

Weighted Intrinsic Viscosity Relationships for Polysaccharide Mixtures in Dilute Aqueous Solutions

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Synopsis

The weighted intrinsic viscosities of polysaccharide mixtures in dilute aqueous solutions have been studied. The purpose of this investigation is to demonstrate that average intrinsic viscosities would scale with the weight fraction of the individual components for polysaccharide mixtures in 0.5N NaOH_(aq). The polysaccharides examined in this study were composed of polymers differing in their molecular weights, degree of branching, and bond linkages. Excellent agreement between theory and experiment was observed for the three different mixed polymer systems examined. This observation validates certain aspects of proposed theoretical treatments which employ this fundamental assumption and allows for further advances in experimental analytical developments of water-soluble polymer systems.

INTRODUCTION

It is generally recognized that polymer properties are ultimately related to the material's fundamental molecular parameters. These parameters include molecular weight, chemical composition, the nature of polymer branching, and many others. The importance of these parameters has motivated the development of several analytical measurement methods capable of determining these parameters. Among these techniques, size exclusion chromatography (SEC)^{1,2} coupled to various on-line detectors has been shown³ to provide much of this fundamental information for soluble polymer samples. More specifically, on-line light scattering (LS) and intrinsic viscosity ($[\eta]$) measurements have proven most useful in these applications. We have shown^{4,5} theoretically that $[\eta]$ and low-angle laser light scattering (LALLS) coupled to SEC can be used to determine absolute weight-average molecular weight, molecular weight distributions, as well as quantitative information about polymer branching. Experimental data were presented recently^{4,5} employing the combined SEC/LALLS technique for polysaccharide samples that are mixtures of linear and branched or variously branched polymers consistent with theory. Our theoretical developments are not restricted to branching analysis and may also be applied to copolymer analysis,^{5,6} although this latter work is not yet completed experimentally.

One assumption that is made by us⁵ within our theoretical development, is that average polymer solution viscosities scale with the weight fraction of the

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individual components in the polysaccharide samples:

$$[\eta]_m = \sum w_i [\eta]_i \quad (1)$$

where: w_i = mass fraction of polymer mixture component i in the sample mixture

$[\eta]_i$ = intrinsic viscosity of polymer component i in the sample mixture

A similar assumption has been proposed by Pannell.⁷ With this assumption, we have been able to advance polymer branching characterization both theoretically and experimentally. However, as reported by several authors,⁸⁻¹¹ Eq. (1) is only valid when there is no special interaction between the polymers in solution. For example, Eq. (1) has been shown to be valid for the case of mixtures of homologous polymers with different molecular weights.^{12,13} If incompatible polymers are mixed, because of attraction and repulsion forces, the conventionally determined intrinsic viscosity of a polymer mixture, $[\eta]_m$, may appear higher or lower than that calculated from Eq. (1).^{8,11} The linear and branched components of starch are similar chemically, and they are unlikely incompatible with each other. But retrogradation (association) phenomenon is known to occur for amylose in water¹⁴ and hence, it is possible that polymer-polymer interaction may exist even in aqueous NaOH solvent and potentially interfere in analytical characterization experiments. Therefore, it is necessary to test polysaccharide compatibility in NaOH_(aq) solvent; the solvent used as eluent for our SEC/LALLS system. The purpose of this research is to determine the validity of Eq. (1) for polysaccharide mixtures in basic aqueous solutions.

EXPERIMENTAL

The specific polysaccharides used were amylose, amylopectin, glycogen, and dextran. Amylose is a linear α -(1,4) linked polysaccharide and was supplied by Serva, Germany (Lot No. 13470). The branched polymers, amylopectin and glycogen are primarily linked via α -(1,4) bonds with about 4-5% and 10% α -(1,6) branches, respectively.^{15,16} These materials were obtained from the Sigma Chemical Co. (St. Louis, MO). Dextran is a mostly linear α -(1,6) linked polysaccharide but contains a few percent α -(1,3) and α -(1,4) short side chains of 1-2 glucose units in length. In this experiment, high- and low-molecular weight dextrans were used. The nominal molecular weights were 500,000 and 70,000 referred to as T500 and T70, respectively. The supplier (Pharmacia Fine Chemicals, Piscataway, NJ) used light scattering to determine the reported molecular weights.

The polymer solutions were prepared by dissolving known mass quantities of the polysaccharides in 0.5*N* NaOH aqueous solution and diluting to a given concentration by volume. The solutions were then filtered through a sintered-glass filter to remove dust particles.

For the intrinsic viscosity studies, several compositional blends of polysaccharide mixtures were prepared. The polysaccharide mixtures investigated

were composed of polymers differing in the degree of branching, bond linkages, and molecular weight. These samples were amylose/amylopectin mixtures, amylose/glycogen mixtures, high-molecular weight dextran (T500)/low-molecular weight dextran (T70) mixtures, and amylose/dextran (T500) mixtures.

Ostwald-Fenske-type viscometers were used in a constant temperature viscometer bath at $30^\circ \pm 0.01^\circ\text{C}$. In order to assume negligible kinetic energy correction, viscometers in which the solvent flow time was greater than 100 s were selected. At least three determinations were made for each sample tested and the flow times agreed to within 0.2 s in all cases.

For each sample, measurements were performed at different concentrations as described elsewhere.¹⁷ For each solution, values of η_{sp} , η_{sp}/c , $\ln \eta_r/c$ were calculated. The intrinsic viscosity, $[\eta]$, was then found by the double extrapolated values of $\ln \eta_r/c$ and η_{sp}/c .

RESULTS AND DISCUSSION

The basic polymer parameters studied are polymer molecular weight, polymer branching, and polymer linkage flexibility. In all cases, the doubly

TABLE I
Intrinsic Viscosities of Polysaccharides Mixtures

Sample	$[\eta]$ (dL/g)
T500:T70 = 1:0	0.507
T500:T70 = 4:1	0.470
T500:T70 = 3:2	0.420
T500:T70 = 2:3	0.349
T500:T70 = 3:7	0.307
T500:T70 = 1:9	0.252
T500:T70 = 0:1	0.247
AMY:GLY = 1:0	0.950
AMY:GLY = 4:1	0.851
AMY:GLY = 3:2	0.635
AMY:GLY = 2:3	0.468
AMY:GLY = 1:4	0.328
AMY:GLY = 0:1	0.071
AMY:AMP = 1:0	0.950
AMY:AMP = 4:1	1.120
AMY:AMP = 3:2	1.182
AMY:AMP = 2:3	1.535
AMY:AMP = 1:4	1.660
AMY:AMP = 0:1	1.840
AMY:T500 = 1:0	0.949
AMY:T500 = 4:1	0.860
AMY:T500 = 3:2	0.738
AMY:T500 = 2:3	0.677
AMY:T500 = 3:7	0.618
AMY:T500 = 1:4	0.534
AMY:T500 = 1:9	0.520
AMY:T500 = 0:1	0.507

Abbreviations: AMY—Amylose; AMP—Amylopectin; GLY—Glycogen; T500—Dextran MW = 500,000; T70—Dextran MW = 70,000.

extrapolated values of:

$$\lim_{c \rightarrow 0} \frac{\ln(\eta_r)}{C} = [\eta] \quad (2)$$

and

$$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{C} = [\eta] \quad (3)$$

were used to determine $[\eta]$ relationships, in accordance with the Huggins¹⁸ and Kraemer¹⁹ relations. In all cases, the values of the intrinsic viscosities agreed to within 0.01 dL/g. The intrinsic viscosities of each sample tested and calculated are given in Table I and plotted as a function of polymer sample weight fraction in Figures 1-4. A least-squares (solid line) analysis of the data, along with the statistical correlation coefficients, are also shown.

In this study, only two different polymer types were included in each system tested. In these cases, Eq. (1) simplifies since

$$i = 1 \text{ or } 2$$

and thus

$$w_2 = (1 - w_1)$$

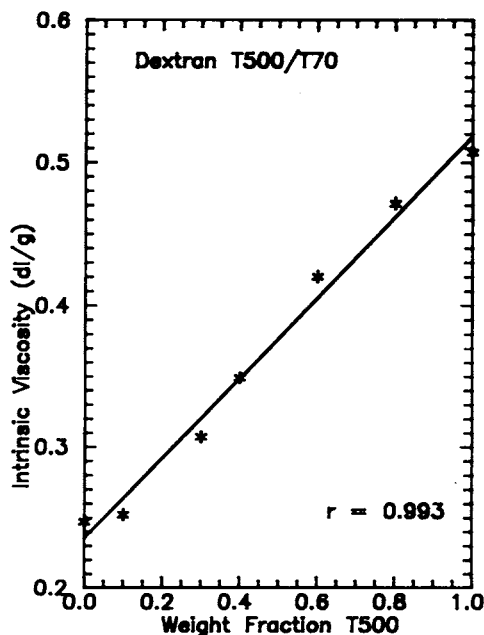


Fig. 1. Plot of intrinsic viscosity vs. weight fraction of T500 for dextran T500/T70 mixtures. $r = 0.993$.

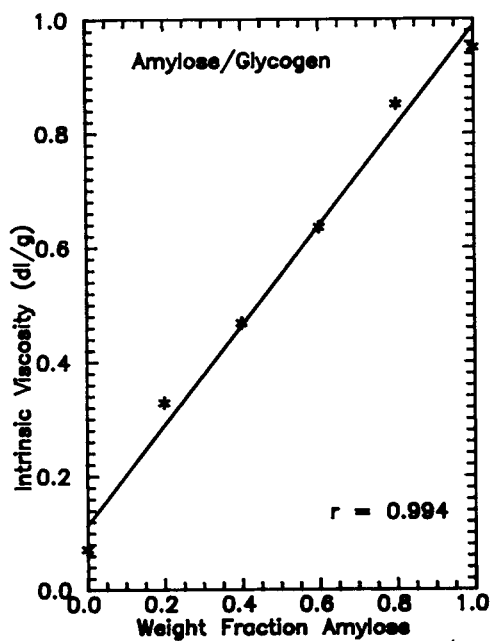


Fig. 2. Plot of intrinsic viscosity vs. weight fraction of amylose for amylose/glycogen mixtures. $r = 0.994$.

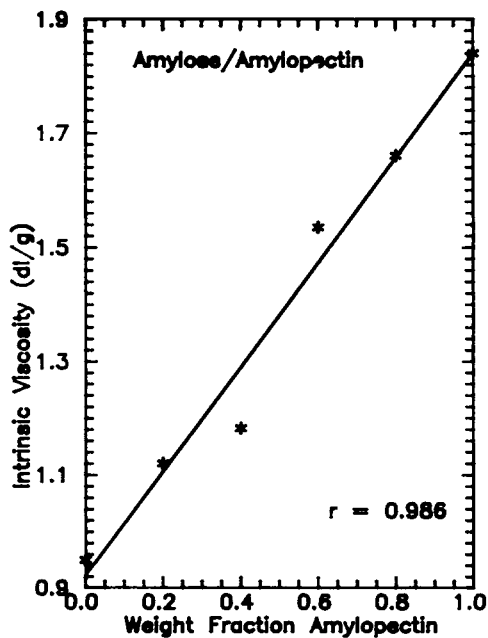


Fig. 3. Plot of intrinsic viscosity vs. weight fraction of amylopectin for amylose/amylopectin mixtures. $r = 0.986$.

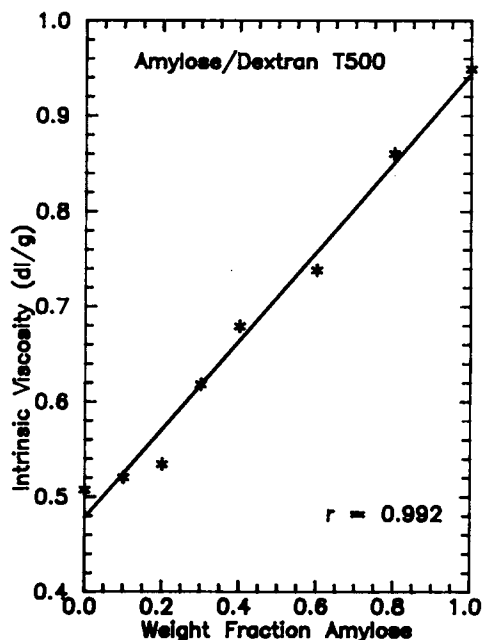


Fig. 4. Plot of intrinsic viscosity vs. weight fraction of amylose for amylose/T500 mixtures. $r = 0.992$.

Consequently, Eq. (1) reduces to

$$[\eta]_m = [\eta]_2 + ([\eta]_1 - [\eta]_2)w_1 \quad (4)$$

where subscripts refer to the two polymer types used in the specific systems tested. Figure 1 displays intrinsic viscosity of mixtures $[\eta]_m$ as a function of weight fraction T500; a high molecular weight dextran. In these experiments, two polymer samples of different molecular weight were mixed, and the intrinsic viscosities determined. Figure 1 indicates that a linear relationship of $[\eta]_m$ and weight fraction of polymer exists; consistent with previous reports.^{12,13} The relationship of intrinsic viscosity with weight fraction of branched polymers mixed with a linear polymer (amylose) is displayed in Figures 2 and 3 for glycogen and amylopectin, respectively. In both cases, a similar linear functionality is observed. This indicates that Eq. (4) is equally valid for mixtures of linear and branched polymers and that these polymer systems are therefore compatible; in other words, the two polymers do not interact in this solvent. Finally, intrinsic viscosity data for two different polysaccharides whose main chain structure is different is presented in Figure 4. The two polymers used in these experiments are dextran and amylose. Dextran is a highly flexible polymer due to the α -(1,6) glycosidic linkages whereas amylose is a more rigid polymer as its α -(1,4) glycosidic bonds are sterically constrained. Even in this case, intrinsic viscosity still scales with the mass fraction of one of the two component polymers in the same manner as the other mixed polymer systems studied here. This indicates that in basic

aqueous solvents, there is no evidence of incompatibility within any of the mixed polysaccharide systems reported in this work.

The excellent agreement between theory and experiment for the three different polymer systems examined allows us to generalize the applicability of Eq. (4), concluding the validity of Eq. (1) and the compatibility of these polymers in this solvent system. That is to say, the average intrinsic viscosity of a polysaccharide mixture does scale with the product of the individual components intrinsic viscosities and their weight fractions. This conclusion is valid for various linear and branched polysaccharides in aqueous NaOH solutions. We can conclude that theories which have employed this relationship are correct in this assumption.

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