

Effect of Temperature on Viscosity of Amylose

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Synopsis

Viscosity parameters were obtained for maize amylose (molecular weight of 107,000) in 1N KOH at 25, 30, 35, and 40°C. Intrinsic viscosity continuously decreased and Huggins' constant k' continuously increased with increasing temperature. The temperature dependence of intrinsic viscosity, $d[\eta]/dT$, was $-2.12 \times 10^{-2}/^{\circ}\text{C}$.

The effect of temperature on the viscous behavior of amylose has been investigated in several solvents. Cowie¹ reported that the intrinsic viscosity of amylose decreased with rising temperature in solutions of formamide and dimethyl sulfoxide (DMSO). However, in solutions of aqueous KCl there was almost no temperature effect. Banks and Greenwood² also noted that the intrinsic viscosity of amylose remained constant in aqueous KCl solutions at different temperatures. They found the temperature effect to be indifferent for amylose in solutions of sodium acetate and pure water as well. On the other hand, Burchard³ reported that the intrinsic viscosity of amylose in water decreased with increasing temperature. Similar decreases, of greater magnitude, were also found in formamide, DMSO, and ethylenediamine.³

No studies have been made of the temperature relations of viscosity of amylose in aqueous KOH. This lack seems especially pronounced because 1N KOH is the classic solvent for amylose.

Materials and Methods

Nepol amylose was obtained from the Staley Mfg. Co. (Decatur, Ill.). This material is separated from a heated suspension of maize starch in water by holding at a lower, but still relatively elevated, temperature to precipitate the solubilized amylose.⁴ The method of Schoch⁵ was followed in purifying the amylose, first with amyl alcohol and then by several fractionations with *n*-butanol. After the second fractionation, the iodine affinity⁵ reached a value of 20.4 g. iodine/100 g. sample. Subsequent fractions did not increase this value. A third fractionation was carried out, and then the precipitated amylose was mixed with 10 times its volume of *n*-butanol and stirred 48 hr. at 3°C., the solvent being changed every 12 hr. The sample was further mixed with ethanol at room temperature,

again stirred for 48 hr., dried in air, and then defatted with ethanol for 48 hr. on a Soxhlet apparatus. Final drying was performed under 100 mm. Hg vacuum at 70°C.

Molecular weight was estimated by evaluating intrinsic viscosity in solutions of 0.5*N* KOH⁶ and 1*N* KOH.⁷ The amylose was dispersed in the aqueous KOH solutions under a nitrogen atmosphere and centrifuged at 10,000*g* for 15 min. to remove impurities. Outflow times were measured to 0.1 sec. with Ostwald-Fenske viscometers in a water bath held at 25 ± 0.01°C.

Temperature effects on intrinsic viscosity were determined in 1*N* KOH, with 30 min. equilibration time permitted for each 10-ml. sample charge. The temperatures used were 25, 30, 35, and 40°C. In order to test whether any degradation might occur at the higher temperatures, outflow time was measured for one sample (after the usual equilibration at each temperature) first at 25°C., then at 40°C., and finally again at 25°C. The outflow time at the end was the same as at the beginning of the testing.

Results and Discussion

Duplicate series of molecular weight (MW) determinations for each of the two KOH concentrations gave average values of 96,000⁶ and 118,-100.⁷ In 1*N* KOH the intrinsic viscosity was 1.39 dl./g., close to the values of 1.34–1.37, determined by Montgomery et al.⁸ for maize amylose under the same conditions.

For the different temperatures, both the intrinsic viscosity and Huggins' constant k' ⁹ are given in Table I. Experimental results are shown in Figure 1. The temperature dependence of intrinsic viscosity, $d[\eta]/dT$, may be calculated from the rectilinear slope of that relationship as $-2.12 \times 10^{-2}/^\circ\text{C}$.

TABLE I
Viscosity Parameters for Amylose in 1*N* KOH

Temperature, °C.	Intrinsic viscosity, dl./g.	Huggins' constant k'
25	1.39	0.19
30	1.29	0.20
35	1.21	0.48
40	1.07	0.88

Similar values of $d[\eta]/dT$ (-1.7 to $-2.4 \times 10^{-2}/^\circ\text{C}$.) were obtained for ethyl cellulose (MW = 119,000–140,000) in organic solvents.¹⁰ Cowie's¹ values of $d[\eta]/dT$ for amylose in DMSO ranged from -0.23 to $-1.90 \times 10^{-2}/^\circ\text{C}$. and in formamide from -0.13 to $-0.70 \times 10^{-2}/^\circ\text{C}$. The more negative values were obtained with greater chain lengths^{1,10} and were therefore interpreted as indicating greater flexibility of the molecule. This evaluation suggests that the amylose molecule is far more flexible

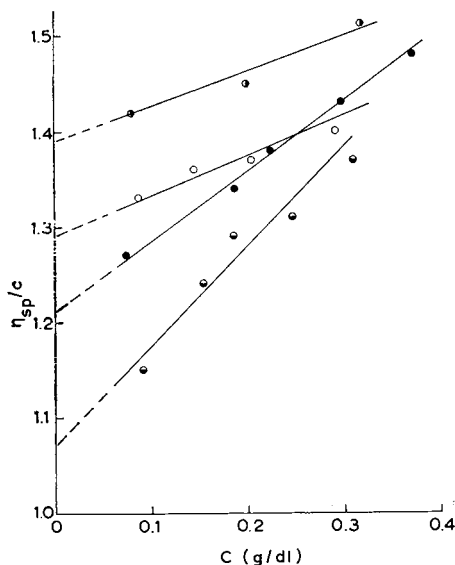


Fig. 1. Experimental averages for values of η_{sp}/c at different concentrations for the temperatures used in this study: (●) 25°C.; (○) 30°C.; (●) 35°C.; (◐) 40°C.

(i.e., more sensitive to temperature change) in 1*N* KOH, in which $d[\eta]/dT$ for molecules of MW = 100,000 is $-2.12 \times 10^{-2}/^{\circ}\text{C}$., than in DMSO, in which $d[\eta]/dT$ for molecules of MW = 3,050,000 is $-1.90 \times 10^{-2}/^{\circ}\text{C}$.¹ Thus, the difference in flexibility of the polymer molecule actually may be reflecting differences in the effectiveness of solvation: Burchard's³ data for $d[\eta]/dT$ for amylose in water, formamide, DMSO, and ethylenediamine were -0.30 , -0.50 , -0.70 , and $-0.92 \times 10^{-2}/^{\circ}\text{C}$., respectively.

Simha¹¹ calculated that k' is approximately 2.0 for uncharged spheres, a value that was confirmed experimentally by Cheng and Schachman.¹² Lower values of k' occur in good solvents, in which the molecule becomes more extended.¹³ This study shows that k' increases very markedly with increasing temperature. It can be inferred that as the temperature rises in the amylose-KOH system, the polymer molecule becomes less extended and increasingly quite coiled. Although Moore and Brown¹⁰ found a discrepant decrease of k' with increasing temperature, they nevertheless also concluded (on other grounds) that chain extension decreased as the temperature increased.

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Résumé

Les paramètres de viscosité ont été obtenus pour l'amylose de maïs (poids moléculaire de 107.000) dans KOH *N/1* à 25°, 30°, 35° et 40°C. La viscosité intrinsèque décroissait continuellement et la constante k' d'Huggins croissait continuellement avec une température croissante. La dépendance de la viscosité intrinsèque en fonction de la température $d(\eta)/dT$ était de $-2.12 \times 10^{-2}/^{\circ}\text{C}$.

Zusammenfassung

Viskositätsparameter wurden für Maisamylose (Molekulargewicht 107.000) in *N/1* KOH bei 25, 30, 35 und 40°C erhalten. Die Viskositätszahl nahm mit steigender Temperatur kontinuierlich ab, und die Huggins-Konstante nahm kontinuierlich zu. Die Temperaturabhängigkeit der Viskositätszahl $d[\eta]/dT$ betrug $-2,12 \cdot 10^{-2}$ pro °C.

Received December 3, 1965

Revised January 10, 1966

Prod. No. 1352