# A rheological investigation of some polysaccharide interactions

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ABSTRACT

This publication contains work on several aspects related to polysaccharide synergy. Firstly a model for predicting the viscosity of non-interacting mixed polysaccharide solutions based upon coil occupancy was derived and experimentally tested for a series of non-ionic cellulose ethers. Good agreement was found between the predicted and experimental values. The model was adapted to accommodate the coil expansion of a polyelectrolyte occurring when it is mixed, and hence diluted, with a non-ionic polysaccharide in aqueous solution. The validity of this approach was examined using solutions of sodium carboxymethylcellulose and hydroxypropyl methylcellulose. The results showed that the enhanced viscosities observed on mixing non-ionic and anionic cellulose ethers can be explained in terms of coil expansion without invoking a mechanism based upon hydrogen bonding, and this was confirmed by sedimentation coefficient measurements. Rheological and ultracentrifugational techniques were used to examine the interaction between xanthan and the fraction of locust bean gum soluble at $35^{\circ}$C observed when solutions of the polysaccharides are mixed cold. Both techniques indicate that significant synergism occurs.

INTRODUCTION

The aim of this work was to examine polysaccharide synergism from a variety of angles. In order to determine clearly that two polysaccharides have interacted from viscosity measurements, it is necessary to possess some way of predicting or estimating the viscosity which a mixed polysaccharide solution would have in the absence of interactions. Various models have been proposed to predict the viscosity of mixed solutions of non-interacting polysaccharides (1,2). Many of these are entirely empirical in

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nature and all have relatively limited adaptability. This work
describes the derivation and experimental validation of a model
for the prediction of the viscosity of mixed polysaccharide
solutions based upon coil occupancy, an approach suggested by
Morris (3).

It has been shown(4) that at concentrations sufficient for
coil overlap to occur, the viscosity of a solution of a single
polysaccharide is given by equation 1.

$$\log \eta^o_{sp} = X\log(C[\eta]) + \log K \qquad (Eq.1)$$

where $\eta^o_{sp}$ is the zero shear specific viscosity, C is the
total polysaccharide concentration, $[\eta]$ is the intrinsic
viscosity, and X and K are constants specific for each
polysaccharide.

By adapting this equation to a two polysaccharide system (A and
B) the following relationship is obtained:

$$(Eq.2)$$

$$\log \eta^o_{sp(A+B)} = (f_A X_A + f_B X_B)\log(C(f_A[\eta_A] + f_B[\eta_B])) + f_A\log K_A + f_B\log K_B$$

where $f_A$ and $f_B$ are the weight fractions of polysaccharides A and
B respectively and subscripts denote the polysaccharides to which
the other terms refer.

Eq.2 has been adapted to account for the changes in intrinsic
viscosity of an ionic polysaccharide,"B", which occur due to
alterations in the total ionic strength, I, of the solution,
which is given by the following relationship:

$$I = I_s + Cf_B\alpha \qquad (Eq.3)$$

Where $I_s$ is the ionic strength of the solvent and $\alpha$ = the weight
fraction counterion content of the polyelectrolyte divided by the
counterion molecular weight.

$$\log \eta^o_{sp(A+B)} = \qquad\qquad\qquad\qquad\qquad (Eq.4)$$

$$(f_A X_A + f_B X_B)\log(C(f_A[\eta_A] + f_B([\eta^*_B] + S.I^{-0.5}))) + f_A\log K_A + f_B\log K_B$$

Where $[\eta^*_B]$ is the intrinsic viscosity of the polyelectrolyte at
infinite ionic strength, and S is a measure of polyelectrolyte
chain stiffness, equal to the gradient of a graph of intrinsic
viscosity against square root of the ionic strength (5).

For weak gel structures the use of steady shear viscosity is less
appropriate and the study of synergism by dynamic rheological
methods is well established (6,7). A system of particular
interest is xanthan gum with locust bean gum where it has been
suggested that xanthan has to be heated for the disordered form
to be attained before the interaction can occur (8). Preliminary

dynamic rheological results are presented for unheated mixtures of these polysaccharides.

Finally, the use of ultracentrifugation to study the interaction between cellulose ethers and that between xanthan and locust bean gum is demonstrated.

MATERIALS AND METHODS

   Hydroxypropylmethylcellulose, HPMC, (Methocel K4M) was donated by Colorcon. Hydroxyethylcellulose, HEC, (Natrosol 250HHX), and Hydroxypropylcellulose, HPC, (Klucel H) were donated by Hercules. Sodium carboxymethylcellulose, NaCMC, (Blanose 12M31FD) was donated by Aqualon. Xanthan (Keltrol F) and locust bean gum were purchased from Kelco and Sigma respectively.
 The fraction of the galactomannan soluble at $35^{\circ}C$ was isolated using a method based upon that of Gaisford et al (9). This temperature fraction was used in all subsequent rheological and ultracentrifugational studies.

   Concentrated solutions (>0.1%) were prepared by dissolving the polysaccharide in the solvent using a high shear Silverson mixer. Dilute solutions were prepared by adding the correct weight of polysaccharide to 80% of the total solvent, shaking until dissolved, then adding the remaining solvent.

   All mixtures of polysaccharide solutions were prepared using single polysaccharide solutions which had been hydrated for 24 hours. The solutions were mixed with an Ultra Turax mixer and allowed to stand for a further 24 hours prior to rheological measurements being performed.

   For each of the cellulose ethers the viscosities of a series of dilute solutions (<0.1%) were determined using an Ostwald viscometer with a flow time for water of 70 seconds. The intrinsic viscosity for each was then obtained using a Huggins plot extrapolation to zero concentration.

   Zero shear viscosities for the concentrated cellulose ether solutions were obtained using a Deer rheometer fitted with concentric cylinder geometry (MG7101).

   The storage and loss moduli for 1.0%w/w solutions of xanthan, locust bean gum, and mixtures of the two were obtained using a Weissenberg rheogoniometer, model R19, fitted with $2^{\circ}$ cone and plate geometry. A frequency range of 0.05 to 0.5 Hz was used.

All rheological measurements were performed at $25^{\circ}C$.

   Sedimentation studies were performed with a MSE Centriscan analytical ultracentrifuge.

RESULTS AND DISCUSSION

   Figures 1 and 2 show the values predicted by equation 2 relative to those obtained experimentally for two sets of mixed

**Figure 1. Predicted and Determined Values of Specific Viscosity
for Methocel K4M / Natrosol 250 HHX mixtures
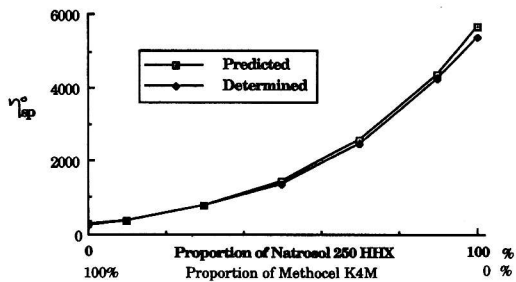(Total polysaccharide concentration 1% w/w)**



**Figure 2. Predicted and Determined Specific Viscosity
values for Methocel K4M / Klucel H mixtures
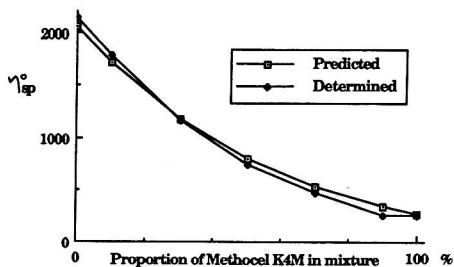(Total polysaccharide concentration 1% w/w)**



**Figure 3. Predicted and Determined Values of Specific Viscosity
For Methocel K4M / Blanose 12M31FD mixtures.
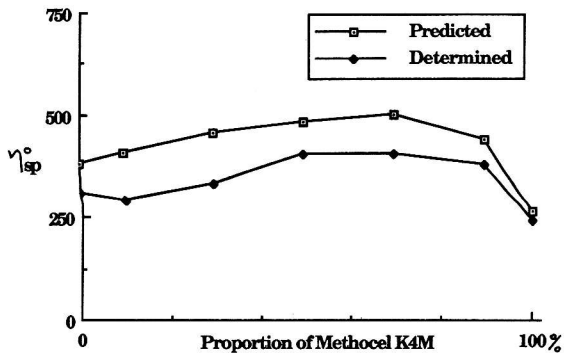(Total polysaccharide concentration 1%)**

Figure 4. Storage and loss moduli for cold mixed solutions of xanthan and the fraction of locust bean gum soluble in water at 35°C.
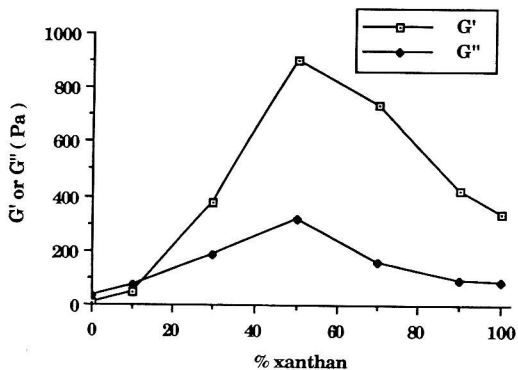


TABLE 1. Sedimentation coefficients of single polysaccharides and mixed systems.

| POLYSACCHARIDE | SEDIMENTATION COEFFICIENT (Svedbergs) |
|---|---|
| Methocel K4M | 2.0 |
| Blanose 12M31FD | 2.4 |
| Methocel K4M (in mixture) | 1.6 |
| Blanose 12M31FD (in mixture) | 2.2 |
| | |
| Xanthan | 7.4 |
| Locust Bean Gum (LBG) | 3.2 |
| Xanthan/LBG mixture | Approx 60 |

solutions of non-ionic cellulose ethers. In each case the solvent
was 0.1M sodium chloride and the total polysaccharide
concentration was 1.0%w/w. There is excellent agreement between
predicted and determined viscosities in each case indicating the
applicability of the model to these systems.

Figure 3 shows the values predicted by equation 4 relative to
those obtained experimentally for mixtures of HPMC and NaCMC. The
solvent was distilled water, and the total polysaccharide
concentration was 1.0%w/w. Agreement between the two curves is
limited especially where the polysaccharide content is
predominantly the polyelectrolyte. The values of the constants X
and K for the NaCMC were obtained from a graph of Log zero shear
specific viscosity against Log coil overlap parameter (C[$\eta$]) at
an added ionic strength of 0.2M. A high ionic strength was chosen
to minimise the effects of errors introduced by the estimation of
the sodium content of the polyelectrolyte. However the
discrepancy between the zero shear specific viscosity of the
1.0%w/w NaCMC solution predicted using these values and that
obtained experimentally is significant. Therefore it appears that
the behavior of the polyelectrolyte coils is not independent of
ionic strength; with increased coil-coil repulsion leading to a
decrease in the number and lifetime of entanglements and hence a
reduction in measured viscosity as the total ionic strength is
reduced.

Importantly, the results show that the enhanced viscosities
produced when an anionic and a non-ionic polysaccharide are mixed
in aqueous solution can be accounted for in terms of
polyelectrolyte coil expansion due to counter-ion dilution on
mixing and it is unnecessary to invoke a mechanism involving
molecular association, as other workers have done (1).

The results of the ultracentrifugation studies, shown in Table
1, indicate that there is no specific association between HPMC
and NaCMC. The sedimentation coefficient of each in the presence
of the other varies little from that obtained in isolation and
these small differences can easily be accounted for by
Johnston-Ogston and viscosity effects. In contrast, the
sedimentation coefficient of the xanthan/locust bean gum mixture
is an order of magnitude greater than either of the individual
polysaccharides. This, along with the relative turbidity of the
mixed solutions signifies that an interaction involving molecular
association has occurred.

Figure 4 shows the storage and loss moduli for various
mixtures of locust bean gum and xanthan solutions in 0.1M sodium
chloride at a concentration of 1.0% w/w. There is an optimum
storage modulus for the mixture containing equal parts of each
polysaccharide;the value of this is approximately 500% greater
than that of the more elastic component (xanthan), at the same
total concentration.

The dynamic rheological and sedimentation data both indicate
that a synergistic   interaction of significant magnitude has
occurred  between xanthan and locust bean gum. At this ionic
strength and in the absence of heat, the xanthan will be fixed in
its   native form. According to the model previously proposed for

this interaction (8) it should not occur in such circumstances. Hence it appears that these two polysaccharides can interact by an additional mechanism. A further report into the nature of this interaction is being prepared.

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