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DETERMINATION OF INTRINSIC VISCOSITY OF STARCHES¹

HARRY W. LEACH²

ABSTRACT

The following improvements are recommended in the determination of intrinsic viscosity of starches: 1) the size 50 Cannon-Fenske capillary viscometer should be used to eliminate viscometer errors; 2) unmodified starches must be pregelatinized in hot water before they are dissolved in 1N sodium or potassium hydroxide; 3) all starch solutions must be clarified by centrifugation or filtration prior to determination of viscosity; 4) while various common methods of graphical analysis give the same results, intrinsic viscosity is preferably derived by plotting inherent viscosity against concentration.

Intrinsic viscosity is essentially a measure of the internal friction or resistance to displacement of high-polymeric molecules in solution. If properly used on a homologous series of a single molecular type, it provides an excellent criterion of relative molecular size. In fundamental starch studies, intrinsic viscosity has become the most useful and widely accepted index of molecular dimensions. Although time-consuming, the procedure is very simple, equipment requirements are modest, and results are precise and interpretable. Since the viscosities are run at very low concentrations and data are extrapolated to infinite dilution, the effects of associative bonding or molecular entanglement are presumably minimized.

However, the starch literature shows a wide diversity of methods for determining intrinsic viscosity, with respect to the solvents employed; the mode of solution of the sample, and the size and type of capillary viscometer used. The choice of viscometer size is particularly confused. Too frequently, the capillary size is omitted from published data on intrinsic viscosity. Even where this information is provided, the viscometer size usually appears much too large for the intended use.

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²Moffett Technical Center, Corn Products Company, Argo, Illinois.

Purposes of the present study were as follows: 1) to determine the dependency of intrinsic viscosity on capillary size by use of representative starchy materials, 2) to ascertain whether differences between viscometers can be eliminated by calibration against known viscosity standards, and 3) to explore methods for effecting solution of the starch sample.

Materials

The following commercial starch products were used: unmodified corn and potato starches, 80-fluidity acid-modified corn starch, and "Ramalin" branched fraction from potato starch (Stein, Hall & Co.). These diverse materials represent respectively two difficultly dispersible granular starches, a readily soluble thin-boiling starch, and a branched fraction which is devoid of any residual granule structure.

Required solutions are 1.00*N* and 5.00*N* potassium hydroxide. These should be titrated and adjusted within 1% of the stipulated values. Alternatively, sodium hydroxide may be substituted, since it effects exactly the same solubilization of the starch and yields the same intrinsic viscosity values as potassium hydroxide.

Routine Cannon-Fenske viscometers were employed, of capillary sizes 50, 75, 100, and 150. Viscosities were run in a constant-temperature bath maintained within $\pm 0.05^\circ\text{C}$. of the stipulated temperature.

Methods and Results

Calibration of Viscometers. The viscometers were calibrated in kinematic viscosity (i.e., centistokes) against distilled water and sucrose solution, 20.00% by weight (2). Flow time of each liquid was determined at 25.0°, 30.0°, and 35.0°C., to give a six-point calibration for each viscometer over the range of 0.7 to 1.6 centistokes. For converting absolute centipoise values to kinematic centistokes, densities of water were obtained from handbook tables, and densities of the sucrose solution were determined at each temperature with a pycnometer. Analysis of these data gave the general calibration equation, $\nu = kt - x$, where ν is the kinematic viscosity in centistokes, k is the slope of the linear relationship in centistokes per second, t is the flow time in seconds, and x is the negative intercept in centistokes on the zero-time axis (Fig. 1). Data for the viscometers used in these studies are as follows:

Viscometer Size	Flow Time of Water at 35°C. sec.	Equation Constants	
		k	x
50	196.8	0.003727	0.0026
75	94.6	0.007929	0.0175
100	46.0	0.01679	0.0397
150	23.7	0.03516	0.1017

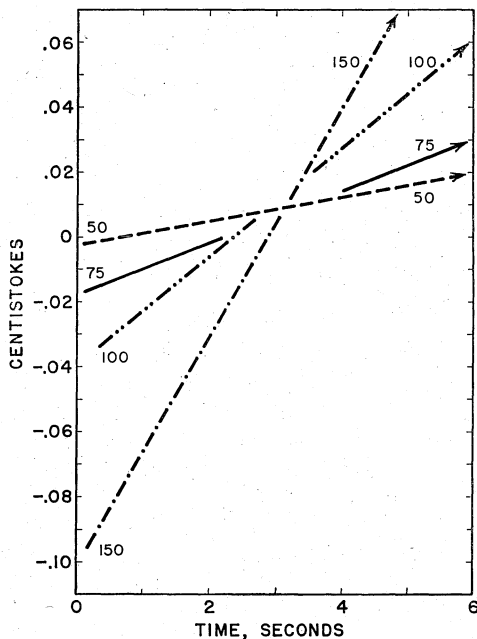


Fig. 1. Lower portions of linear calibrations of various viscometers, showing intercepts on zero-time axis.

Average deviations of the six calibration points from strict linear adherence to the above equation were 0.18, 0.17, 0.12, and 0.28% for the size 50, 75, 100, and 150 viscometers, respectively. The above equation constants are therefore well within the required accuracy in the range of 0.7 to 1.6 centistokes used for intrinsic viscosity determination. When calibration data were expressed in absolute viscosity (i.e., as centipoises), deviations from strict linearity were substantially higher, namely, 0.82 to 0.92%. For this reason, kinematic viscosities were used in the present study, even though no correction for solution density is actually required in the determination of intrinsic viscosity.

As a check on the accuracy of the above constants, the average kinematic viscosities (by all four viscometers) of 1N potassium hydroxide and 1N sodium hydroxide at 35°C. were 0.788 ± 0.002 and 0.865 ± 0.002 centistokes, respectively. These show excellent agreement with values of 0.786 and 0.864, as calculated from data of Hitchcock and McIlhenny (6).

Solution of Starch Samples. The starch samples were dissolved by the method of Lanski *et al.* (7). This involves suspending the weighed sample in water, cooking the stirred paste for 30 min. in a boiling

water bath, cooling to room temperature, and adding 5N potassium hydroxide to give a final alkali concentration of 1.00N. According to this procedure, the final starch solution is filtered through fine glass-wool to remove traces of fiber or other undissolved material. This mode of filtration did not adequately remove suspended insolubles which impede flow in the smaller capillaries. However, by centrifuging the alkaline solution for 5 min. at 2,200 r.p.m. (900 g), any haze was removed, and a minute trace (1-3 mg.) of insoluble sediment was deposited. Microscopic examination showed the latter to be very fine fiber, less than 35μ in size. Incidentally, viscosity determinations before and after centrifugation provide an excellent criterion of total solubilization of the starch. An appreciable decrease in viscosity indicates removal of swollen but invisible aggregates, which block the capillary and therefore increase the apparent viscosity.

As an alternative procedure, the starch solution may be suction-filtered through a fritted glass filter of medium porosity (10- to $15\text{-}\mu$ pore size). This technique is more rapid than centrifugation, but it can only be used with modified starches whose viscosity is sufficiently low to permit rapid filtration without significant evaporation losses.

Various unsuccessful attempts were made to dissolve the starch directly in cold 1N alkali, without the intermediate pregelatinization in hot water. While this may be feasible with the individual starch fractions and with various thin-boiling products, all unmodified granular starches must first be pasted in hot water prior to solution in alkali. In various tests, 0.2-0.4 g. of corn starch was dispersed by stirring for 10-60 min. in cold 1.0-2.5N alkali. In all cases, hazy "grainy" dispersions were obtained which gave gel-like sediments on centrifuging, obviously indicating the presence of a substantial amount of swollen starch particles. Also, centrifugation reduced the viscosity of these dispersions by 10 to 20%, owing to removal of this undissolved swollen material.

Determination of Intrinsic Viscosity. Solutions of the four representative starch products were prepared in 1N potassium hydroxide at the concentrations specified below, and then clarified by the indicated procedure:

<i>Starch Product</i>	<i>Concentration</i> g./100 ml.	<i>Clarification</i>
Unmodified potato starch	0.3	Centrifuged
Unmodified corn starch	0.4	Centrifuged
"Ramalin" branched fraction	0.5	Filtered
80-Fluidity corn starch	1.0, 2.0	Filtered

Flow times were determined at 35.0°C. with each of the four calibrated viscometers, using the above solutions at five or more different

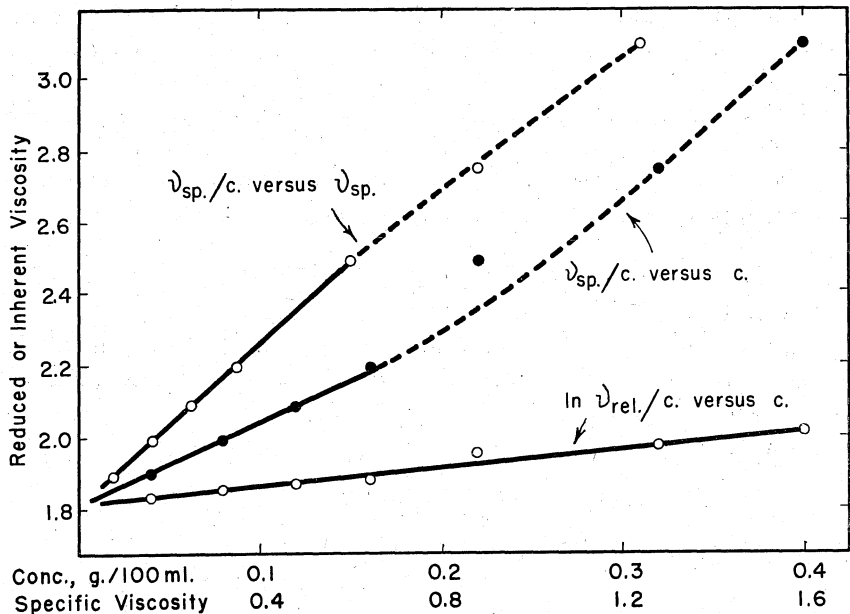


Fig. 2. Modes of determining intrinsic viscosity of corn starch.

dilutions to cover a fivefold range in concentration. Flow time data were converted to kinematic viscosities (in centistokes) by means of the appropriate viscometer constants, and these values then expressed as relative viscosity (v/v_0) or as specific viscosity ($(v/v_0) - 1$) with respect to the kinematic viscosity (v_0) of the 1N potassium hydroxide solvent.

Intrinsic viscosities were obtained by three different methods of graphical analysis of data, in each case extrapolating to the zero abscissa (Fig. 2):

A) Reduced viscosity (i.e., specific viscosity divided by starch concentration) versus concentration:

$$\left[\frac{v_{sp}}{c} \right]_{c \rightarrow 0}$$

B) Inherent viscosity (natural log of relative viscosity, divided by concentration) versus concentration:

$$\left[\frac{\ln v_{rel}}{c} \right]_{c \rightarrow 0}$$

C) Reduced viscosity versus specific viscosity:

$$\left[\frac{v_{sp}}{c} \right]_{v_{sp} \rightarrow 0}$$

These systems of plotting have been used by various investigators (4,5,8) to determine the intrinsic viscosity of starch fractions. As shown in Table I, values for intrinsic viscosity by these three methods did not generally differ to a significant degree. The preferred technique is method B (i.e., inherent viscosity vs. concentration), for two reasons: 1) the relation is linear up to higher starch concentrations, and 2) the lower slope of the plot permits more precise extrapolation (Fig. 2).

Discussion and Conclusions

A very general error in determining intrinsic viscosity is the use of a capillary viscometer with too fast a flow time for the fluid measured. The ranges in which the various routine Cannon-Fenske viscometers may be used are specified by the manufacturer (3) as follows:

<i>Size</i>	<i>Approx. Centistokes per Second</i>	<i>Operable Range</i> <i>centistokes</i>
50	0.004	0.8-3.2
75	0.008	1.6-6.4
100	0.015	3-12
150	0.035	7-28

In other words, no flow-time measurement in a Cannon-Fenske viscometer should be less than 200 sec. (1). If a liquid passes through a particular viscometer in a shorter time, then a capillary of smaller bore should be substituted.

The reason for this stipulation becomes obvious from Fig. 1, which shows the lower portions of the calibration curves for each instrument. None of the extrapolated curves passes through the zero-zero origin, and the intercept on the zero-time axis (i.e., the correction x in the calibration equation) increases progressively as the capillary bore increases. In the case of those viscometers of large capillary bore, too much of the potential energy of the hydrostatic head is wasted in various side actions which do not assist the flow of liquid through the capillary: 1) turbulent flow at the entry to and exit from the capillary, 2) acceleration of the liquid from rest to high-speed flow in the capillary, and 3) expenditure of energy in the form of frictional heat. The net effect of these side actions is to retard the flow in the capillary and thus increase the apparent viscosity. Hence, at a level of 1.00 centistoke, the errors for the specific 50, 75, 100, and 150 viscometers used are 0.26, 1.75, 3.97, and 10.17% (i.e., the corrections x for each viscometer).

Universal practice is to calculate intrinsic viscosity directly from

raw flow-time data in seconds. Comparison of results by this method with those obtained from corrected kinematic data shows that the error decreases progressively as the capillary bore becomes smaller (Table I). With the No. 50 viscometer, the difference between cor-

TABLE I
EFFECT OF CAPILLARY SIZE, VISCOMETER CORRECTION, AND MODE OF PLOTTING ON THE INTRINSIC VISCOSITY

STARCH	VISCOMETER SIZE	UNCORRECTED INTRINSIC VISCOSITY ^a	CORRECTED INTRINSIC VISCOSITY ^b			
			Mode of Plotting			Average
			A	B	C	
Unmodified potato starch	50	2.73	2.72	2.72	2.72	2.72
	75	2.58	2.66	2.63	2.66	2.65
	100	2.41	2.55	2.55	2.55	2.55
	150	2.20	2.55	2.55	2.55	2.55
Unmodified corn starch	50	1.81	1.81	1.81	1.81	1.81
	75	1.71	1.71	1.76	1.75	1.74
	100	1.63	1.66	1.74	1.73	1.71
	150	1.46	1.61	1.73	1.69	1.68
"Ramalin" branched fraction	50	1.08	1.08	1.08	1.08	1.08
	75	1.03	1.05	1.05	1.05	1.05
	100	0.98	1.03	1.02	1.04	1.03
	150	0.91	1.03	1.02	1.04	1.03
80-Fluidity corn starch	50	0.27	0.27	0.27	0.27	0.27
	75	0.27	0.27	0.27	0.27	0.27
	100	0.27	0.27	0.27	0.27	0.27
	150	0.24	0.27	0.27	0.27	0.27

^a Average values by the three modes of plotting, using flow time data directly.

^b Corrected by appropriate viscometer calibration equation.

rected and uncorrected values vanishes. Hence, by using this smaller capillary, there is no necessity to calibrate the viscometer against known liquids, and raw flow-time data can be used directly. These same considerations necessarily apply to the use of the Cannon-Ubbelohde viscometer.

However, even when data are corrected for viscometer errors, the intrinsic viscosities still show a considerable dependency on capillary size, increasing as the bore is decreased (Table I). These anomalies are attributed not to the viscometer itself, but rather to the inherent "misbehavior" of high-polymeric molecules in solution, including such factors as the following:

- 1) Excessive inertia of large spatially-extended molecules, whereby the solvent may flow *through* the solute, rather than the solute flowing *with* the solvent;
- 2) Deformation and probable rotational motion of the large molecules in the flow gradients within the capillary;
- 3) Momentary association, entanglement, and clumping of molecules,

to give an extended network even at very high dilution.

- 4) "Molecular domain" of fully solvated starch molecules appears to correspond to a concentration of about 0.15%. At this concentration, all of the solvent molecules are within the outer boundaries of the extended starch molecules, which then have no free space in which to move.

All of these flow-retarding actions have an increasing influence as the molecular dimensions of the solute increase and as the capillary bore decreases. These high-polymer influences cannot be eliminated or compensated for merely by calibrating the instrument against such simple substances as water and sucrose solutions, which do not exhibit anomalous misbehavior. In the strictest sense, it is not possible to obtain any "true" viscosity measurement on starch which is totally free of instrument influences, reaction between solute molecules, and solute-solvent interaction.

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