose ethers did not occur under the conditions used in this investigation. In only one instance did a pulp-methylcellulose sample have a sour odor and in this case the analytical results, using both the anthrone and viscometric techniques, agreed well, indicating no appreciable degradation of the additive.

Sampling Procedures

All sorption runs were made in 8-ounce, narrow-mouth, screw-cap bottles, 200-ml. Pyrex centrifuge jars, or small stock bottles of 400 to 500 ml. capacity. Two hundred ml. of a given concentration of methylcellulose were pipetted into a bottle or jar and brought to bath temperature. Pulp (usually one gram--ovendry basis) at 16 to 30% consistency was weighed to the nearest milligram and introduced into the bottle or jar and then dispersed by rapid mechanical stirring for several minutes. The bottle (or jar) was capped (or stoppered) tightly and rotated end-over-end at constant temperature for a minimum of 9 days. The bath at 25° C. was controlled within $\pm$ 0.2° C., the bath at 3.3° C. within $\pm$ 0.3° C., and the bath at 38.0° C. within $\pm$ 0.5° C. At the end of the rotation period, the samples were allowed to settle at least overnight before sampling the supernatant liquor.

Since a variety of sampling methods were used during the present study, these procedures will be given in detail and designated by a code number. References to procedures later in the text will cite these numbers. Methods making use of anthrone will have the code letter A

and those employing viscosity the letter V. The procedures are tabulated in Table XI. The order of the three operations--centrifugation, filtration, and dilution--can be readily ascertained, since the initial operation involved either the unsettled pulp or the supernatant liquor from settled pulp. For example, in method A4, the supernatant liquor was first centrifuged, then filtered, and then diluted, whereas in method A1 the unsettled pulp was first filtered, then centrifuged, and then diluted.

Celite filters were made by briefly stirring 0.5 gram analytical grade Celite in 50 ml. of 0.01 gram/100 ml. methylcellulose solution. From this slurry, 3-mm. pads of Celite were formed on coarse microfilters and sucked dry. The filtrate from these filters was frequently slightly turbid as the result of dislodged Celite particles. This turbidity was readily removed by centrifuging 2 minutes in a small clinical centrifuge before sampling for anthrone analysis.

The centrifuge had a centripetal field of approximately 1.5×106 cm./sec.^{2}. Samples were centrifuged with 0.1 gram glass wool to prevent disturbance of particles centrifuged out.

TABLE XI

SAMPLING PROCEDURES

Anthrone

Method	Centrifugation			Sample	Filter	Filtration		Dilution of
	Sample	Volume, ml.	Time, min.			Volume, ml.	Initial Volume Discarded, ml.	
A1	Filtrate	25	15	Unsettled pulp	Coarse micro-filter as filter stick	25	None	Centrifugate
A2	Filtrate	25	15	Unsettled pulp	Coarse micro-filter as filter stick	25	10	Centrifugate
A3	None	--	--	Supernatant liquor	Fine sealing tube as filter stick	5	10	Filtrate
A4	Super-natant liquor	25	15	Centri-fugate	Fine sealing tube as filter stick	5	5	Filtrate
A5	Super-natant liquor	25	15	Diluted sample	Celite coarse microfilter	6-9	10-12	Centrifugate

Viscosity

Method	Centrifugation			Sample
	Sample	Volume, ml.	Time, min.	
V1	None	--	--	Supernatant liquor
V2	Super-natant liquor	25	15	Centrifugate

Analytical Procedure

Anthrone. The analytical procedure using anthrone is as follows:

1. The reagent consists of 2 grams of anthrone dissolved in 1830 grams of concentrated sulfuric acid. The acid is shaken vigorously to insure good dissolution of the anthrone. The reagent is stored at room temperature and is aged one day before use.

2. Five ml. of the solution to be tested is diluted volumetrically so that the diluted concentration of methylcellulose lies between 0.001 and 0.005 gram/100 ml. In sampling method A5, this dilution was done prior to filtration.

3. Five ml. of the diluted solution is placed in a 25 x 25-mm. test tube and 10 ml. of anthrone reagent is added cautiously to form a double layer. The contents of the test tube are poured rapidly into a clean test tube and then returned to the original tube.

4. The test tube is stoppered and the mixture allowed to air cool. The transmittance of the solution is read in a 1-cm. absorption cell using a model 14 Coleman universal spectrophotometer at 625 mm wavelength, using reagent and water as a reference liquid. Air entrapped in mixing occasionally deposits on the face of absorption cells. This can be removed by evacuation in a desiccater for several minutes.

5. For calibration, two samples of 0.005 gram/100 ml. methylcellulose were run and a straight line drawn through the sample average

on a log transmittance vs. concentration plot. Calibration is pre-
ferably done at the time samples are run or at least within one day
of the running of the samples. The concentration of samples is
obtained from the calibration curve. The concentration of supernatant
liquor is calculated by multiplying the sample concentration by the
appropriate dilution factor.

6. Sorption of additive is computed by subtracting the
equilibrium concentration times the liquid volume of the system from
the initial methylcellulose.

Viscosity. The viscometric analytical technique is given in
detail below.

1. Ten ml. of the sample to be tested are introduced (at
bath temperature) into a Cannon-Fenske Ostwald-type Series 50 viscometer
(60) through a Corning coarse microfilter. The liquid held in the
microfilter stem can be forced out by gentle air pressure. The vis-
cometer is held in a bath at 25° C. (maintained constant within $\pm$ 0.01° C.).
After allowing 5 minutes for temperature equilibration, the solution
efflux time is measured in duplicate with a stopwatch to the nearest
0.1 second. Kinetic energy corrections are not required for water
solutions in Series 50 viscometers.

2. The relative viscosity of the solution is computed from
the efflux times of solution and solvent, respectively. The relative
viscosity of the methylcellulose in the supernatant liquor is obtained by
subtracting the log of the pulp residual viscosity from the log of the

liquor relative viscosity to obtain the log of the methylcellulose relative viscosity. The concentration of methylcellulose is then computed using the Arrhenius viscosity equation.

3. Sorption is calculated by subtracting the equilibrium concentration times the liquid volume of the system from the initial methylcellulose.

EXPERIMENTAL DATA

EFFECT OF TIME ON SORPTION

The time required to attain sorption equilibrium is important. Unless equilibrium is attained, analytical results will be dependent on this variable. To determine the time necessary for sorption to be complete, experiments were run at 25° C., using approximately 1 gram of pulp in 200 ml. of 400-cp. grade methylcellulose. The results for cotton linters and bleached sulfite pulp are given in Tables XII and XIII.

Twenty-five ml. samples were removed at intervals and analyzed with anthrone, using the sampling methods indicated. In calculating sorption, allowance was made for methylcellulose previously removed in analytical samples. For example, in Run 1 for 655-cc. S.-R. cotton linters, the total sorption at one hour was the initial methylcellulose less the methylcellulose removed in the samples at 0.167 and 0.5 hour, and less the methylcellulose present in the liquid volume of the system at one hour. For the 335-cc. S.-R. cotton linters, the 36- and 240-hour analyses were for separate pulp samples. The analyses for 12 and 72 hours were obtained from the same pulp sample.

Taking successive analytical samples in the manner indicated results in an increase in the consistency of the pulp in the sorption system. The consistency varies from about 0.5% at the beginning of a run to 1.0-1.3%, depending on the number of samples taken. The tacit assumption is made that consistency has no effect on the amount sorbed.

TABLE XII

RATE OF SORPTION OF METHYLCELLULOSE
BY COTTON LINTERS

Time, hr.	Liquid Volume System, ml.	Concentration, g./100 ml.	Cumulative Sorption g./g. Pulp x 10^2	Wet Pulp, g.	OD Pulp, g.	Sampling Method
			Run 1 - 655 S.-R.			
0.167	202	0.00410	0.20	3.00	0.845	A1
0.5	177	0.00385	0.26			
1.0	152	0.00362	0.30			
26.5	127	0.00302	0.39			
49.5	102	0.00268	0.43			
			Run 2 - 655 S.-R.			
0.167	202	0.00407	0.20	3.00	0.874	A1
0.5	177	0.00403	0.21			
2.0	152	0.00345	0.32			
8.0	127	0.00273	0.42			
20.0	102	0.00260	0.44			
50.0	77	0.00230	0.46			
			Run 3 - 655 S.-R.			
1.0	202	0.00315	0.28	3.50	1.282	A2
4.0	177	0.00275	0.34			
10.0	152	0.00220	0.40			
24.0	127	0.00180	0.44			
36.5	102	0.00156	0.46			
53.0	77	0.00146	0.47			
			Unbeaten			
1.0	202	0.00465	0.05	3.50	1.191	A2
4.0	177	0.00424	0.11			
10.0	152	0.00443	0.09			
24.0	127	0.00432	0.09			
36.5	102	0.00413	0.11			
53.0	77	0.00373	0.14			
			335 S.-R.			
12.0	202	0.00314	0.52	3.11	0.703	A3
36.0	202	0.00268	0.66	3.07	0.694	
72.0	177	0.00228	0.71	3.11	0.703	
240.0	202	0.00090	0.82	4.42	1.00	

Note: 400-cp. methylcellulose
Initial concentration 0.005 gram/100 ml. in 200 ml. volume;
25° C.

TABLE XIII

RATE OF SORPTION OF METHYLCELLULOSE
BY 700 S.-R. BLEACHED SULFITE PULP

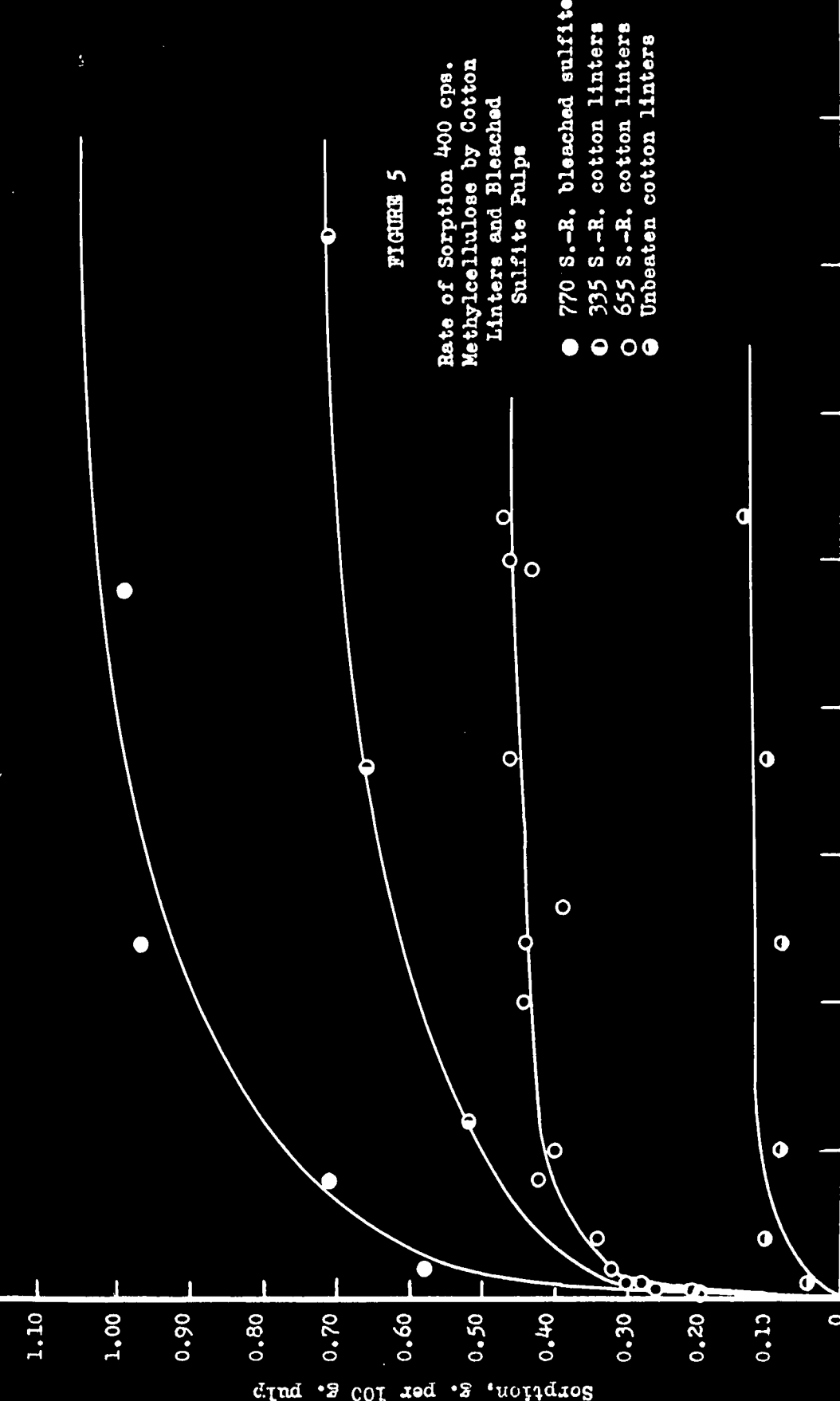| Time, hr.	Liquid Volume System, ml.	Concentration, g./100 ml.	Cumulative Sorption, g./g. Pulp x 10^2	Wet Pulp, g.	OD Pulp, g.	Sampling Method
		Initial Concentration, 0.0150 g./100 ml.				
2.0	204	0.0119	0.58	4.52	1.00	A5
8.0	179	0.0112	0.71			
24.0	154	0.0098	0.97			
48.0	129	0.0097	0.99			
		Initial Concentration, 0.0500 g./100 ml.				
2.0	204	0.0432	1.21	4.52	1.00	A5
8.0	179	0.0438	1.21			
24.0	154	0.0431	1.21			
48.0	129	0.0420	1.46			

Note: 770-cc. S.-R. bleached sulfite
400-cp. methylcellulose
25° C.

For a classical sorption system, such as that of acetic acid in water on charcoal, this is true. In other words, the amount sorbed depends on the total charcoal present, not on the charcoal per unit volume. However, there is some indication that increasing pulp consistency reduces retention of methylcellulose. This will be discussed in more detail later. Even if sorption decreases with increasing consistency, the conclusions to be drawn regarding time to constant sorption are not invalidated, although some objection might legitimately

be raised to rate equations obtained in the manner mentioned above.

Some of the data of Tables XII and XIII are plotted in Figure 5. The instantaneous rate of sorption is given by the slopes of the curves in Figure 5, and it can readily be seen that the rate at a given time increases with the degree of beating; this might be expected since pulp surface, from all available evidence, also increases with beating. The sorption is characterized by a rapid initial rate followed by a gradually decreasing rate, and appears to be largely complete in about 70 hours for the 770-cc. S.-R. bleached sulfite and well-beaten cotton linters, in 50 hours for the 655-cc. S.-R. cotton linters, and in about 10 hours for the unbeaten linters.

Sorption rate is a function of initial concentration, as may be concluded from a study of Table XIII. For the bleached sulfite pulp with an initial concentration of 0.0150 gram/100 ml., 50% of the total sorption at 48 hours was complete in two hours but, for an initial concentration of 0.0500 gram/100 ml., 83% of the 48-hour sorption was complete in this same time. (Apparently, the necessity of diluting samples 1:10 for analysis in the 0.0500 gram/100 ml. run introduced analytical errors which masked the small changes occurring between 2 and 24 hours.) A comparison of the curves of Figure 5, with respect to the effect of the initial concentration on the rate of sorption, cannot be made since different pulps are involved and (as will be shown later) bleached sulfite sorbs more than cotton linters at similar degrees of beating.

FIGURE 5

Rate of Sorption 400 cps.
Methylcellulose by Cotton
Linters and Bleached
Sulfite Pulps

● 770 S.-R. bleached sulfite
◐ 335 S.-R. cotton linters
○ 655 S.-R. cotton linters
◑ Unbeaten cotton linters

Although the curves in Figure 5 might be interpreted as indicating a nearly constant sorption after 70 hours, it is desirable to present other evidence in this regard. In Table XIV are given analyses of cotton linter pulps at various times up to 288 hours. These data show that, for initial concentrations of 0.0150 gram/100 ml. and above, sorption is complete in about 100 hours. For lower concentrations, at least 180 hours are required. Accordingly, a minimum time of 220 hours or 9 days was adopted for all further runs to insure sorption equilibrium.

The data in Tables XII and XIII, when plotted as log time vs. log sorption (and also log concentration), yield straight lines. This relation is of the form $X/M = at^n$, where X/M is sorption in grams per 100 grams of pulp, t is the time in hours, and a and n are constants which are given in Table XV. From the data presented, there appears to be a relationship between the constant a and the degree of beating, as well as the absolute concentration in the system, whereas the exponent n is affected relatively little. The a constant increases with the degree of beating and with increasing concentration. Beating seems to have only a small effect after it is initiated. Since only a limited amount of data was available, however, no detailed correlation was attempted. In addition, it was found that the rate of sorption was not proportional to the instantaneous concentration or to the difference between equilibrium and instantaneous concentrations. The data also did not fit the equation of Ladergren as given by Swan and Urquhart (61), which states that the sorption rate is proportional to the difference between saturation and instantaneous sorptions. Gustaver's equation (62),

TABLE XIV

TIME REQUIRED BY COTTON LINTERS
FOR CONSTANT SORPTION

Initial Concentration, g./100 ml.	Freeness, cc. S.-R.	Time, hr.	Concentration At Given Time, g./100 ml.
0.0050	795	69	0.00225
		180	0.00182
		276	0.00170
0.0150	795	92	0.00935
		180	0.00900
		276	0.00915
0.0250	795	93	0.0177
		180	0.0174
		288	0.0176
0.0050	635	121	0.00178
		180	0.00163
		276	0.00138
0.0150	635	122	0.00855
		192	0.00850
		276	0.00840
0.0250	635	132	0.0172
		192	0.0171
		288	0.0169

Note: Sampling Method A3
400-cp. methylcellulose at 25° C.

TABLE XV

RATE EQUATION* CONSTANTS FOR
COTTON LINTERS AND BLEACHED SULFITE PULPS

	Constant	
Pulp	a	n
Cotton linters		
unbeaten	0.06	0.17
655-cc. S.-R.	0.29	0.12
335-cc. S.-R.	0.35	0.15
770-cc. S.-R.		
Bleached sulfite		
0.0150 g./100 ml.		
initial concentration	0.49	0.12
0.0500 g./100 ml.		
initial concentration	0.95	0.10

*For the equation $X/M = at^n$

which relates rate of sorption to the instantaneous sorbate present and the free surface available, was not applicable.

It must be emphasized that the equations deduced from the rate data obtained in this study are actually parabolic in form and, consequently, would never show a constant sorption, no matter how large a value of time was substituted. Therefore, these rate equations apply only to the early stages of sorption and would probably give erroneous results for times greater than about 50-70 hours for beaten pulps and about 15 hours for unbeaten pulps. An analogous situation arises when applying the Freundlich adsorption isotherm, which is also parabolic in

form, to sorption systems which come to a constant or saturation sorption. The Freundlich equation may not be used to predict sorption for concentrations which approach the saturation concentration.

The rate studies on the sorption of 400-cp. methylcellulose have shown that a considerable time is required for sorption equilibrium to occur. At 0.5 to 1.3% consistency, sorption is complete in 100 hours or less for concentrations of methylcellulose of 3% or more on the fiber. For lower concentrations, at least 180 hours are required. Although complete equilibrium requires a protracted time, sorption was found to be 40% complete for unbeaten and 70% complete for beaten cotton linters (at a concentration of 1% of additive on the pulps), in a time of two hours. At this same time, slightly beaten bleached sulfite pulp had sorbed 60% of the saturation value for 3% additive on the fiber and 80% for 10% additive on the fiber. The rate equations obtained were of the form $X/M = at^n$, where X/M is the sorption, t is the time, and a and n are constants. It was pointed out that this type of equation is parabolic in form and, therefore, is applicable only to the early stages of sorption. From these equations, it was concluded that the rate of sorption increases with increasing concentration of additive and with increased beating, although concentration had the most pronounced effect.

EFFECT OF BEATING ON SORPTION

The general procedure in investigating the effect of variables on the extent of sorption was to run at least two and, in most cases,

three or more samples at varying initial concentrations in order to obtain a curve of equilibrium concentration versus sorption. A comparison was then made between curves rather than between points.

Bleached Sulfite Pulp

In Table XVI are tabulated the results obtained with bleached sulfite pulps of different degrees of beating, using 400-cp. methylcellulose at a temperature of 25° C. The initial concentration and the equilibrium concentrations for the anthrone and viscosity methods are given. The sampling procedures refer to the outline given in Table XI. The viscometric data are plotted in Figure 6 and the anthrone data in Figure 7 with equilibrium concentrations as abscissas and sorptions as ordinates.

The curves in Figure 6 and Figure 7 were obtained by fitting the data of Table XVI to a Freundlich adsorption isotherm (46, 48) which gives an equation of the type $X = ax^n$ or more specifically $X/M = ac^n$, where X/M is the sorption in grams per 100 grams pulp, c is the equilibrium concentration in grams/100 ml. and a and n are constants. The best straight lines were drawn through these data on a log-log plot of equilibrium concentration versus sorption. These lines are the best fit of a straight line to the experimental data and were drawn in this fashion to indicate the applicability of an adsorption isotherm of the Freundlich type.

A study of Figures 6 and 7 reveals that the data fit an equation of this type reasonably well, although there is considerable variability in the analytical results. A curve of somewhat sigmoid shape, similar to

TABLE XVI

EFFECT OF EQUILIBRIUM CONCENTRATION ON SORPTION BY BLEACHED SULFITE PULP

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
Unbeaten					
0.0150	0.0110	0.77	0.0068	1.62	A5, V2
0.0300	0.0256	0.80	0.0209	1.76	
0.0500	0.0428	1.30	--	--	
0.1000	0.0930	1.13	--	--	
0.0050	0.0034	0.31	--	--	A3, V1
0.0100	0.0068	0.63	--	--	
0.0200	0.0158	0.81	0.0090	2.17	
0.0300	0.0251	0.93	0.0182	2.30	
0.0500	0.0465	0.56	0.0373	2.42	
770 S.-R.					
0.0050	0.0012	0.76	--	--	A3, V1
0.0100	0.0040	1.19	--	--	
0.0200	0.0119	1.58	0.0063	2.72	
0.0300	0.0202	1.88	0.0155	2.84	
0.0500	0.0393	2.00	0.0328	3.32	
0.0150	0.0058	1.72	0.0046	2.06	A5, V2
0.0300	0.0181	2.30	0.0123	3.50	
0.0500	0.0355	2.77	0.0298	4.12	
0.1000	0.0806	3.60	0.0733	5.08	
0.0500	0.0410	1.65	0.0347	2.93	A5, V2
0.0500	0.0406	1.74	0.0339	3.10	
0.1000	0.0900	1.68	0.0758	4.57	
0.1000	0.0884	2.00	0.0775	4.22	

TABLE XVI (continued)

EFFECT OF EQUILIBRIUM CONCENTRATION ON SORPTION BY BLEACHED SULFITE PULP

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
570 S.-R.					
0.0150	0.0049	2.00	0.0028	2.43	A5, V2
0.0300	0.0163	2.68	0.0129	3.37	
0.0500	0.0327	3.32	0.0267	4.55	
0.1000	0.0764	4.40	0.0648	6.77	
0.0150	0.0060	1.78	0.0044	2.10	A5, V2
0.0300	0.0171	2.51	0.0150	2.94	
0.0500	0.0343	3.00	0.0308	3.72	
0.1000	0.0790	3.88	0.0688	5.97	
0.0100	0.0034	1.31	—	—	A4, V1
0.0200	0.0093	2.10	—	—	
0.0300	0.0166	2.61	0.0108	3.80	
0.0500	0.0323	3.51	0.0277	4.35	
0.0500	0.0365	2.51	0.0331	3.25	A5, V2
0.1000	0.0838	2.92	0.0726	5.18	
300 S.-R.					
0.0100	0.0024	1.51	—	—	A4, V1
0.0200	0.0066	2.65	—	—	
0.0300	0.0124	3.46	0.0042	5.14	
0.0500	0.0230	4.27	0.0200	5.90	

TABLE XVI (continued)

EFFECT OF EQUILIBRIUM CONCENTRATION ON SORPTION BY BLEACHED SULFITE PULP

300 S.-R.

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
0.0300	0.0161	2.70	0.0065	4.65	A5, V2
0.0500	0.0323	3.38	0.0223	5.43	
0.1000	0.0794	3.70	0.0627	7.15	
0.0500	0.0290	4.05	0.0277	4.32	A5, V2
0.1000	0.0726	5.12	0.0612	7.47	
0.0500	0.0334	3.15	0.0224	5.41	A5, V2
0.0500	0.0361	2.60	0.0249	4.89	
0.1000	0.0764	4.33	0.0677	6.12	
0.1000	0.0796	3.69	0.0618	7.33	

Note: 400-cp. methylcellulose at 25° C.

FIGURE 6

Effect of Equilibrium Concentration on Sorption
Bleached Sulfite Pulp--Viscometric Analysis
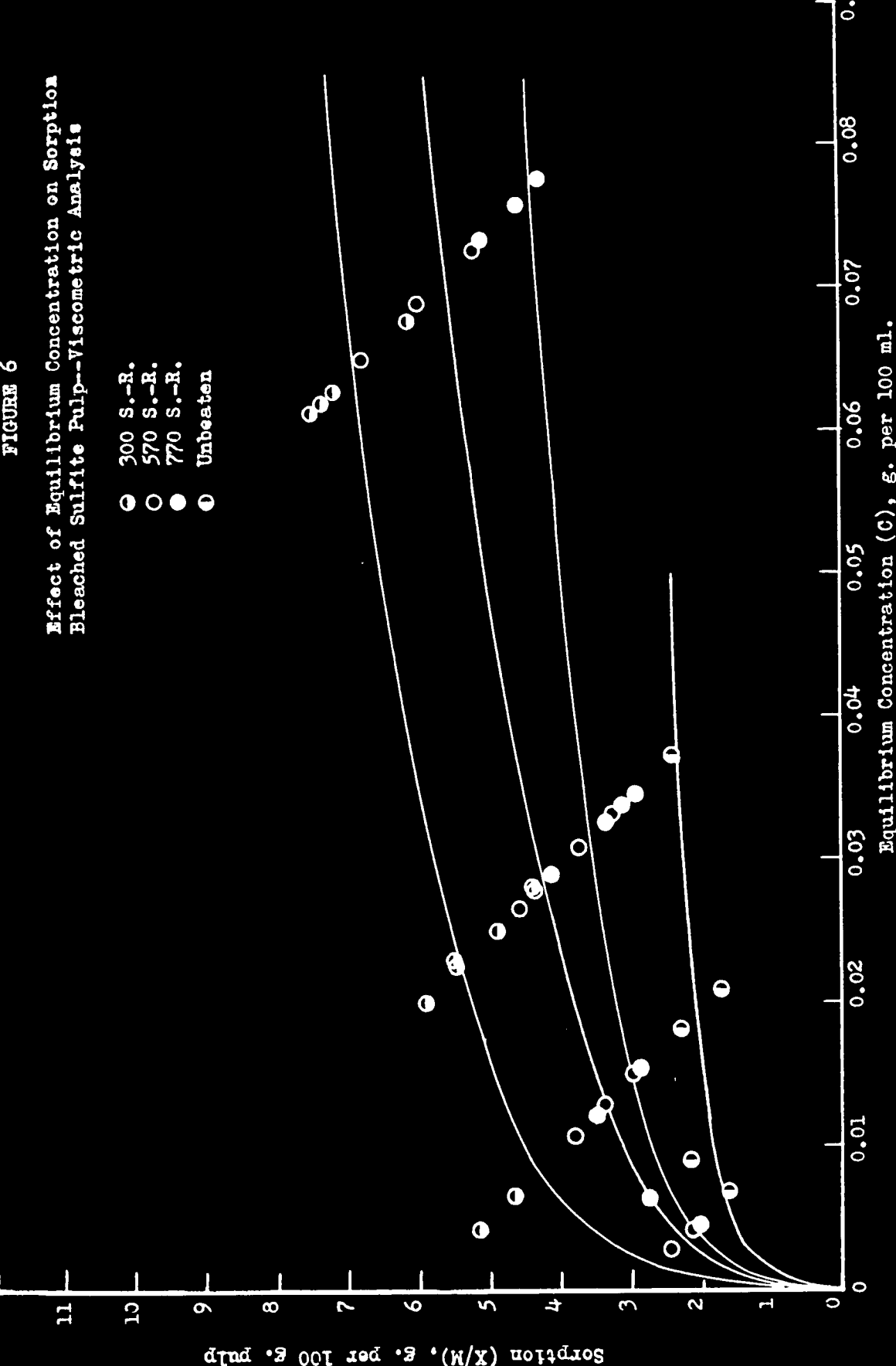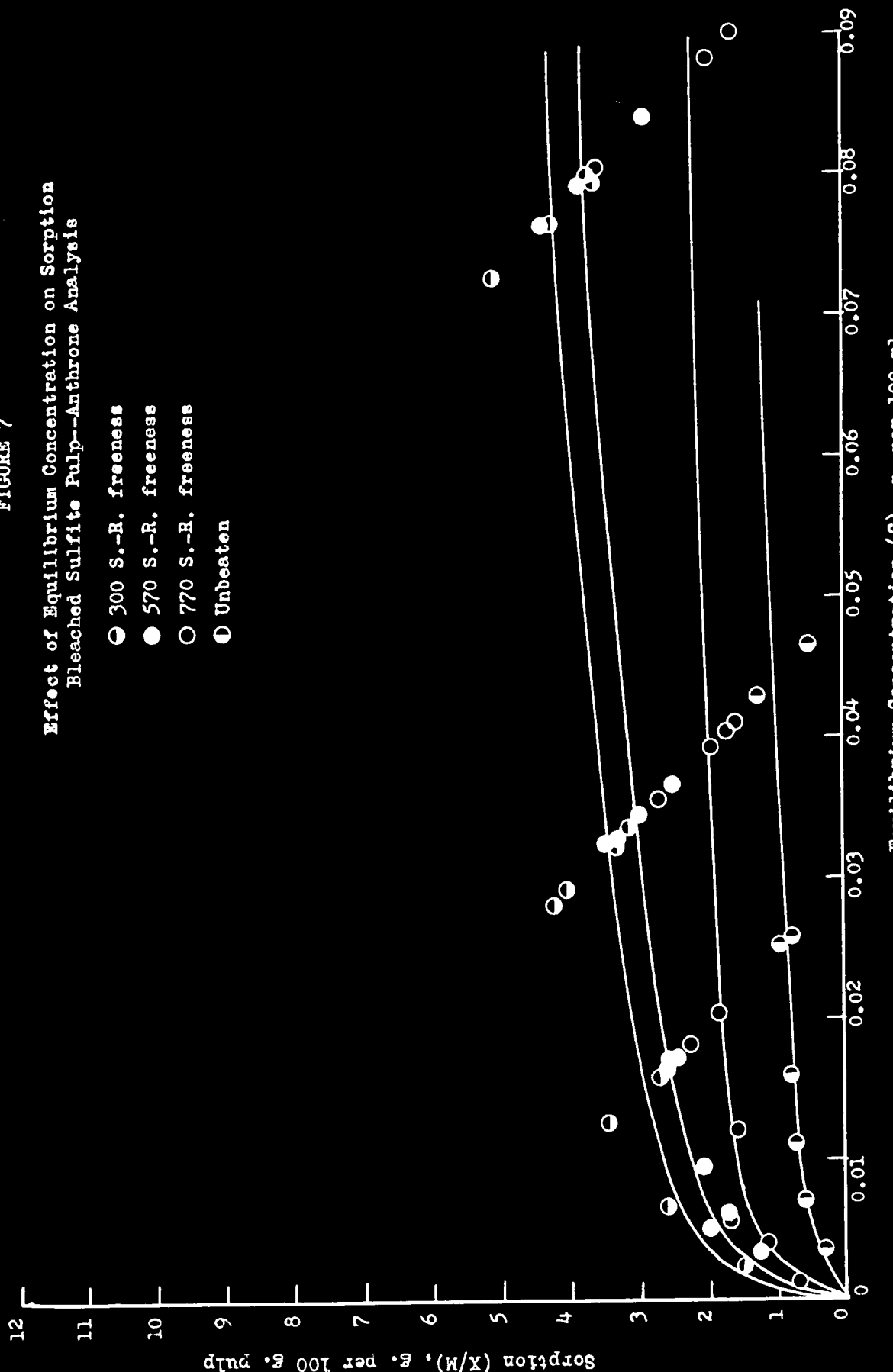
◐ 300 S.-R.
○ 570 S.-R.
● 770 S.-R.
◑ Unbeaten

Equilibrium Concentration (C), g. per 100 ml.

Sorption (X/M), g. per 100 g. pulp

FIGURE 7

Effect of Equilibrium Concentration on Sorption
Bleached Sulfite Pulp—Anthrone Analysis

that obtained in the adsorption of moisture vapor by cellulose, would fit the data better than the parabolic curves shown but, inasmuch as the variability of the results was so great, no attempt was made to apply such a curve.

The data will also fit moderately well an isotherm of the Langmuir type (46, 48) which is an hyperbola: $c/(X/M) = 1/ab + c/b$ where X/M is sorption in grams/100 grams pulp, c is the equilibrium concentration in grams/100 ml., and a and b are constants. This equation has the advantage, in sorption studies, that the curve becomes essentially parallel to the X axis therefore indicating a sorption saturation, whereas the Freundlich parabolic curve does not do so. The Freundlich isotherm is therefore applicable only to data which are not too near the region of saturation. Since the best curve through the present experimental data is of sigmoid shape as previously mentioned, the Freundlich isotherm gives a little better fit than the Langmuir equation. The Brunauer-Emmett-Teller (46) adsorption equation for molecular multilayer adsorption was not applied to the data obtained but it conceivably might fit more precise data quite well, since this equation is applicable to sigmoid type adsorptions.

Table XVI and Figures 6 and 7 show that the analytical results obtained with the anthrone method and with the viscometric method agree very poorly. In general, viscosity gives sorptions which are 1.5 to 2 times those obtained with the anthrone method. In addition to the poor agreement between the two methods, considerable variability is apparent for a given method between runs made under presumably identical conditions

using samples of the same pulp. The variability of the results may conceivably be associated with either the analytical method, the method of treatment, or may be inherent in the system being studied. This variability, which will be discussed in detail later, makes it difficult to draw precise quantitative conclusions from the data, but the qualitative effect of the several variables can be readily ascertained. These qualitative relationships constitute the main purpose of this study and a more quantitative interpretation will have to await refinement of the analytical techniques, methods of treatment, or statistical analysis for a characteristically variable system.

Figures 6 and 7 indicate clearly that sorption is a function of beating and increases with the degree of pulp treatment. In the case of both analytical techniques, the sorption by the well-beaten pulp is about 3 to 4 times that for the unbeaten pulp. Sorption increases rapidly at first with increasing equilibrium concentration and then increases less rapidly as higher concentrations are approached. The highest concentration of additive used (0.1% or 20% on the pulp at 0.5% consistency) was not sufficient to saturate the pulp since the sorption curves are not parallel to the X-axis in this region, although more nearly so with the anthrone than the viscosity methods. However, it is obvious that the pulp is nearly saturated at 20% of additive and little would be gained by increasing the methylcellulose to pulp ratio.

The reader may be interested in the straight lines of negative 45° slope formed by the groups of points in Figures 6 and 7. These straight lines result from the method of computation of the sorption and

intersect the X-axis at the initial methylcellulose concentration
and the Y-axis at the amount of methylcellulose added on the pulp. The
lines have no other significance.

Bleached Kraft Pulp

In Table XVII and Figure 8 are given the results of runs with
bleached kraft pulp at different degrees of beating. The effect of beating
in the case of the bleached kraft is much less pronounced than with the
bleached sulfite pulp, although sorption quite definitely increases with
beating. There is no significant difference between sorption by the
775-cc. and the 580-cc. S.-R. freeness pulps, and the well-beaten pulp
sorbs only about 1.5 times the methylcellulose retained by the unbeaten
stock. These results are necessarily quite tentative, because of the
limited data available. Additional runs would undoubtedly alter averages
but not trends.

Cotton Linter Pulp

In Table XVIII are tabulated results of experiments using
cotton linters beaten to various freenesses. The agreement between
the two analytical methods is much better for the linters than for the
bleached sulfite or bleached kraft pulps. Although the samples for
anthrone analysis were largely obtained by fritted glass filtration, in-
stead of by Celite filtration, the agreement of the methods is undoubtedly
the result of the nature of the beaten cotton linters and will be dis-
cussed in detail later. The viscometric method requires no correction for
residual viscosity of the pulp and, consequently, no variability in results
because of this correction can occur.

TABLE XVII

EFFECT OF EQUILIBRIUM CONCENTRATION ON SORPTION BY BLEACHED KRAFT PULP

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
Unbeaten					
0.0150	0.0097	1.02	0.0103	0.90	A6, V2
0.0300	0.0255	0.80	0.0223	1.45	
0.0500	0.0422	1.40	0.0361	2.63	
0.0150	—	—	0.0069	1.59	V2
0.0500	—	—	0.0335	3.17	
725 S.-R.					
0.0050	0.0015*	0.64	—	—	A6, V2
0.0150	0.0084**	1.29	0.0069	1.59	
0.0300	0.0215	1.62	0.0166	2.61	
0.0500	0.0360	2.65	0.0323	3.41	
580 S.-R.					
0.0150	—	—	0.0075	1.47	A6, V2
0.0300	0.0184	2.23	0.0159	2.74	
0.0500	0.0365	2.52	0.0315	3.55	
0.0150	—	—	0.0057	1.83	V2
0.0500	—	—	0.0317	3.50	
0.1000	—	—	0.0758	4.47	

TABLE XVII (continued)

EFFECT OF EQUILIBRIUM CONCENTRATION ON SORPTION BY BLEACHED KRAFT PULP

325 g.-R.

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
0.0150	0.0046	2.06	0.0046	2.06	A5, V2
0.0300	0.0148	2.97	0.0141	3.10	
0.0500	0.0312	3.60	0.0282	4.22	
0.1000	—	—	0.0550	8.78	V2

Note: 400-cp. methylcellulose at 25° C.
* Fine filter stick from supernatant liquor.
** Direct analysis of centrifugate.

Effect of Equilibrium Concentration on Sorption
Bleached Kraft Pulp--Viscometric Analysis

◐ 325 S.-R. freeness
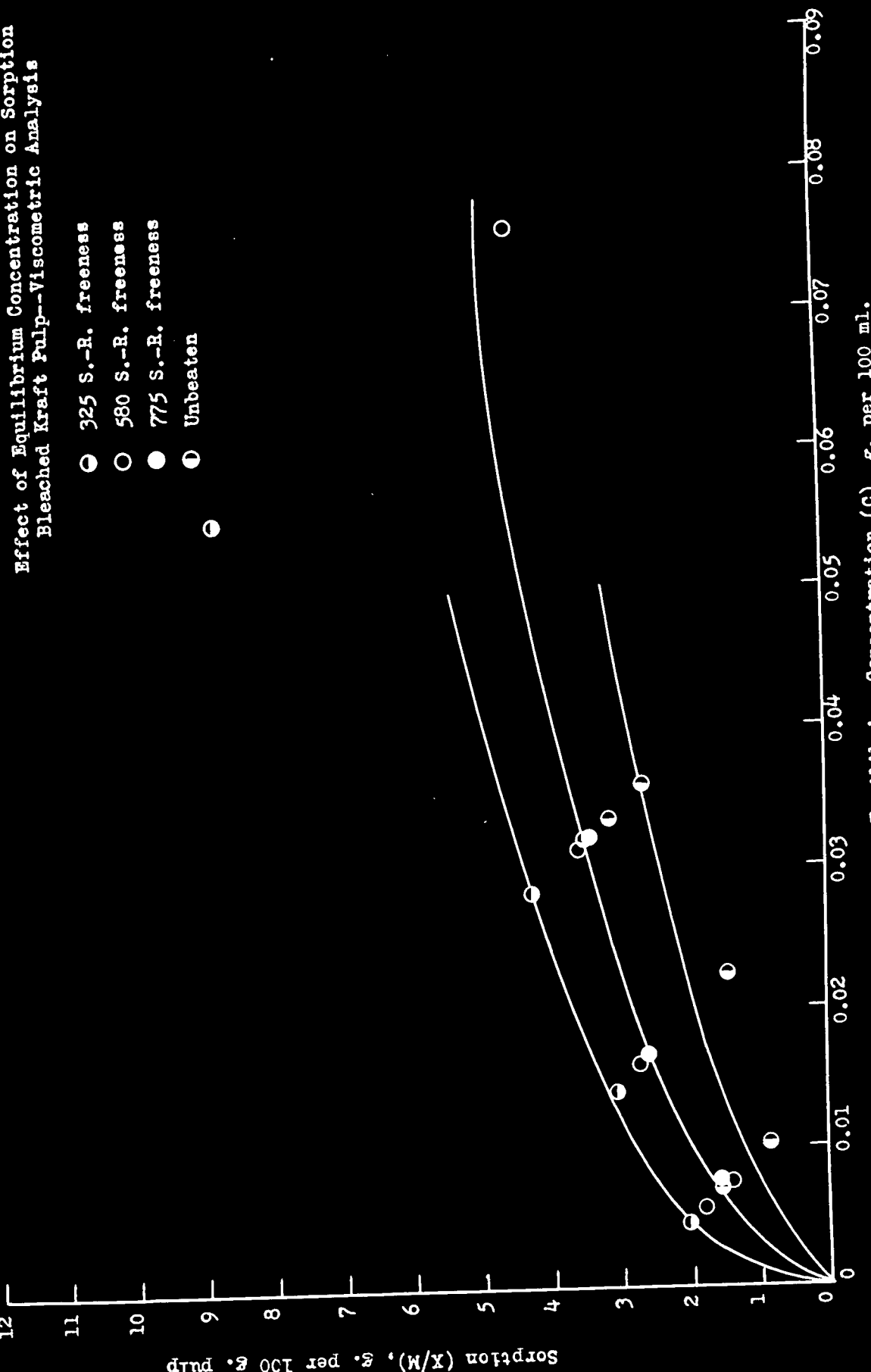○ 580 S.-R. freeness
● 775 S.-R. freeness
◑ Unbeaten

TABLE XVIII

EFFECT OF EQUILIBRIUM CONCENTRATION ON SORPTION BY COTTON LINTERS

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
Unbeaten					
0.0050	0.0036	0.27	—	—	A3, V1
0.0100	0.0081	0.35	0.0093	0.11	
0.0200	0.0178	0.38	0.0186	0.22	
0.0300	0.0280	0.30	0.0289	0.12	
705 S.-R.					
0.0050	0.0017	0.64	—	—	A3, V1
0.0150	0.0092	1.11	—	—	
0.0250	0.0172	1.38	—	—	
635 S.-R.					
0.0050	0.0014	0.71	—	—	A3
0.0150	0.0084	1.28	—	—	
0.0250	0.0169	1.55	—	—	
0.1000	0.0844	2.80	—	—	A5
470 S.-R.					
0.0100	0.0034	1.31	0.0031	1.37	A3, V1
0.0200	0.0112	1.72	0.0121	1.54	
0.0300	0.0199	1.95	0.0176	2.43	
0.1000	0.0730	5.12	—	—	A5

TABLE XVIII (continued)

EFFECT OF EQUILIBRIUM CONCENTRATION ON
SORPTION BY COTTON LINTERS

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
		335 S.-R.			
0.0100	0.0039	1.20	0.0043	1.12	A3, V1
0.0200	0.0118	1.60	0.0131	1.33	
0.0300	0.0200	1.92	0.0219	1.52	
0.1000	0.0852	2.64	—	—	A5

Note: 400-cp. methylcellulose at 25° C.

The viscosity data for cotton linters are meager but they show that sorption increases with beating. Surprisingly enough, the 335-cc. S.-R. freeness pulp sorbed a little less methylcellulose than the 470-cc. S.-R. freeness pulp. Anthrone, however, shows about the same sorption for both of these pulps, except for the last result with the 470-cc. S.-R. pulp, which appears to be too high. The anthrone method also indicates that sorption increases with beating and that well-beaten pulps sorb about 4 to 5 times the methylcellulose sorbed by the unbeaten pulps. The increase in sorption did not occur as regularly with beating as with the bleached sulfite pulp.

Unbleached Kraft and Unbleached Sulfite Pulps

For the unbleached pulps the viscometric analytical method was used exclusively and, since the pulps had practically no residual viscosity, only a small correction was necessary. Unbeaten and one beaten interval (about 600-cc. S.-R. freeness) were run for each pulp; the results are given in Table XIX. Again, it will be noted that sorption increases with beating. For 610-cc. S.-R. unbleached kraft pulp, the increase in sorption was about threefold over that of the unbeaten pulp and approximately the same for the 630-cc. S.-R. unbleached sulfite pulp when compared with the unbeaten sulfite pulp.

Sorption Constants

Table XX gives the Freundlich isotherm constants for the pulps studied in the present investigation. A possible physical interpretation of these constants will be mentioned in the discussion of results.

TABLE XIX

EFFECT OF EQUILIBRIUM CONCENTRATION ON SORPTION BY
UNBLEACHED KRAFT AND UNBLEACHED SULFITE PULP

Initial Concentration, g./100 ml.	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
Unbeaten Kraft			
0.0150	0.0111	0.74	V2
0.0500	0.0445	0.97	
610-cc. S.-R. Kraft			
0.0150	0.0068	1.61	V2
0.0500	0.0382	2.20	
0.1000	0.0834	2.98	
Unbeaten Sulfite			
0.0300	0.0258	0.78	V2
0.0500	0.0426	1.38	
630-cc. S.-R. Sulfite			
0.0300	0.0183	2.25	V2
0.0500	0.0307	3.75	
0.1000	0.0784	4.03	

Note: 400-cp. methylcellulose at 25° C.

TABLE XX

FREUNDLICH SORPTION ISOTHERM CONSTANTS

Viscometric Analysis

400-cp. Methylcellulose

25° C.

Degree of Beating	Constant a	Constant n
Bleached Sulfite Pulp		
Unbeaten	4.5	0.20
770 S.-R.	8.1	0.24
570 S.-R.	12.2	0.30
300 S.-R.	13.3	0.24
Bleached Kraft Pulp		
Unbeaten	19.0	0.59
775 S.-R.	22.1	0.54
580 S.-R.	13.6	0.41
325 S.-R.	18.2	0.39
Unbleached Sulfite Pulp		
Unbeaten	--	--
630 S.-R.	10.8	0.34
Unbleached Kraft Pulp		
Unbeaten	1.8	0.20
610 S.-R.	5.3	0.25
Cotton Linters		
Unbeaten	1.0	0.23
470 S.-R.	5.3	0.25
335 S.-R.	5.3	0.25

COMPARISON OF SORPTION BY PULPS AT SIMILAR DEGREES OF BEATING

The relative sorptivity of papermaking pulps for methylcellulose is of interest, both from a theoretical and from a practical viewpoint. In Figures 9 and 10, the various pulps used in this study are compared at similar degrees of beating. For viscometric analysis at approximately 600-cc. S.-R. freeness, the bleached sulfite pulp sorbed methylcellulose to a greater extent than the kraft or unbleached sulfite pulps. Bleached kraft and unbleached sulfite sorbed about the same amount and are just significantly lower than the bleached sulfite. Unbleached kraft, however, showed a lower sorptivity, which corresponded roughly to unbeaten bleached sulfite.

Anthrone analysis at 600-cc. S.-R. freeness showed a similar relationship between bleached sulfite and bleached kraft, and indicated that cotton linters were significantly lower than the above pulps. The sorption of the linters corresponded to that shown by 770-cc. S.-R. freeness bleached sulfite pulp.

In Figure 10, bleached sulfite pulp is compared with cotton linters and bleached kraft at about 300-cc. S.-R. freeness. These data show that bleached sulfite and bleached kraft have approximately the same relative sorptivities as at 600-cc. S.-R. freeness, and that cotton linters retain much less methylcellulose than the other pulps.

Anthrone analysis at 300-cc. S.-R. freeness showed no difference between bleached sulfite and bleached kraft pulps but, again, cotton linters gave a sorption which was a little greater than that given by 700-cc. S.-R. freeness bleached sulfite pulp.

Sorption of Methylcellulose by Different Pulps
at Similar Degrees of Beating

● Bleached sulfite—570 S.-R. freeness

○ Bleached kraft—580 S.-R. freeness

◑ Unbleached sulfite—630 S.-R. freeness

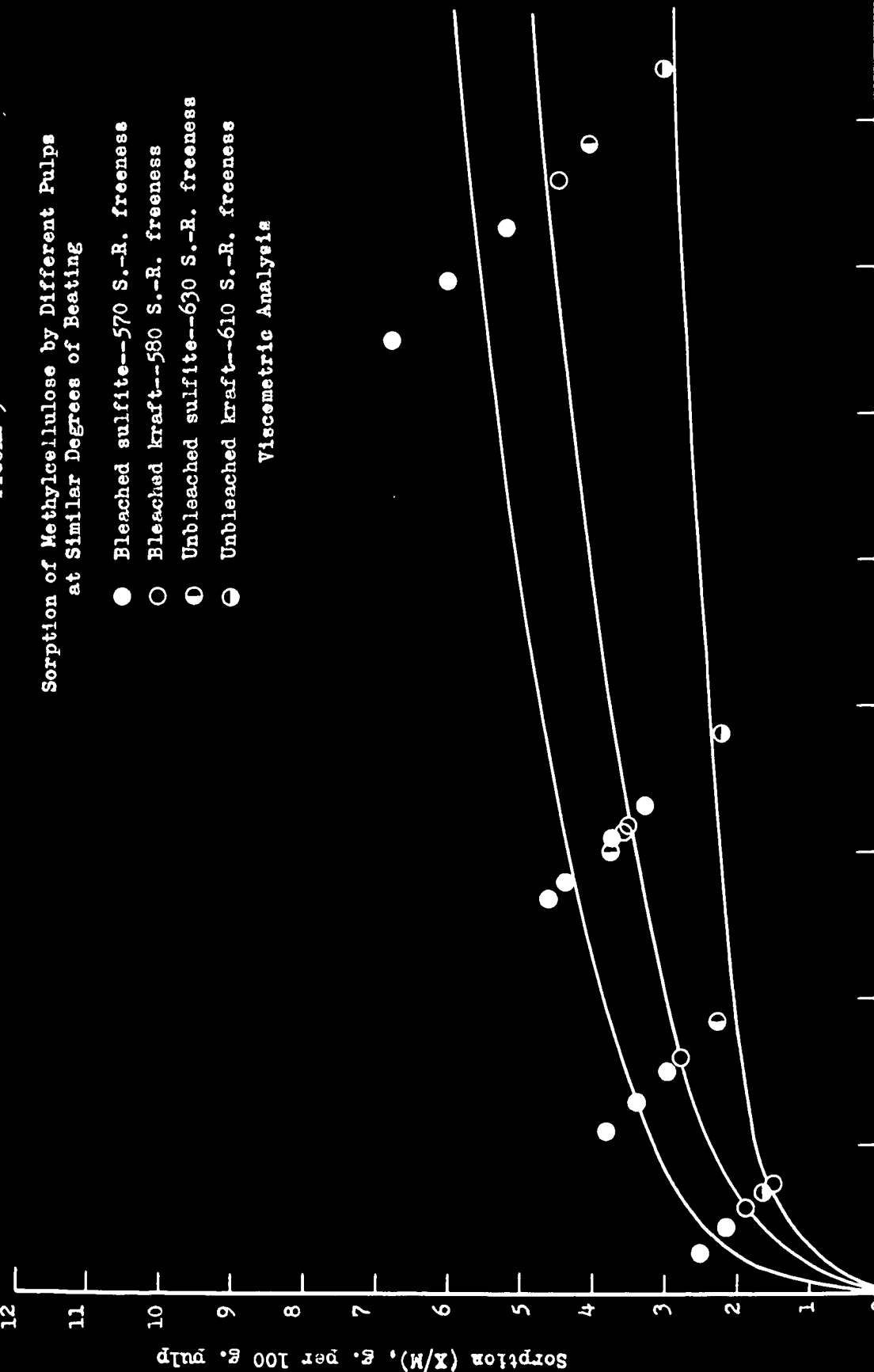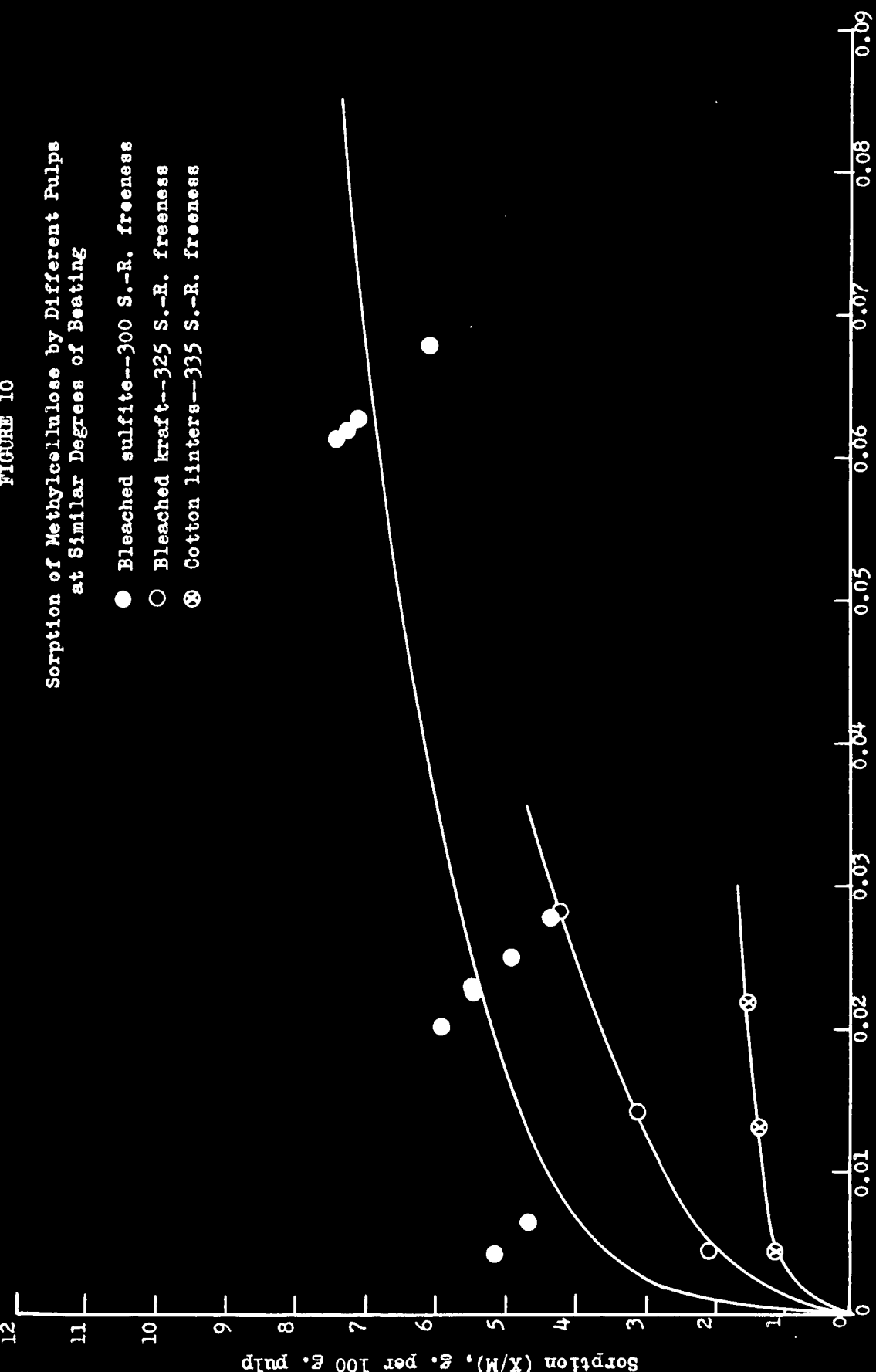◐ Unbleached kraft—610 S.-R. freeness

Viscometric Analysis

FIGURE 10

Sorption of Methylcellulose by Different Pulps
at Similar Degrees of Beating

- Bleached sulfite—300 S.-R. freeness
○ Bleached kraft—325 S.-R. freeness
⊗ Cotton linters—335 S.-R. freeness

Equilibrium Concentration (C), g. per 100 ml.

Sorption (X/M), g. per 100 g. pulp

In summary, the pulps studied may be arranged in the following order of sorptivity at similar degrees of beating. Bleached sulfite has the greatest sorptivity followed closely by bleached kraft and unbleached sulfite, which are approximately equal. From comparisons with bleached sulfite, it was concluded that cotton linters showed greater sorptivity than unbleached kraft, and that these latter two pulps retained much less additive than the other pulps.

EFFECT OF MOLECULAR WEIGHT ON SORPTION

The effect of molecular weight on sorption is a particularly interesting variable, since the efficacy of the viscometric method of analysis depends on the absence of selective retention of a particular molecular species by the pulps under investigation. In Table XXI and Figures 11 and 12 are presented data obtained by both the viscometric and anthrone analytical techniques for 770-cc. S.-R. freeness bleached sulfite pulp, with curves drawn through the 400-cp. methylcellulose data. It may be observed from Figure 11 that none of the viscosity grades of methylcellulose deviate significantly from the values for the 400-cp. sample, except for a single point for the 100-cp. methylcellulose (an apparent anomaly) and the ethylcellulose data.

In Figure 12 a similar situation exists, except that only one point of the ethylcellulose data deviates significantly from the 400-cp. methylcellulose curve. The ethylcellulose results obtained viscometrically must be questioned, because of the very low viscosity of this material. This, in turn, made the residual viscosity of the pulp a major portion of the observed viscosity, thus materially decreasing

TABLE XXI

EFFECT OF MOLECULAR WEIGHT ON SORPTION

770-cc. S.-R. Bleached Sulfite Pulp

| Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
25-cp. Methylcellulose					
0.0150	0.0095	1.06	0.0029	2.41	A5, V2
0.0500	0.0402	1.82	0.0294	4.02	
0.1000	0.0872	2.26	0.0754	4.70	
100-cp. Methylcellulose					
0.0150	0.0079	1.39	0.0072	1.53	A5, V2
0.0500	0.0362	2.63	0.0308	3.73	
0.1000	0.0712	5.52	0.0660	6.55	
4000-cp. Methylcellulose					
0.0150	0.0066	1.67	0.0056	1.88	A5, V2
0.0500	0.0362	2.63	0.0358	2.72	
0.1000	0.0832	3.07	0.0718	5.37	
Ethylcellulose					
0.0103	0.0009	1.88	—	—	A5, V2
0.0342	0.0216	2.44	0	6.84	
0.0684	0.0480	3.91	0.0165	10.32	

TABLE XXI (continued)

EFFECT OF MOLECULAR WEIGHT ON SORPTION

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures

300-cc. S.-R. Bleached Sulfite Pulp

25-cp. Methylcellulose

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
0.0150	0.0076	1.43	0.0059	1.79	A5, V1
0.0500	0.0393	1.94	0.0267	4.52	
0.1000	0.0840	2.78	0.0669	6.28	

FIGURE 11

Effect of Molecular Weight on Sorption
by 770 S.-R. Bleached Sulfite Pulp

● 400 cps. methylcellulose
◐ 25 cps. methylcellulose
◑ 100 cps. methylcellulose
○ 4000 cps. methylcellulose
⊗ Ethylcellulose

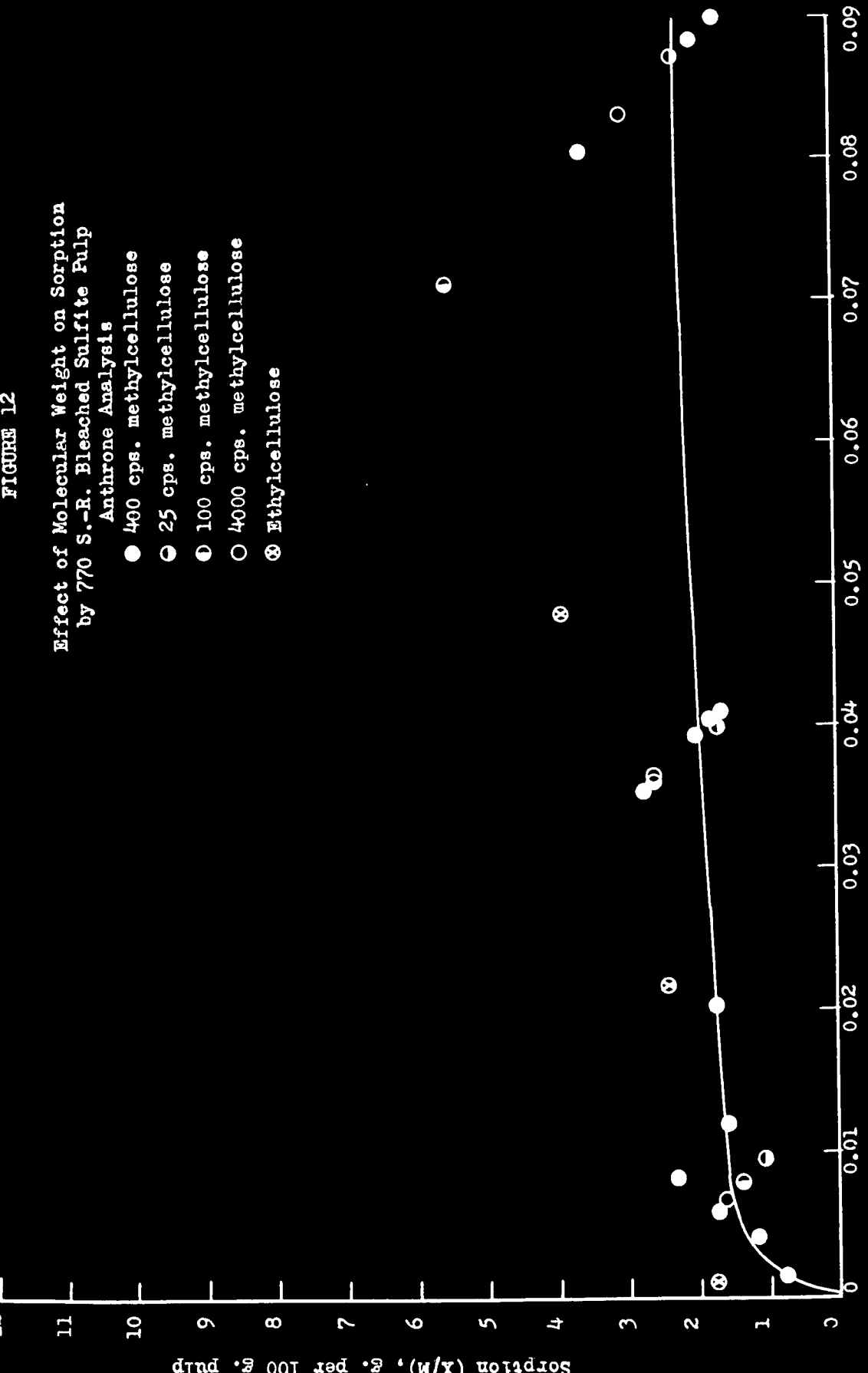Equilibrium Concentration (C), g. per 100 ml.

Sorption (X/M), g. per 100 g. pulp
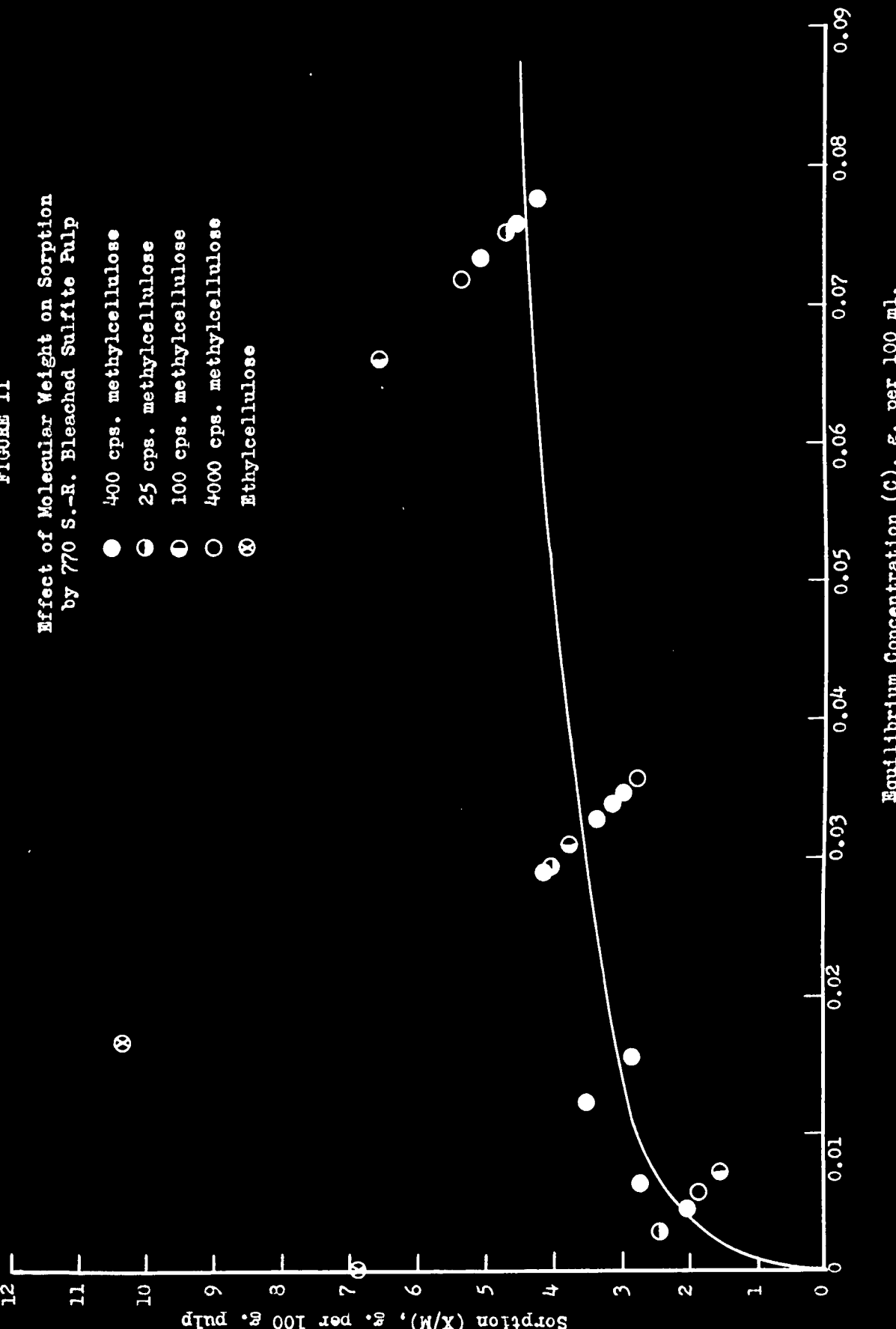
FIGURE 12

Effect of Molecular Weight on Sorption
by 770 S.-R. Bleached Sulfite Pulp
Anthrone Analysis

● 400 cps. methylcellulose

◑ 25 cps. methylcellulose

◐ 100 cps. methylcellulose

○ 4000 cps. methylcellulose

⊗ Ethylcellulose

Equilibrium Concentration (C), g. per 100 ml.

Sorption (X/M), g. per 100 g. pulp

confidence in the findings.

Table XXI also includes data on the addition of 25-cp. methylcellulose to 300-cc. S.-R. bleached sulfite pulp. The viscometric data do not differ significantly from that obtained with 400-cp. methylcellulose but, unfortunately, the sorption as determined with anthrone is considerably lower and corresponds to the sorption obtained with 400-cp. methylcellulose on 770-cc. S.-R. freeness pulp. No explanation for this situation has been found and, in view of the other findings, the anthrone data for the 300-cc. S.-R. freeness pulp must be disregarded.

It was concluded that sorption of methylcellulose by pulps is not accompanied by a selective retention of particular molecular species, and that ethylcellulose is sorbed to a slightly greater extent than methylcellulose.

EFFECT OF ROSIN AND ALUM ON SORPTION

In Table XXII are reported results on the effect of rosin and alum on the retention of 400-cp. methylcellulose by 570-cc. S.-R. freeness bleached sulfite pulp. The rosin used was a commercial (Grade F) wood rosin containing 30% free rosin and 70% solids. One ml. of a 4% solution of this rosin was added to the appropriate methylcellulose solutions (before addition of the pulp) to give 4% rosin on the pulp. One and one-half ml. of reagent grade papermaker's alum $(Al_2(SO_4)_3 \cdot 18H_2O)$ in 4% solution was added to the methylcellulose solutions to give 6% alum on the pulp. For the experiments employing both rosin and alum, the rosin was first added to the methylcellulose solution, followed by

TABLE XXII

EFFECT OF ROSIN AND ALUM ON SORPTION

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption g./100 g. pulp	Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
4% Rosin on Pulp					
0.0150	0.0052	1.94	0.0048	2.01	A5, V2
0.0300	0.0154	2.84	0.0115	3.63	
0.0500	0.0333	3.17	0.0247	4.91	
0.1008	0.0760	4.00	0.0568	8.30	
4% Rosin - 6% Alum on Pulp					
0.0500	0.0272	4.39	0.0117	7.57	A5, V1
0.1000	0.0742	4.80	0.0514	9.30	
6% Alum on Pulp (0.00045 Molar Solution)					
0.0150	0.0054	1.89	0	3.00	A5, V1
0.0300	0.0168	2.65	0.0087	4.23	
0.0500	0.0326	3.27	0.0193	6.06	
0.1000	0.0802	3.45	0.0663	6.47	
66.6% Alum on Pulp (0.005 Molar Solution)					
0.0500	--	--	0.0122	7.51	V1
0.1000	--	--	0.0280	14.28	

TABLE XXII (continued)

EFFECT OF ROSIN AND ALUM ON SORPTION

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
		66.6% Alum on Pulp (0.05 Molar Solution)			
0.0500	—	—	0.0095	8.03	VI
0.1000	—	—	0.0055	18.86	

Note: 400-cp. methylcellulose, 570-cc. S.-R. bleached sulfite pulp, 25° C.

the pulp, and then the alum. The procedure followed in making the 0.005 and 0.05 molar alum-methylcellulose solutions included the addition of 200 ml. of solution to the salt in an 8-ounce bottle, then shaking until the alum was completely dissolved. The pulp was then added as explained in the "Experimental Procedures" section.

Rosin and alum in the presence of methylcellulose and in concentrations corresponding to those obtained in samples diluted for filtration had no appreciable effect on the anthrone analysis. Specifically, 0.004 g./100 ml. of rosin and 0.006 g./100 ml. of alum in 0.005 g./ 100 ml. methylcellulose did not affect the anthrone calibration.

In analyzing with the viscosity technique, it was found that the presence of the salt reduced the Arrhenius viscosity constant for 400-cp. methylcellulose only slightly. For no salt this constant was 2.11, for 0.00045 molar alum 2.09, for 0.005 molar alum 2.07, and for 0.05 molar alum 2.04. Rosin at a concentration of 0.04 g./100 ml. reduced the Arrhenius viscosity constant to 1.99. Increasing alum and rosin concentrations apparently tend to collapse the hydration layer and reduce the viscosity of the methylcellulose at a given concentration. The Arrhenius viscosity equation was obeyed in an excellent manner in the presence of the alum. Viscosities were, of course, determined relative to the solvent, which was the particular salt solution used in a given experiment. The viscosity of the 0.00045 molar alum solution was essentially that of water, and the 0.005 molar alum had a viscosity relative to water of 1.014; the 0.05 molar alum had a viscosity of 1.116.

The data in Table XXII, when compared with Figures 6 and 7, show that there is no effect of the 4% rosin on retention. (In arriving at a conclusion from a set of data, obviously anomalous values were disregarded. Such is the case with the viscometric analytical value at 0.1000 g./100 ml. initial concentration.) There is also no effect of the 6% alum on retention. However, the combination of 4% rosin and 6% alum shows a distinct effect on retention when evaluated visco-metrically. The anthrone results, on the other hand, show that rosin-alum are not significant. No experiments were made to determine the effect of the combination rosin-alum on methylcellulose viscosities and, for computational purposes, it was assumed that the rosin and the alum were removed from solution by precipitation on the fibers. Therefore, the viscosity data are questionable, and it must be concluded that, at 0.5% consistency, 4% rosin and 6% alum exert little or no influence on the retention of methylcellulose by moderately beaten bleached sulfite pulps.

In the case of the higher concentrations of alum, a very great effect on sorption may be noted. For the 0.05 molar alum solution, the methylcellulose is nearly quantitatively retained.

SORPTION REVERSIBILITY

Effect of Concentration

From a theoretical viewpoint, the reversibility of a sorption system can give important clues to the nature of the forces involved and, in a practical sense, can serve to determine those laboratory or industrial

conditions which will be most effective. A "reversible" process is one which can be reversed by making infinitesimal changes in conditions of state--for example, concentration or temperature. In the case where a lag exists in the response of the process to the changes in conditions, "hysteresis" is said to occur. A process is irreversible if it does not respond to reverse changes in conditions but goes essentially in one direction only.

Tabulated results of experiments on reversibility of the pulp-methylcellulose-water system may be found in Tables XXIII and XXIV. The procedure included the addition of distilled water to a system at equilibrium in order to dilute the methylcellulose. After rotation for at least nine days, the equilibrium concentration was again determined and the sorption computed, making allowances for the initial sample removed. If initial and final sorptions are equal, then no changes have occurred as a result of the dilution and the sorption is irreversible. If the sorption decreases to correspond to the new equilibrium concentration, then the sorption is reversible. If the sorption decreases only partially, so that it lies between the initial sorption and that corresponding to the new equilibrium concentration, then hysteresis has taken place. A study of Tables XXIII and XXIV indicates that the initial and final sorptions agree fairly well, considering the analytical variability (previously mentioned in the section) in the effect of beating, and taking into account the fact that the final sorption values are nearly equally distributed about the initial values. The viscometric sorptions in particular agree well and, as will be pointed out later, more confidence can be placed in this method than in

TABLE XXIII

CONCENTRATION HYSTERESIS

Initial Concentration, g./100 ml.	Initial Liquid Vol. System, ml.	Initial Anthrone Equilibrium Concentration, g./100 ml.	Initial Sorption g./100 g. pulp	Water Added, ml.	Final Liquid Volume System, ml.	Final Anthrone Equilibrium Concentration, g./100 ml.	Final Sorption g./100 g. pulp
570-cc. S.-R. Bleached Sulfite							
0.0150	179	0.0060	1.78	200	379	0.0036	1.48
0.0300	179	0.0171	2.51	200	379	0.0078	2.61
0.0500	179	0.0343	3.00	200	379	0.0139	3.87
0.1000	179	0.0790	3.88	200	379	0.0375	3.83
720-cc. S.-R. Bleached Sulfite							
0.0150	198*	0.0058	1.72	200	398*	0.0046	1.02
0.0500	179	0.0355	2.77	200	379	0.0173	2.56
0.1000	179	0.0806	3.60	200	379	0.0400	2.86
795-cc. S.-R. Cotton Linters**							
0.0050	154	0.0021	0.56	25	179	0.0017	0.58
—	179	0.0017	0.58	50	229	0.0013	0.58
635-cc. S.-R. Cotton Linters							
0.0250	174	0.0169	1.51	150	320	0.0088	1.62
470-cc. S.-R. Cotton Linters							
0.0100	184	0.0034	1.31	150	334	0.0017	1.35
0.0200	184	0.0112	1.72	150	334	0.0055	1.94

TABLE XIII (continued)

CONCENTRATION HYSTERESIS

Initial Concentration, g./100 ml.	Initial Liquid Vol. System, ml.	Initial Anthrone Equilibrium Concentration, g./100 ml.	Initial Sorption, g./100 g. pulp	Water Added, ml.	Final Liquid Volume System, ml.	Final Anthrone Equilibrium Concentration, g./100 ml.	Final Sorption, g./100 g. pulp
			335-cc. S.-R. Cotton Linters				
0.0100	184	0.0039	1.20	150	334	0.0022	1.21
0.0200	184	0.0118	1.60	150	334	0.0060	1.76

*Leak in sample container
**0.75 gram of ovendry pulp in system

TABLE XXIV

CONCENTRATION HYSTERESIS

Initial Concentration, g./100 ml.	Initial Liquid Vol. System, ml.	Initial Viscosity Equilibrium Concentration, g./100 ml.	Initial Sorption, g./100 g. pulp	Water Added, ml.	Final Liquid Volume System, ml.	Final Viscosity Equilibrium Concentration, g./100 ml.	Final Sorption, g./100 g. pulp
			570-cc. S.-R. Bleached Sulfite				
0.0300	129	0.0108	3.80	200	351*	0.0047	3.63
0.0500	129	0.0277	4.35	200	332	0.0106	4.40
			300-cc. S.-R. Bleached Sulfite				
0.0300	130	0.0042	5.14	200	362*	0.0012	5.24
0.0500	130	0.0200	5.90	200	341*	0.0070	6.11

*Leak in sample container.

Note: The residual viscosity was considered to be diluted by the distilled water added in the same manner as the methylcellulose.

that of the anthrone. These data, therefore, support the conclusion that the sorption of methylcellulose by pulps is irreversible with respect to concentration changes. In short, methylcellulose will adsorb but not desorb.

In order to ascertain whether the manner of addition could influence the retention of methylcellulose, equilibrium systems of pulp-methylcellulose-water were treated with additional methylcellulose in moderately concentrated solution, so that the resulting equilibrium concentration would be materially increased. These data are given in Table XXV. The sorptions obtained from the sorption versus equilibrium concentration curves of Figure 7 are listed for comparison in the last column. The agreement between these values and the final sorption values is good.

Effect of Temperature

Table XXVI and Figure 13 report results of experiments designed to show the effect of temperature on sorption reversibility. A run was made at 38° C. and another at 3.3° C. After sampling to determine the equilibrium concentration, the 38° C. samples were rerun at 3.3° C. and the 3.3° C. samples at 38° C. It may be observed from Figure 13 that sorption increases with temperature, and that sorption appears to be a function of the particular temperature reached (and independent of the path) for ascending temperatures. However, for descending temperatures a hysteresis effect is observed, since the 38° C. run, when rerun at 3.3° C., had a higher sorption than the initial 3.3° C. run. It was concluded, therefore, that sorption was

TABLE XXV

CONCENTRATION HYSTERESIS

Initial Concentration, g./100 ml.	Initial Anthrone Equilibrium Concentration, g./100 ml.	Initial Sorption, g./100 g. pulp	Material Added	Final Anthrone Equilibrium Concentration, g./100 ml.	Final Sorption, g./100 g. pulp	Calculated From Figure 7 Final Sorption, g./100 g. pulp
0.0150	0.0049	2.00	25 ml. 0.1 g./100 ml. MC	0.0139	2.55	2.50
0.0300	0.0163	2.68	25 ml. 0.5 g./100 ml. MC	0.0694	3.95	3.70

Note: 570-cc. S.-R. bleached sulfite pulp
400-cp. methylcellulose at 25° C.

TABLE XXVI

TEMPERATURE HYSTERESIS

Initial Concentration, g./100 ml.	38.0° C.		3.3° C.	
	Anthrone Equilibrium Concentration, g./100 ml.	Sorption, g./g. Pulp x 10^2	Anthrone Equilibrium Concentration, g./100 ml.	Sorption, g./g. pulp x 10^2
	38.0° C. to 3.3° C.			
0.0150	0.0026	2.47	0.0076	1.59
0.0300	0.0004	4.08	0.0182	2.51
0.0500	0.0250	4.90	0.0346	3.19
0.1000	0.0666	6.40	0.0824	3.57
	3.3° C. to 38.0° C.			
0.0150	0.0026	2.32	0.0088	1.19
0.0300	0.0110	3.48	0.0220	1.52
0.0500	0.0236	4.76	0.0406	1.72
0.1000	0.0642	6.32	0.0880	2.07

Note: 400-cc. methylcellulose, 570-cc. S.-R. freeness bleached sulfite pulp.

FIGURE 13

Temperature Hysteresis

○ Sorption at 38° C.

◐ Sorption to equilibrium at 3.3° C. followed by sorption at 38° C.

● Sorption at 3.3° C.

◑ Sorption to equilibrium at 38° C. followed by sorption at 3.3° C.

Equilibrium Concentration (C), g. per 100 ml.

Sorption (X/M), g. per 100 g. pulp
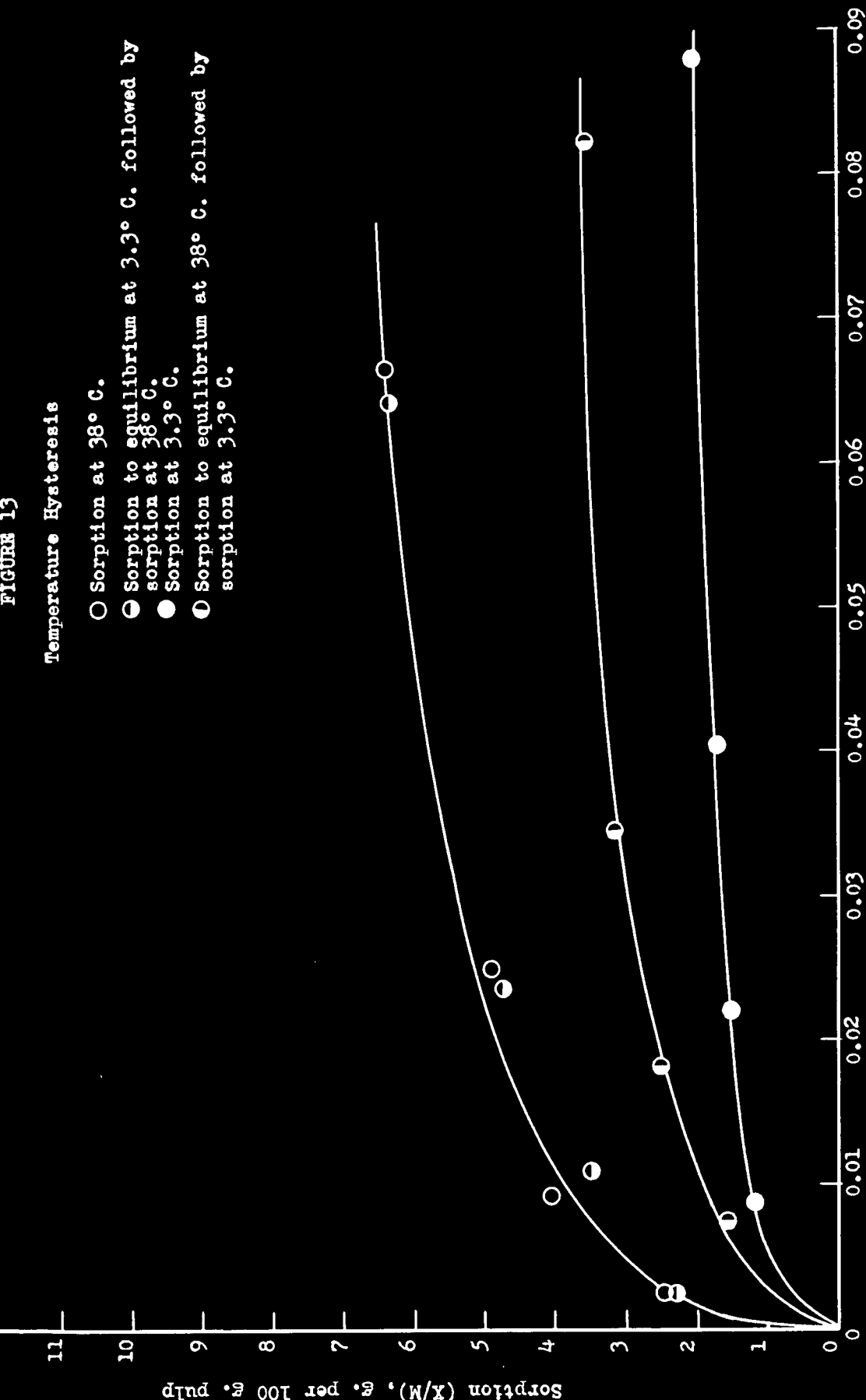
not completely irreversible with respect to temperature but showed

a hysteresis effect.

In summary, it has been shown in this section that sorption

of methylcellulose by pulps is irreversible with respect to concentration

and exhibits a hysteresis effect with respect to descending temperatures.

EFFECT OF TEMPERATURE ON SORPTION

Table XXVII contains data on the effect of temperature on the

retention of 400-cp. methylcellulose by 570-cc. S.-R. freeness bleached

sulfite pulp. The anthrone data from Table XXIII are plotted in Figure

14. No residual viscosity constants were available for 3.3° C. and

38° C., and the residual viscosity obtained at 25° C. was used throughout

for viscometric computations. However, it seems reasonable that tempera-

ture should affect this value to such an extent so that the viscosity

concentrations can only be approximately correct.

From Figures 13 and 14, the marked effect of temperature on

sorption can be readily seen. Retention increases with increasing

temperature, in contrast to a classical type adsorption in which sorption

decreases with increasing temperature. The effect of temperature is

even more pronounced than the effect of beating (Figures 6 and 7), and

raising the temperature 13° C. resulted in doubling the sorption as

measured by viscosity and increased the sorption 50% as measured with

anthrone as compared with sorptions at 25° C.

The anthrone data of Table XXVII were plotted on log-log

graph paper, and the best straight line was drawn through the points
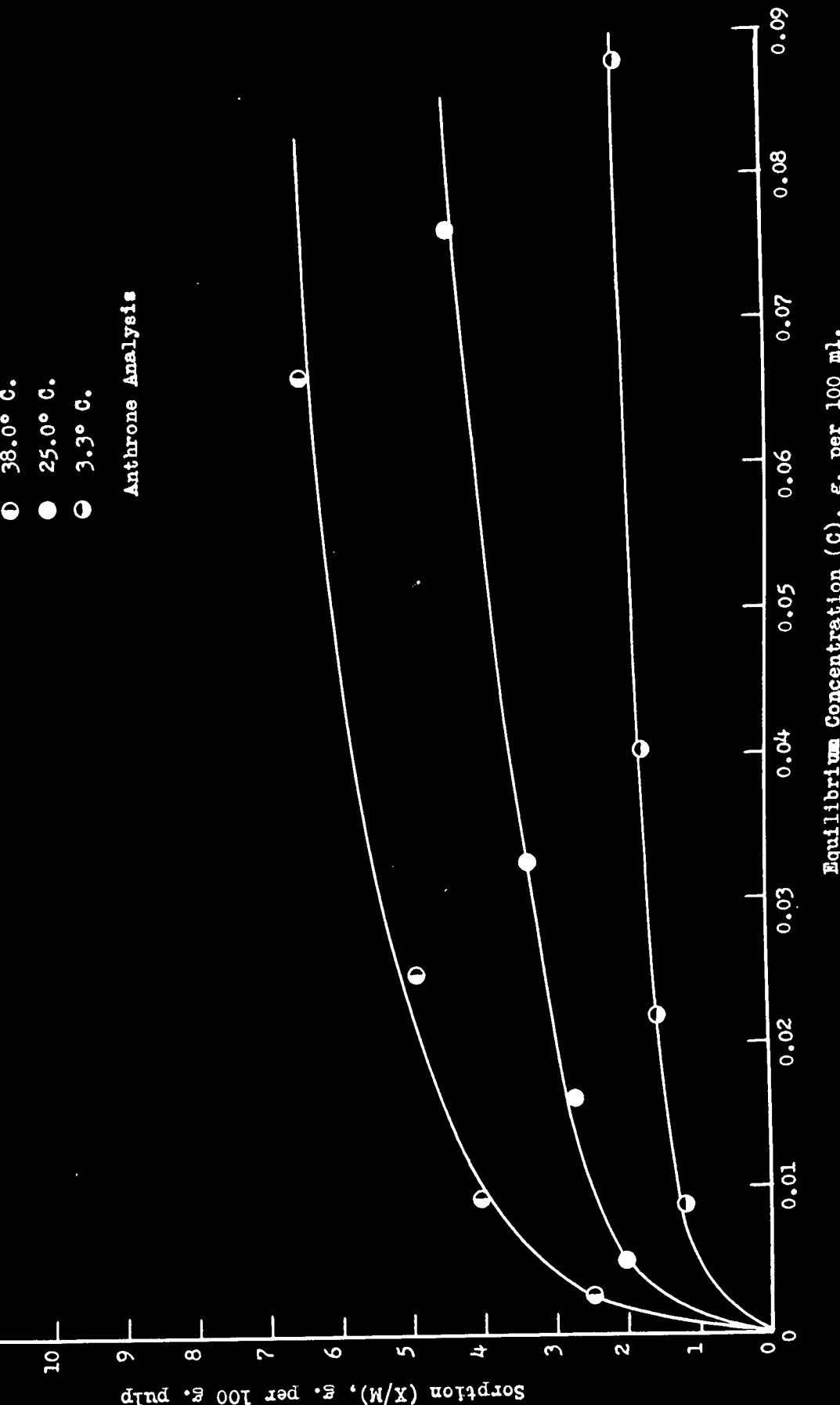
TABLE XXVII

EFFECT OF TEMPERATURE ON SORPTION OF METHYLCELLULOSE

Initial Concentration, g./100 ml.	Anthrone Equilibrium Concentration, g./100 ml.	Anthrone Sorption, g./100 g. pulp	Viscosity Equilibrium Concentration, g./100 ml.	Viscosity Sorption, g./100 g. pulp	Sampling Procedures
		3.3° C.			
0.0150	0.0088	1.20	0.0034	2.31	A5, V2
0.0300	0.0220	1.52	0.0166	2.61	
0.0500	0.0406	1.72	0.0347	2.92	
0.1000	0.0880	2.05	0.0799	3.70	
		25° C.			
0.0150	0.0049	2.00	0.0028	2.43	A5, V2
0.0300	0.0163	2.68	0.0129	3.37	
0.0500	0.0327	3.32	0.0267	4.55	
0.1000	0.0764	4.40	0.0648	6.77	
		38° C.			
0.0150	0.0026	2.47	0	3.00	A5, V2
0.0300	0.0094	4.08	0.0052	4.94	
0.0500	0.0250	4.90	0.0180	6.33	
0.1000	0.0666	6.42	0.0395	11.94	

Note: 570-cc. S.-K. bleached sulfite, 400-cp. methylcellulose.

Anthrone Analysis

● 38.0° C.
● 25.0° C.
◐ 3.3° C.

Equilibrium Concentration (C), g. per 100 ml.

Sorption (X/M), g. per 100 g. pulp

in the manner previously described for fitting the data to a Freundlich isotherm. From this plot values of equilibrium concentrations for the three temperatures at a given sorption were obtained. These data may be substituted in the Clausius-Clapeyron equation to obtain the differential heat of retention.

$$Q = -\Delta H = (RT_2 T_1/T_2 - T_1) \ln C_2/C_1$$

where Q = heat evolved or absorbed,

ΔH = heat of retention,

T_1 and T_2 are absolute temperatures corresponding
to equilibrium concentrations, and

C_1 and C_2 at a selected sorption.

It may be seen from this equation that a plot of log C versus the reciprocal absolute temperature will give a straight line whose slope multiplied by the gas constant R, and the factor for conversion of natural logs to naperian logs will give ΔH. Such a plot is given in Figure 15 with the lines corresponding to selected sorptions that are tabulated. In Table XXVIII the slopes of the various lines are given, together with the calculated heats of retention. For comparison, the heats calculated from the viscosity data are included. The agreement between methods is good, considering the probable errors in the viscosity technique mentioned previously, and serves to inspire confidence in the comparative nature of the anthrone data. The heat of retention does not appear to vary greatly for sorptions above 1.6% on the pulp.

FIGURE 15

Effect of Temperature on Sorption
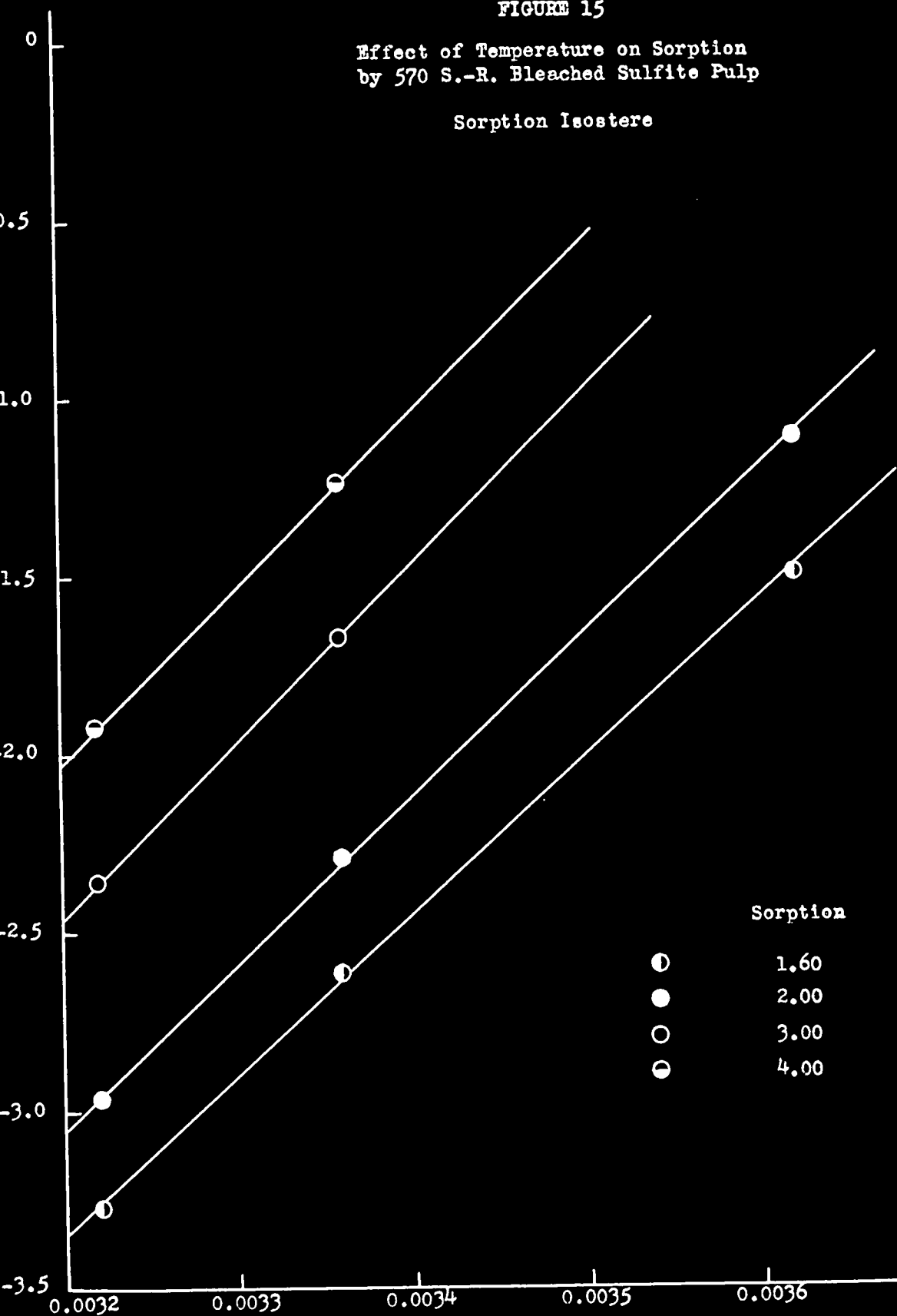by 570 S.-R. Bleached Sulfite Pulp

Sorption Isostere

Reciprocal Absolute Temperature °K.

TABLE XXVIII

HEAT OF RETENTION OF METHYLCELLULOSE

Sorption, g./100 g. pulp	Slope Log Concentration-Reciprocal Temperature Curve	ΔH_R
	Anthrone Method	
1.60	4400	20,200
2.00	4600	21,100
3.00	4930	22,600
4.00	4870	22,300
Av.		21,500
	Viscosity Method	
4.00	3870	17,700
5.00	4070	18,600

Experimental runs using 300-cc. S.-R. freeness bleached sulfite pulp and methylcellulose of 400 and 25 cp. viscosity grades were also made. Although these data were somewhat meager (only two points were run on the 38° C. and 3.3° C. curves), they gave heats of retention approximating that obtained from the 570-cc. S.-R. pulp. It was concluded, therefore, that heats of retention varied little with the degree of beating of the pulp or with the molecular weight of the methylcellulose.

Since retention of methylcellulose increases with increasing temperature, in a manner similar to the increase in adhesion of copolymers to cellulose with increase in temperature, a classical-type adsorption phenomenon cannot be exclusively involved. Accordingly, a line of reasoning similar to that of Hofrichter and McLaren (32) was followed in obtaining

an actual heat of adsorption. These investigators postulated that the heat of adhesion was equal to an exothermic heat of adsorption and an endothermic heat of fluidity or cohesion. The evolution or absorption of heat on adhesion depends on the relative magnitudes of cohesion and adsorption. They found adhesion to be endothermic and, consequently, concluded that the heat of cohesion was greater than the heat of adsorption.

Since Hofrichter and McLaren worked with hot melts in their investigations, the idea of heat of fluidity or cohesion is hardly applicable to high polymer solutions in good solvents. As will be discussed later, there is every reason to believe that a gelation of methylcellulose occurs at the fiber-solution interface on sorption of methylcellulose from water solution. Therefore, the heat of gelation was substituted for Hofrichter and McLaren's heat of cohesion. Thus, the heat of retention was made equal to the heat of adsorption plus the heat of gelation. Heats of gelation of methylcellulose were obtained by application of the Clausius-Clapeyron equation to gelation temperatures obtained by the Dow Chemical Company (3). These data are listed in Table XXIX together with the calculated molar heat of gelation and the specific heat of gelation. The specific heat of gelation was obtained by dividing the molar heat by the molecular weight obtained from data furnished by Dow. The gelation temperatures and molecular weights are averages of a number of batches of the Methocel grades listed. From Table XXIX it may be seen that the heat of gelation is relatively constant with respect to molecular weight, and that the heat of gelation decreases with increasing concentration.

TABLE XXIX

HEAT OF GELATION OF METHOCEL*

Methocel Grade	Concentration, % (by wt.)	Gelation Temperature, °C.	Δ H, Cal./mole	Δ H, Cal./gram
4000	2.6	51.4	32,600	0.23
	3.0	50.5		
25	2	55.0	29,600	0.78
	5	48.5		
15	2	50.0	26,200	0.86
	5	51.5		
	5	51.5	11,800	
	10	40.0		
10	2	53.5	30,200	1.19
	5	52.0		
	5	52.0	13,400	
	10	41.5		

*From Dow Methocel Brochure (3), Figures 6-9 (p. 47-50).

The values from 2 to 5% concentration were used in computing the heat of sorption; the average molar heat of gelation was taken as 29,700 cal./mole.

The form of the Clausius-Clapeyron equation used was that employed by Meyer and van der Wyck (65) for calculating the heat of gelation of gelatin.

$$Q = -\Delta H = \frac{RT_2 T_1}{T_2 - T_1} \ln W_2/W_1.$$

where W_1 and W_2 are the concentrations by weight of solutions saturated at absolute temperatures T_1 and T_2.

The equation relating heats of retention, adsorption, and gelation is:

$$\Delta H_R = \Delta H_S + \Delta H_G,$$

where the subscripts refer to retention, sorption, and gelation. Substituting the experimentally determined heats of retention and gelation, the value for the heat of sorption is found to be:

$$\Delta H_S = \Delta H_R - \Delta H_G$$

$$= 21,500 - 29,700$$

$$= -8200 \text{ cal./mole (exothermic)}.$$

In comparison, the value of the heat of sorption computed by Hofrichter and McLaren from the adhesion data of hot melts was - 17,500 cal./mole (exothermic).

The modified Clausius-Clapeyron equations used in computing the heats of gelation and retention may be readily derived from the van't Hoff isochore, in turn obtained from the Gibbs-Helmholtz equation (42). The van't Hoff or reaction isochore is:

$$d l_n K/dT = \Delta H_2/RT,$$

where K = equilibrium constant,

T = absolute temperature (°K.),

ΔH = heat reaction, cal./mole, and

R = gas constant, cal./mole.

The general expression for the true thermodynamic equilibrium constant for a single reactant and a single product is:

$$K = \alpha_2 / \alpha_r$$

where α_2 = activity of product

α_r = activity of reactant

Integration of the reaction isochore gives:

$$\int_{K_1}^{K_2} d\ln K = \Delta H/R \int_{T_1}^{T_2} T^{-2} \, dT$$

$$\ln (K_2/K_1) = (-\Delta H/R)(1/T_2 - 1/T_1)$$

K_1 and K_2 are the equilibrium constants at absolute temperatures T_1 and T_2.

For a sorption process, an equilibrium exists between a substance sorbed on a substrate and the same substance in solution:

$$K_1 = \alpha P_1/\alpha R_1; \quad K_2 = \alpha P_2/\alpha R_2$$

where the subscript P refers to the sorbed state

and R the sorbate state.

Substituting in the integrated isochore:

$$\ln (\alpha P_2/\alpha R_2)(\alpha P_1/\alpha R_1) = (\Delta H/R)(1/T_2 - 1/T_1)$$

Setting $\alpha R_2 = \alpha P_1$ (in effect choosing a constant sorption),

$$\ln (\alpha R_1/\alpha R_2) = (\Delta H/R)(1/T_2 - 1/T_1)$$

In dilute solutions, such as those used in the present study, activities may be replaced by concentrations:

$$\ln (C_1/C_2) = (\Delta H/R)(1/T_2 - 1/T_1)$$

$$-\Delta H = (RT_2 T_1/T_2 - T_1) \ln (C_2/C_1)$$

where C_1 and C_2 are equilibrium concentrations corresponding to a given sorption at temperatures T_1 and T_2.

In the case of the formula used to obtain heats of gelation, an equilibrium between a saturated water solution of methylcellulose and methylcellulose in the gel (solid) phase was postulated.

$$Sol \rightleftharpoons Gel$$

The equilibrium constant would be:

$$K = \alpha_G / \alpha_S$$

where α_G = activity of the gel and

α_S = activity of the sol.

The activity of the gel is, of course, one:

$$K = 1/\alpha_S$$

Substitution in the integrated isochore and replacement of activities by weight concentrations gives:

$$\ln W_1/W_2 = \Delta H/R \ (1/T_2 - 1/T_1)$$

since $K_1 = 1/\alpha_{S_1}$ and $K_2 = 1/\alpha_{S_2}$

Rearranging

$$-\Delta H = (RT_2T_1/T_2 - T_1) \ln W_2/W_1$$

where W_1 and W_2 are equilibrium saturated sol concentrations corresponding to absolute temperatures T_1 and T_2.

A note on the replacement of activities with concentrations is in order. Activities are "effective" concentrations and are usually expressed in molalities (moles/1000 grams solvent). The simplest concept is simply to consider the concentrations which appear in the modified isochores as ratios and, therefore, independent of units used for expressing the concentrations.

The criteria for the use of these equations must be considered. The assumption is made, when using the van't Hoff isochore, that the heat of reaction (used here generically) is independent of temperature. This is known experimentally to be untrue. However, little error is made in making such an assumption over the relatively narrow temperature range involved. The van't Hoff equation is further applicable to a constant pressure-constant volume system. These are essentially the conditions under which methylcellulose was sorbed on pulp, and the questions of equilibrium and reversibility are pertinent. The sorption of methylcellulose comes to a constant state as nearly as can be measured. This is not a true thermodynamic equilibrium, however, in which infinitesimal changes in concentration, for example, would reverse the sorption. In fact, sorption has been shown to be completely irreversible with respect to concentration in that methylcellulose will sorb but not desorb on pulp under isothermal conditions. However, the Gibbs-Helmholtz equation on which the van't Hoff isochore is based is applicable to irreversible systems (66), and requires only thermodynamic equilibrium in initial and final states of the process. Thus, the efficacy of the heat of reaction calculations depends on the approach to true equilibrium of the system pulp-methylcellulose-water. Although a true equilibrium is not attained, it can be argued that deviations will exist at each temperature and will be in the same direction, so that differences in actual equilibrium conditions will approximate differences in true equilibrium conditions. Since the heats are based on differences, it may be concluded that the results are valid to a first approximation.

EXPERIMENTS ON VOLUME CHANGE ON SORPTION, SORPTION BY CELLOPHANE, EFFECT
OF CONSISTENCY, AND EFFECT OF HIGH RATES OF SHEAR ON RETENTION

Heymann (4, 5) has shown that solutions of methylcellulose
increase slightly in volume on gelation. Since the sorption of methyl-
cellulose by pulps might conceivably consist of a gelation at the fiber
surface, an attempt was made to show such a volume change in a sorption
system consisting of pulp, methylcellulose, and water. A mercury
dilatometer similar to that used by Heymann was used in preliminary
experiments but was abandoned for a Neville-Theis (62) type dilatometer,
modified by a side arm with a stopcock. No positive conclusions could
be drawn from these experiments, since the volume change effect was
apparently too small to measure conveniently, and the difficulties in
excluding air from the sorption system proved to be unsurmountable in
the time available.

Experiments were conducted on the retention of methylcellulose
by known areas of cellophane (viscose sausage casing), after batchwise
extraction to remove glycerin. Preliminary experiments with anthrone
indicated some slight sorption and additional experiments, using the
viscosity technique, showed approximately 0.85 gram methylcellulose
retained for one square meter of wet sausage casing at an equilibrium
concentration of about 0.09 g./100 ml. Sorption at 0.045 g./100 ml.
was roughly 0.3 gram. However, the efficacy of these determinations
depends on the accuracy of the determination of the water in the cello-
phane which is not available for diluting the methylcellulose. Since
one square meter of sausage casing weighs about 50 grams, the amount of

water introduced with wet cellophane (or soaked up by dry cellophane)
is appreciable. This same uncertainty exists in the case of pulps,
but the amount of water in one gram of pulp which is not available for
diluting the methylcellulose cannot possibly be over several grams and
can consequently be ignored in a solution of 200 ml.

This water not available for diluting the methylcellulose
was determined for the sausage casing by soaking extracted strips of
casing in water, and carefully blotting to remove all surface water,
then weighing before and after oven drying. Mild pressures (such as
couching with a handsheet couch roll) had no effect on the imbibed water.
It was found that the 2-mil high-stretch sausage casing had an imbibed
water content of 1.25 grams per gram of cellophane. This water was
assumed to be unavailable to the methylcellulose and due allowance
was made in making sorption calculations.

The sorption of methylcellulose appears to have possibilities
as a method for surface area measurement of pulps. However, only the
barest beginning has been made in the present study.

The effect of consistency on the sorption of methylcellulose
by pulps was not studied in detail, but preliminary experiments indicated
decreasing sorption with increasing consistency. This may result from
greater friction between fibers as consistency is increased, thus pre-
venting any loosely held methylcellulose from being retained.

An experiment designed to show the effect of moderate rates of
shear on the retention of methylcellulose by pulps was conducted. Two

samples of 300-cc. S.-R. bleached sulfite pulp at equilibrium with 400-cp. methylcellulose were stirred in a Waring blendor for 4 minutes and reanalyzed viscometrically. The equilibrium concentration decreased in both cases, thus indicating that additional sorption had taken place and that no sorbed methylcellulose had been removed by the action of the blendor. The apparent increased sorption may have been the result of a somewhat increased surface, because of the action of the blendor, or to the concentration of high molecular methylcellulose in the copious quantities of foam formed. This tended to give very low viscosities and very low equilibrium concentrations.

DISCUSSION OF RESULTS

ANALYTICAL PROCEDURES

General

The search for a suitable analytical procedure for measuring
the retention of a carbohydrate gum by cellulose is by no means ended.
The variability which exists within and between the anthrone and the
viscosity techniques is, quite naturally, of considerable concern be-
cause precision in an analytical method is always comforting, although
it is certainly true that precision does not necessarily insure accuracy.
The existence of this variability implies that certain variables have
been inadequately controlled in the experiments run thus far, and future
work on an analytical method should certainly be directed toward dis-
covering the cause of this variability and eliminating it. It could
conceivably develop that this variability is inherently characteristic
of the system under investigation, and that it cannot be eliminated.
In such a case, recourse would have to be had to statistical analysis,
which would involve many more data than those reported in this work.

Although the data obtained on the system pulp-methylcellulose-
water are quite variable when considering either the anthrone or the
viscosity technique, it is felt that this variability does not detract
from qualitative arguments and conclusions. There seems little doubt,
for example, that sorption increases with beating, although how much
it increases is debatable. In almost every case, those qualitative
conclusions obtained with the viscosity technique also apply to the

anthrone technique.

It should be emphasized, however, that the disparity between the anthrone and viscosity methods is due largely to the method of computing the sorption. As was pointed out previously, the calculated sorption depends on small differences and, consequently, is very sensitive to the equilibrium concentration. In Figure 16 are plotted the viscosity versus the anthrone analytical values for bleached sulfite pulp. It may be noted that the difference between the two methods is only about 10-12% of the average concentration at higher concentrations and about 20% at low concentrations. Nevertheless, this small discrepancy results in a ratio of viscosity to anthrone of 1.5 to 2 in calculated sorptions.

The variability noted in the results does not lie in the analytical techniques themselves, because analyses on a given bottle could be repeated in an excellent manner as long as four weeks apart. The variability, therefore, lies in the system of procedures. The time of sorption was not uniform but was a minimum of nine days. Time could conceivably cause the variations noted if sorption continued slowly over an extended period. The analytical reproducibility, however, indicates that sorption did not vary regularly with the length of a run, suggesting that there is no time effect. (Additional evidence in this regard was given in the section on the effect of time on sorption.)

In general, somewhat better precision within a run (a smooth curve could be drawn through the points on a Freundlich isotherm plot)

FIGURE 16

Comparison of Anthrone and Viscosity
Analytical Techniques

Bleached Sulfite Pulp

Anthrone Analysis, g. per 100 ml.
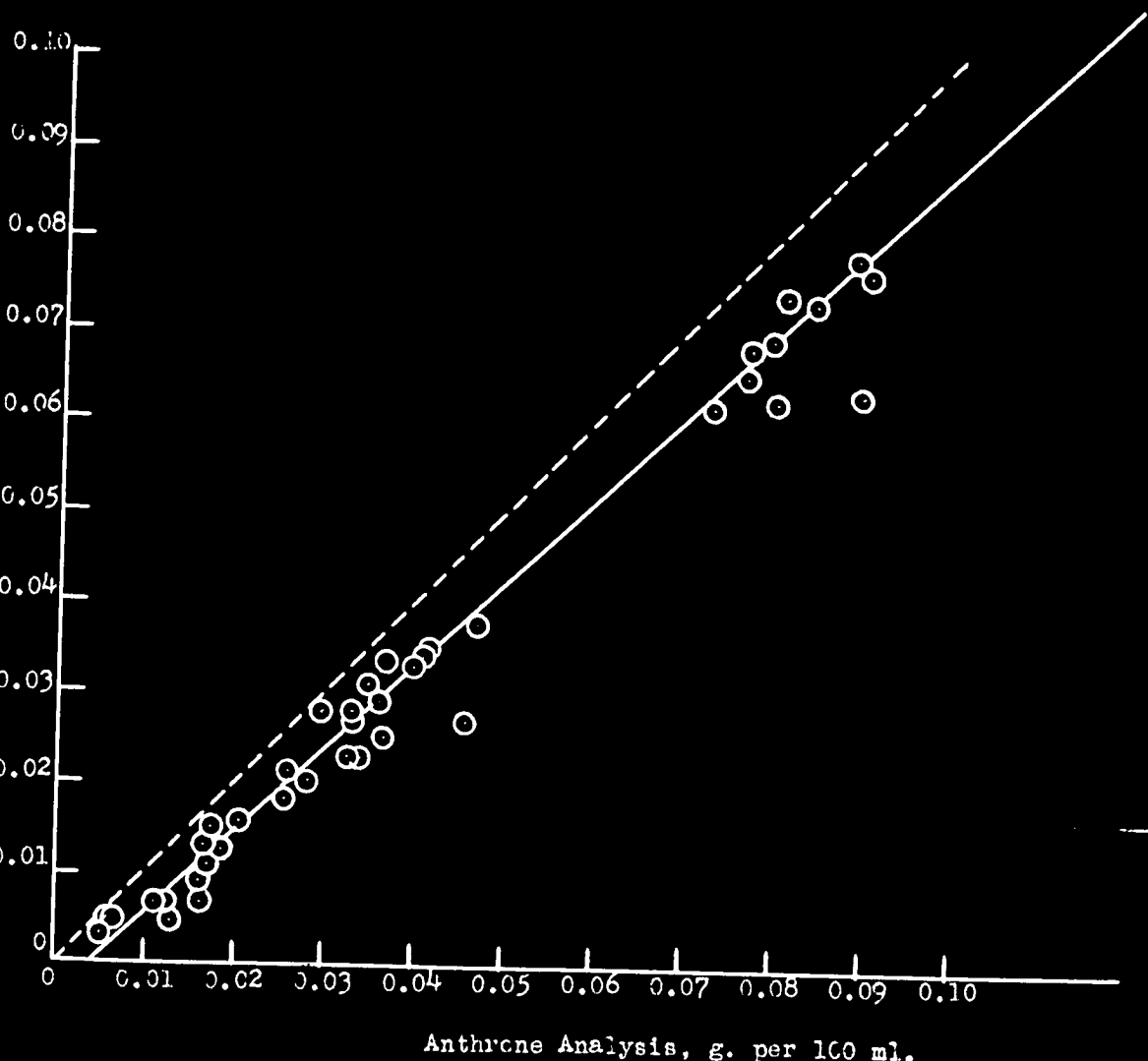
was noted than between runs. This suggests that certain variables influenced a given run but were not common to all runs. Temperature variation is a possibility, but great care was taken to avoid any temperature fluctuations. Moreover, temperature deviations could have been as large as 1° C. and still have affected the sorption less than 10%. The stirring procedures for dispersing the pulp were not uniform (stirring was simply continued until the pulp was dispersed), and possibly this operation deserves future study when considering analytical techniques. It is most unlikely, however, that stirring could have been uniform within a run and nonuniform between runs. The time of rotation also varied between runs but was constant for a given run, so that it could possibly account for the results obtained.

A further possibility is variation in the actual ovendry weight of the pulp sample. It was calculated that all one-gram pulp samples lay within the range 0.97-1.03 grams, and it was deemed unlikely that samples would be outside the range 0.98-1.02 grams. Therefore, gross variations in weights of samples could not have occurred. The loss of weight by evaporation while the wet pulp was being weighed was checked and found to be considerably less than 10 mg. and, therefore, had a negligible effect on the ovendry weight of pulp.

Bacterial degradation of methylcellulose has been shown to be nonexistent under the conditions of the experiments.

Anthrone

The anthrone technique will be considered in more detail. The

general method for testing filtration procedures for use with anthrone
analysis was to mix pulp-water supernatant fines with known concentra-
tions of methylcellulose and filter these mixtures through Celite or
fritted glass filters. It was shown that the methylcellulose under such
conditions could be recovered almost quantitatively.

Krepamer (28) and Broadbent and Harrison (29) have indicated
that methylcellulose is a pulp deflocculator and dispersing agent.
Therefore, it is reasonable to suppose that the concentration and average
size of the settled supernatant cellulose fines will be greater in the
presence of methylcellulose. This is qualitatively shown by the notice-
ably greater turbidity and longer settling times exhibited by pulps with
added methylcellulose in comparison with untreated pulps. This turbidity
also increases with methylcellulose concentration. The Celite and
fritted glass filters may readily remove the supernatant fines present
in a pulp-water suspension but are not able to remove quantitatively
cellulose fines in the presence of the methylcellulose.

As has been mentioned previously, the incomplete separation
of cellulose from the gum would result in an equilibrium concentration
which was too high and a calculated sorption which was too low. Anthrone
determined sorptions were, in almost every case, lower than those
determined by viscosity. If viscosity is assumed to indicate the true
level of sorption, then such a trend would be expected.

The anthrone analytical variability could be explained in
part by a variation in the distribution of fines from one pulp sample to
another. This may have occurred during filtration of the pulp from the

beater since pulp fines would tend to concentrate in the lower layers of the filtered pad. In those pulp samples which had a greater percentage of fines, the supernatant cellulose concentration and the equilibrium concentration would be greater, whereas the sorption would decrease. The variation in fines might also influence the level of sorption, but this effect would probably be less than the effect of unfiltered cellulose fines on the equilibrium concentration.

The residual viscosity has a possible influence on the depth of color obtained with anthrone. Table IX shows that the material which gives the residual viscosity is largely removed in Celite filtration, apparently through sorption by the Celite. (Conclusions from Table IX, however, are complicated by lack of knowledge of whether a given concentration results from suspended cellulose or soluble hemicellulose substances.) The concentration which may result from residual viscosity can, therefore, be ignored.

Viscosity

Viscosity must give a true indication of concentration of a high molecular weight substance in the presence of pulp, provided that there is no selective sorption of a particular molecular weight species and provided that any substance leached from the pulp either has no viscosity or can be satisfactorily taken into account. Further suppositions are that the pulp "residual viscosity" (if present) acts independently of the additive, and that the additive displays no viscometric anomalies. It must also have the ability of being satisfactorily represented by an equation relating viscosity to concentrations. The last requirement

is that the presence of the additive should in no way influence the extent of leaching out or, in other words, influence the amount of the residual viscosity.

The requirements of nonselective sorption, independent action of additive and residual viscosity, and lack of viscometric anomalies appear to have been adequately considered for the system pulp-methylcellulose-water. The data on the effect of molecular weight on sorption indicate that selective sorption is nonexistent. Experiments with mixtures of pulp-water supernatant liquor and known methylcellulose concentrations and with mixtures of aspenwood hemicelluloses and methylcellulose solutions have shown that the pulp extract and aspen hemicelluloses act independently with methylcellulose and that log viscosities are additive as would be expected. Methylcellulose has also been shown to obey the Arrhenius equation (relating viscosity and concentration) in an excellent manner.

The correction for residual viscosity and the influence of methylcellulose on residual viscosity remain to be discussed. Actually, these considerations are the same. A not inconsiderable variability was noted in the residual viscosities determined on pulp-water systems. This variability undoubtedly existed in the presence of the methylcellulose and could partially account for viscometric analytical variation. Any difference in distribution of fiber fines between pulp samples could affect the level of sorption contributing to overall variability. The possibility that methylcellulose eliminates the residual viscosity seems unlikely, since the methylcellulose would have to form a semipermeable membrane at a fiber interface to prevent leaching out. However,

the methylcellulose may inhibit extraction as the result of satura-
tion of the solution with respect to a given molecular weight. Since
the residual viscosity is in all probability due to short-chain,
water-soluble hemicellulose material, this also seems unlikely, because
saturation with respect to short-chain materials certainly could not
exist in the dilute methylcellulose solutions employed.

A brief summary of the evidence in regard to the nature of
the pulp residual viscosity is in order. The residual viscosity cannot
be inorganic, since the neutral salts required to give a similar viscosity
simply are not present in one gram of pulp. In addition, the pH of all
pulp extracts was near 7, showing the absence of acids, bases, or
non-neutral salts. On the other hand, hemicelluloses in small concen-
tration could readily give such viscosities (67). The residual vis-
cosity cannot be centrifuged out, indicating that substances in solution
are responsible.

THEORY OF SORPTION

The Nature of Methylcellulose Sorption

The experimental results will be reviewed in order to elucidate
the mechanism of retention of methylcellulose by pulps.

The results obtained with pulps beaten to various degrees of
freeness indicated that sorption for well-beaten pulps was approximately
three to four times that obtained for unbeaten pulps. Since freeness is a
rough measure of surface area, and the surface area of pulps increases
three to five times with beating (68, 69), it can be concluded that

sorption of methylcellulose is a surface phenomenon and that the
term "adsorption" is applicable to this process. The variation of re-
tention obtained with beating agrees with the findings of Obermanns
for sorption of hemicelluloses and of the Dow Company on the sorption of
Methocel. In addition, theoretical considerations lend weight to these
conclusions. The dimensions of the methylcellulose molecule have been
reported to be 7-9 A. in diameter and the D.P. x 5.15 A. in length.
According to Heuser (20), cellulose is present in the fiber in micelles,
which consist of 100-170 individual polyglucose chains in bundles of
50-60 A. wide and 600-1000 A. long. The micellar bundles are separated
by a system of hollow spaces consisting of canals of largely varying
widths ranging from 1000 down to 10 A. The micelles themselves are
fissured by small cracks of about 10 A. The dyeing of cotton gives
further evidence as to the size of the spaces. Lehner and Smith (21)
conclude that 18 A. is the upper limiting size for dyes which dye cotton.
It seems relatively unlikely, therefore, that the long methylcellulose
chains could penetrate such a structure more than superficially since,
even if chain ends were to penetrate the cellulose (like threading a
needle), the ends would soon meet cellulose spaces of the same magnitude
as the molecular diameter.

In Table XX the Freundlich adsorption constants for various
pulps were given. Generally speaking very little success has been had
in attempting to attach any theoretical significance to these empirical
constants. However, Gyangi (72) has made a very interesting attempt in
this direction. By starting with the general distribution equation for
a substance distributed between two phases, and constructing a mathematical

model consisting of incremental cubes, Gyangi showed that, for an

adsorption which takes place anywhere on a given surface, the Freundlich

exponent n should equal 2/3. If adsorption is limited to edges of cubes

(i.e., lines on the surface), the Freundlich exponent would be 1/3 and,

for the extreme case where point adsorption is involved, the exponent

would be zero. It was further pointed out that for $n = 1/3$, the solute

should be confined to certain lines in the solid phase, and these lines

may be identified with the exposed edges of microcrystals of the solid

phase or scratches or imperfections in them.

From the data of Table XX, it can readily be seen that the

exponents for the sorption of methylcellulose by pulps are quite close

to the value of 0.33 specified by Gyangi, as indicative of line ad-

sorption except for the first two constants for bleached kraft pulp. It

is to be expected that sorption on the surface of a cellulose fiber would

be linear and correspond to the orientation of cellulose micelles in the

gross surface of the fiber. As will be pointed out later, however, this

does not necessarily mean that the methylcellulose itself is linearly

attached to the cellulose in sorption, but merely that the points of

adhesion between pulp and additive lie in a line.

In comparing the sorptivity of pulps at approximately equal

freenesses, it was found that bleached sulfite exhibited the greatest

adsorbing power, followed by bleached kraft and unbleached sulfite and,

finally, cotton linters and bleached kraft. As was shown by Robertson

and Mason (68), freeness is essentially a function of particle size and

packing in the fiber pad; the latter is dependent on fiber stiffness.

Therefore, to attain the same freeness, stiff fibers must have a smaller particle size and, hence, a greater surface area. These facts further increase the disparity between the sorptions of bleached and unbleached sulfite and bleached kraft on the one hand and linters and unbleached kraft on the other, since at the same freeness the latter pulps would have a greater surface. It may be postulated that the hydrophilic nature of the pulp surface [which decreases in the order noted for sorption (30)] plays an important role in the retention of methylcellulose by pulps; the more hydrophilic pulps would retain greater amounts of additive.

Gelation of Methylcellulose

In a subsequent section, the gelation of methylcellulose will be considered in relation to its retention by wood pulps. In this section, the gelation will be considered separately, with particular reference to thermodynamic effects. Water solutions of methylcellulose of sufficient concentration and molecular weight coagulate and gel on heating to the range 40-65° C. Gelation is accompanied by a slight volume increase in the system. Heymann (4) investigated these phenomena and suggested that methylcellulose exists in water solution as highly hydrated sol particles which must be dehydrated before a gel can form. The volume change noted on gelation was thought to be the result of the removal of the "adsorbed-solvated" water layer, which had a greater density than the surrounding liquid. This behavior may be contrasted with that of agar and gelatin, whose solutions gel on cooling and exhibit a volume decrease on gelation. In the case of methylcellulose, water

does not play an extensive part in the formation of the gel structure, whereas the reverse is true for gelatin and related substances.

It may be postulated, in the case of gelation of methylcellulose, that two processes are involved which are occurring simultaneously. One process involves dehydration of the methylcellulose particle and consists in the breaking of the hydrogen bonds between water layers and the hydroxyl groups of the methylcellulose. At a given temperature, there is an equilibrium between water molecules entering and leaving the water shell around a methylcellulose particle. Since the energy possessed by a water molecule is directly a function of the absolute temperature, raising the temperature will increase the number of water molecules which possess the requisite energy to leave the shell until a new equilibrium is reached. As the temperature rises, the water shell grows smaller, allowing closer approach of the methylcellulose particles to one another and, at the same time, decreasing the relative solution viscosity (a result to be expected since dehydration is in essence a decrease in effective particle dimensions). Other manifestations of this process are reduction in clarity of solutions with increasing temperature. The dehydration process is endothermic (heat must be added to the system), because hydrogen bonds are being broken.

As the water shell around a methylcellulose molecule decreases to such an extent that close approach between adjacent molecules is possible, molecular aggregation begins to occur, and the solution becomes hazy. This aggregation is the beginning of the second process associated with gelation, in which hydrogen bonding occurs between methylcellulose

molecules--either directly or with "bridges" of single water molecules. This second process is exothermic, since hydrogen bonds are being formed. As aggregation continues, groups of molecules coalesce to form a more or less rigid structure, and the methylcellulose sets to a tough stringy gel. Since gelation occurs as the temperature is raised, it is an endothermic process and has a positive heat. Therefore, it can be reasoned that the heat of gelation corresponds to the difference between the respective heats of dehydration and aggregation. Because the heat of gelation is positive, the heat of dehydration (also positive) must be larger than the negative heat of aggregation or, in other words, more hydrogen bonds are broken in dehydration than are formed in aggregation.

In Table XXIX it was seen that the heat of gelation of methylcellulose, based on the data from the Dow Methocel brochure, was independent of the viscosity average molecular weight. Speaking generally, a relationship exists between viscosity and number average molecular weight and, for highly disperse systems, the ratio of the former to the latter is approximately two. This ratio decreases to one for monodisperse systems. Since the methylcellulose samples used were polydisperse (un-fractionated), it may be stated that the heats of gelation are also independent of the number average molecular weights. The common factor among the grades of Methocel listed are the number of chain ends per mole. Thus, it may be concluded that gelation involves the molecule as a whole but that the chain ends do not take part in bonding methylcellulose particles. This is not surprising, since it is to be expected that chain ends would have much greater mobility and average kinetic

energy than the bulk of the chain. From the average heat of gelation of about 30,000 cal./mole, and the approximate heat of hydrogen bonding of 7500 cal./mole, it can be calculated that on the average four moles of hydroxyl groups per mole of methylcellulose, or two hydroxyl groups per chain end, do not take part in gelation.

Mechanism of Retention

At a given temperature and a given concentration, a molecule of methylcellulose in water solution is in equilibrium with water molecules entering and leaving the outer layers of the hydration shell. Raising the temperature or increasing the concentration will shift the equilibrium and decrease the extent of the hydration shell. An equation which gives a relationship between relative viscosity and the partial specific volume of the dispersed phase of hydrophilic colloids is that of Bunits. This equation is discussed by Gortner (73). Since relative viscosity is related to concentration, this equation also gives the influence of concentration on the dispersed phase partial specific volume. The Bunits equation is: $\eta_r = (1 + 0.5\phi)/(1 - \phi)^4$, where η_r = relative viscosity and ϕ = volume fraction of the system occupied by the disperse phase. For the 400-cp. methylcellulose, the partial specific volume for 0.1 g./100 ml. concentration is 102 cc./gram and for 0.01 g./100 ml. it is 120 cc./gram. Thus, increasing the concentration of a hydrophilic colloid results in a decrease in the hydration shell.

If wood pulp is introduced isothermally into the system methylcellulose-water, the methylcellulose molecules begin to strike the surface of the cellulose (itself having a hydration layer). Most of the

methylcellulose molecules do not adhere to the cellulose because of
the protection of the respective hydration shells, which are about
40 Å. thick for methylcellulose as computed from the Kunitz equation.
Occasionally, however, methylcellulose molecules, having a much higher
energy than the average, strike the cellulose surface at a point where
the respective hydration shells are momentarily thin, and hydrogen bonds
are formed with the pulp through "bridges" of several water molecules.
These bonds are relatively easily broken since water molecules in the
outer layers of the respective hydration shells are not firmly bound.
If the methylcellulose molecules are close enough to the pulp to hydrogen
bond directly or through a single water molecule bridge, the adhesion
is a relatively stable one and only a few methylcellulose molecules are
able to escape.

As additional methylcellulose molecules strike the surface of
the pulp and form stable bonds, the point is rapidly reached where
hydrogen bonding between adjacent molecules begins to take place.
Ordinarily, when such bonds form in solution, they are rapidly broken
because of the mobility of the respective molecules. Now, however, the
bonding molecules are greatly restricted through attachment at some
point to the cellulose surface, and the comolecular bonds are much
more stable. As other molecules continue to adhere to the pulp, the
surface becomes more crowded and molecular mobility is further reduced
which, in turn, increases the stability of the comolecular bonds. Addi-
tional molecules find it increasingly difficult to penetrate the adhering
methylcellulose molecules at the pulp surface, and the rate of sorption

continues to decrease steadily. At equilibrium, there exists at the
pulp surface a semirigid structure of methylcellulose molecules,
analogous to the gel formed on heating a methylcellulose solution in
water of sufficient concentration. At low equilibrium concentrations,
the gel structure is less rigid and compact than at higher concentrations.

Increasing the concentration isothermally results in a de-
creased hydration shell, allowing a greater number of methylcellulose
molecules to possess sufficiently thin hydration shells and the requisite
energy to strike the pulp surface and adhere--in short, the rate of
sorption increases. As equilibrium is approached, the gel structure at
the fiber surface becomes more compact and rigid than at lower concen-
trations because of the greater number of molecules adhering--i.e.,
sorption is increased. This increased sorption is the result of the
decreased hydration shell resulting from bulk concentration effects,
thus allowing a closer packing at the fiber surface. As the concentration
is increased, saturation of the fiber results (at about 0.1 g./100 ml.),
because the packing at the fiber surface becomes so great that additional
molecules cannot penetrate to the fiber surface. This occurs because
the partial specific volume and, consequently, the hydration layer, as
determined by the Kunitz equation, approaches a minimum with increasing
concentration. In view of the above, the question might be raised as
to why no attempt was made to apply a Kunitz-type equation instead of
a Freundlich isotherm to the concentration-sorption data. The data
were so variable that little was to be gained by doing so. However,
future refinement of the analytical techniques might possibly show that
this equation is applicable.

The gel-like structure at the fiber surface is conceived as being somewhat oriented. The preferred orientation would seem to be with the molecules of methylcellulose perpendicular to the gross fiber surface. This is deemed most probable because the hydration layer at molecular chain ends is certainly less thick than elsewhere, and the energy possessed by such an end segment is greater on the average than other chain segments, thus making such chain ends more likely to adhere to the cellulose. The number of molecules actually sorbed is about four times less than that calculated by assuming a cross-sectional area of 100 sq. A. and a stacked railroad tie packing. This is in excellent agreement when it is considered that a 100 sq. A. cross section is probably too small for a hydrated methylcellulose molecule, even in a gel structure. Further evidence that retention involves such an orientation is given by the conclusion that chain ends are not involved in the ordinary gelation of methylcellulose on heating, and by the fact that the heat of true adsorption of -8200 cal./mole corresponds to about one gram-atom of hydrogen bonding per mole or, on the average, about one hydroxyl group per methylcellulose chain involved in true adsorption. It will be remembered that heat of retention was endothermic and comprised an endothermic heat of gelation and an exothermic heat of adsorption. Since the heat of gelation is greater in magnitude, the heat of retention must be endothermic.

The retention of methylcellulose is irreversible with respect to isothermal concentration changes because of the reduced mobility of the molecule attached to the fiber surface, which prevents rehydration and

dispersion. Decreasing the temperature below the original sorption temperature, however, results in removal of methylcellulose from the sorbed layers (Figure 13). Although decreasing the temperature decreases the mobility of the adsorbed molecules and, consequently, their likelihood of being desorbed, this is more than offset by the tendency to rehydrate and increase the equilibrium water envelope which, in turn, forces the gel structure at the fiber surface to expand and tear loose the greater part (but not all) of the adsorbed methylcellulose.

Increasing the sorption temperature increases the retention of methylcellulose, because the water shell is smaller and the packing at the fiber surface is greater. The reverse takes place at lower temperatures where the retention is less.

The presence of highly hydrated anions, such as sulfate ion in sufficient concentration, exerts a dehydrating effect on the methylcellulose molecule. The relative viscosity for a given concentration is reduced in such a salt solution and the retention of methylcellulose is greatly increased. Again, this may be associated with a smaller water shell and better packing at the fiber surface.

Average molecular weight has no specific effect on retention since, for all the samples of methylcellulose studied, the molecular weight was sufficiently great that the gel at the fiber surface could readily form and maintain a semisolid structure. It is to be anticipated that a molecular weight will be reached where the average chain length is insufficient to permit a gel to form. This should result in decreased retention.

One further remark should be made about the slow rate of methylcellulose sorption. For endothermic processes, the heat of activation for the process must be at least equal to the heat of reaction. In the over-all methylcellulose retention process, therefore, the heat of activation must be at least 21,500 cal./mole (endothermic). This heat of activation lies in the upper part of the range which Glasstone (47) describes as that of activated adsorption. This author further states that the rate of adsorption is usually relatively slow and irreversibility not uncommon.

PRACTICAL IMPLICATIONS

A brief resume of the experimental results with respect to paper mill applications will serve to point up the practical value of the present study.

In using methylcellulose as a wet-end additive, the time variable is very important. Since time to sorption equilibrium is long, methylcellulose should be added as far back in the papermaking system as is practical. This would probably be the beater or the stock chest ahead of the beater. Even then, equilibrium could not be reached in the time available from the point of application to the machine headbox, although sorption would certainly be largely complete in this time. The rate of sorption could be increased by increasing the amount of refining given to the pulp or by increasing the concentration of the methylcellulose.

Other factors may also influence the point of addition, however. Preliminary experiments indicated that sorbed methylcellulose is resistant to high rates of shear, but this aspect requires additional study. It is known, for example, that starch is scraped from cellulose fibers in passing through a Jordan. Beating and jordaning may affect methylcellulose similarly. In addition, other experiments suggested that there may be an effect of consistency on sorption and this might also raise objections to the addition of the methylcellulose to the beater, where consistencies are about 5%. A compromise would have to be reached between time, consistency, and any tendency for the beating operation to remove sorbed methylcellulose.

Mill operators will find that retention of methylcellulose will be much greater in summer when the raw water supply is warm than in winter when the water is cold. Any method of heating the water will increase retention, and it might be possible to sorb methylcellulose under such conditions that sorption can occur in warm water, followed by resuspension of the pulp in cold water. This method would take advantage of the temperature hysteresis effect noted earlier.

No difference among various grades of methylcellulose will be noted as far as retention is concerned.

Other factors being equal, increasing the beating of a given pulp or the concentration of methylcellulose will increase the extent of methylcellulose retention.

Addition of methylcellulose to the wet-end system, where the alum and rosin concentration are greatest, will enhance retention. This point will, of course, be the beater.

No problem exists with regard to diluting the stock after sorption has taken place, since no desorption will occur unless accompanied by temperature reduction.

GENERAL SUMMARY AND CONCLUSIONS

The retention of methylcellulose by various papermaking pulps
has been measured by two entirely different analytical techniques. One
method makes use of a sensitive colorimetric carbohydrate test (anthrone),
and the other method makes use of the relationship between viscosity and
concentration for highly polymeric substances. This is exemplified by
the Arrhenius viscosity equation; log relative viscosity is equal to
a constant times the concentration. In both methods, the sorption was
computed from the difference between initial and equilibrium concentrations.

It was found that the results with either analytical method
left much to be desired with respect to precision. In general, the
viscometric method gave sorptions which were twice as great as those
obtained with the anthrone method. However, it was also noted that the
same relative values were obtained with either method. For example, the
anthrone determined sorptions for bleached sulfite pulp varied from
about 1% (on the pulp) for unbeaten to 4% for well-beaten pulps, whereas
the viscosity determined sorptions varied from 2.5-7.5%.

The reasons for this variability in each of the analytical
techniques were discussed in detail. It was concluded that the viscosity
method gave results which were more nearly absolute than the anthrone
method, but that either method gave comparative data. The variability
with either method was apparently not due to temperature fluctuations,
bacterial degradation, lack of a stable equilibrium system, or variation
in weights of pulp samples. The possibility that the pulp samples were

not uniform with respect to fiber size distribution was suggested, since the pulps had been dewatered from the beater by filtration, in which operation there is a distinct probability that pulp fines concentrated at the pulp-filtering medium interface. Although the filtered pulp pads were pulled apart into small tufts and mixed thoroughly before sampling, the tufts were hardly small enough to assure an absolutely uniform pulp for a sample of only one gram of ovendry pulp (about five grams of wet pulp). Larger samples would minimize this variation.

It was postulated that another factor which could contribute to the anthrone variability, and which could also account for the difference in sorption level between anthrone and viscosity, was the probable increase in concentration of pulp fines present in the settled supernatant liquor of the system pulp-methylcellulose-water over that of pulp-water alone. This was considered probable since methylcellulose has been shown to be a good deflocculating agent, and the settled turbidities of pulp-methylcellulose-water were greater and persisted longer than the turbidities of the pulp-water system. The Celite filters were therefore subjected to a greater load for the actual samples than they were for preliminary tests with mixtures of pulp-water supernatant liquor and methylcellulose solutions. It is probable that cellulose fines penetrated the filters and increased the apparent concentration of methylcellulose in the filtrate. This would result in a higher equilibrium concentration and a lower sorption.

The over-all variability in the viscosity method was thought to be a combination of the variability as the result of the residual viscosity

and that due to nonuniform distribution of pulp fines in the samples.
It was previously shown that the pulp residual viscosity could be re-
moved by extraction with hot or boiling water, and this is recommended
for future investigations. The problem of obtaining a uniform pulp sample
is a very difficult one, because it is necessary to keep the pulp wet
(i.e., at least 40% moisture) in order to avoid irreversible drying
effects, and such pulp is difficult to mix thoroughly and intimately.
Perhaps the pulp from the beater could be dewatered on a muslin-covered
wash box and mixed completely at the same time. After the pulp had
attained 12-15% consistency, it could be pressed to remove additional
moisture without much segregation of the fines. The pulp should then
be picked apart into small tufts and again mixed before storage.

Studies of the effect of time on the retention of methylcellulose
by pulps showed that the sorption required a period of 180 hours to attain
equilibrium for 1% additive on the pulp at 0.5% consistency. However,
for beaten pulps sorption was 70% complete in two hours. The rate of
sorption increased with beating because of the resulting greater pulp
specific surface, and with the initial concentration of methylcellulose.
Retention could be fitted to a parabolic equation $X/M = at^h$, where X/M
is the sorption in grams per 100 grams pulp, t is the time in hours, and
a and n are constants. n was approximately the same for all the pulps
studied and had an average value of 0.12. a depended on the degree of
beating and the initial concentration. It was pointed out that this
equation is applicable only to the earlier stages of sorption because
it does not indicate an equilibrium condition, although constant sorption
was shown to occur.

Retention of methylcellulose increased with increasing degree
of beating and increasing equilibrium concentration. The data could be
reasonably well represented by equations of the Freundlich and Langmuir
isotherm type, but the analytical variability was such that positive
conclusions could not be drawn. It was suggested that the constant n
in the Freundlich isotherm indicated that retention was confined to
lines on the cellulose surface. The retention of methylcellulose for
well-beaten pulps was generally found to be three to four times the
retention of unbeaten pulps. From this evidence and theoretical con-
siderations of molecular dimensions, it was concluded that the retention
of methylcellulose is a true adsorption and is a function of the surface
present.

Comparison of various pulps at similar degrees of beating
showed that bleached sulfite pulp had the greatest sorptivity, followed
closely by bleached kraft and unbleached sulfite. Cotton linters and
unbleached kraft retained much less methylcellulose than the other pulps.
It was pointed out that relative sorptivity corresponded with relative
hydrophilic character of the pulps, and the hypothesis was advanced that
the hydrophilic nature of the pulp surface influences retention greatly.

Experiments with four viscosity grades of methylcellulose
having molecular weights varying from 31,000 to 126,000 indicated no
significant differences between the grades with respect to retention by
770-cc. S.-R. bleached sulfite pulp. The viscosity method showed a much
greater retention of ethylcellulose than the methylcellulose, but the
anthrone method indicated no difference. It was concluded that the anthrone

method was more comparatively correct in this instance, and that there was no particular effect of alkoxyl groups on retention.

Four per cent rosin and 6% alum on the pulp at 0.5% consistency had no effect on the retention of the methylcellulose. For the combination of rosin and alum, viscosity indicated a significant effect, whereas anthrone did not. Again, it was shown that anthrone was more probably correct, and it was concluded that rosin and alum in the concentrations used did not affect retention. Alum concentrations of 60 and 600% on the pulp, however, greatly increased retention of methylcellulose which, for the latter concentration, was almost quantitative. This can be explained by the dehydrating effect of the sulfate ion on the methyl-cellulose. Gross precipitation was not involved, because the addition of the alum to the methylcellulose solution alone caused no coagulation.

Retention of methylcellulose was shown to be irreversible with respect to decreasing concentration under isothermal conditions. In brief, methylcellulose will sorb but not desorb. Lowering the tempera-ture, however, results in removal of some of the methylcellulose from the fiber. A temperature hysteresis effect was thus demonstrated for descending temperatures.

The effect of temperature on sorption was investigated and found to be greater than the effect of beating. Raising the temperature from 25° to 38° C. doubled the retention of methylcellulose as determined by viscosity for 570-cc. S.-R. sulfite pulp. Sorption isotherms were run at 38°, 25°, and 3.3° C. by the anthrone method, and the heat of retention was determined from these data by the use of a modified

Clausius-Clapeyron equation. This heat of retention was found to be 21,500 cal./mole (endothermic). From the Dow Methocel brochure, data were obtained which enabled a calculation of the heat of gelation of methylcellulose. This was about 29,700 cal./mole (endothermic) and was independent of molecular weight. The hypothesis was advanced that retention of methylcellulose is a combination of an endothermic gelation process and an exothermic adsorption process. The heat of retention, therefore, is equal to the sums of the heat of gelation and the heat of adsorption. Since the heats of retention and gelation were known, the heat of adsorption could be calculated to be -8200 cal./mole (exothermic).

Some miscellaneous experiments on sorption volume change, sorption by cellophane, and the effect of consistency and high rates of shear on retention were reviewed briefly.

A suggested theory of retention of methylcellulose by pulps was advanced which accounts for the observed phenomena. It was suggested that methylcellulose is oriented at the fiber surface, and that the molecular chain ends of the methylcellulose are principally involved in retention. The effect of increasing concentration, increasing temperature, and increasing salt concentration is to decrease the hydration shell around the methylcellulose molecule, which permits a closer packing at the fiber surface and an increased sorption. It would be anticipated that the effect of these variables would decrease in the order salt, temperature, and concentration, and this was experimentally observed.

Practical implications of the present study were discussed, and it was concluded that methylcellulose should be added to the paper-making system as far back in the wet end as possible, and that the warmer the mill water, the better the retention. Beater addition was considered advantageous with respect to concentration of additive and salts present, and possibly disadvantageous with respect to consistency and beating effects.

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