

## Viscosity of Dilute and Semi-Dilute Aqueous Pectin Solutions

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## ABSTRACT

Provided proper solvent conditions are chosen for a given pectin such that the Huggins coefficient,  $k_1$ , is close to 0.33, a one-point measurement allows a precise determination of the intrinsic viscosity,  $[\eta]$ . However extrapolation techniques are preferred. Viscosity measurements in the coil-overlap region for a commercial pectin resulted in a critical concentration ( $c^*$ ) of 0.7g/dl.

## INTRODUCTION

The increasing use of hydrocolloids in different food products, e.g. drinking yoghurt and jam has resulted in a growing interest in the basic rheological behavior of pectin solutions. Pectins are naturally occurring polysaccharides, consisting of linearly linked galacturonic acid. In native pectin about 70% of the carboxylgroups are methyl-esterified. One of the simplest methods of gaining information about the size and shape of a polymer in solution is by viscosity measurements<sup>(1)</sup>. Viscosity measurements were performed on a commercial pectin sample by use of capillary viscometry and a controlled stress rheometer. From dilute solution data,  $[\eta]$  which is a measure of the specific hydrodynamic volume is calculated. From the semi-dilute viscosity data the coil-overlap parameter ( $c[\eta]$ ) is calculated and  $c^*$  is determined. Furthermore the importance of the  $k_1$ , is discussed in connection to a one-point determination of  $[\eta]$ .

## MATERIALS AND METHODS

Cannon-Fenske viscometers (nos. 50 and 75) were used to investigate a commercial high

methoxyl pectin, GENU pectin type B rapid set (Degree of esterification, 71.4%). Samples were dissolved in either 0.17M acetic acid/0.083M K-acetate (pH 4.4), or in 0.017M acetic acid/0.083M K-acetate (pH 5.4). Intrinsic viscosity values were determined by the following methods of calculation: Huggins-Kraemer (HK) plots where the common intercepts equal  $[\eta]$  and the Solomon-Ciuta (SC) equation which in favorable cases allows a determination of  $[\eta]$  from a one-point finite concentration measurement<sup>(2)</sup>. In the semi-dilute region the viscosity measurements were performed on a Haake RS100 rheometer using a double-gap (DG41) geometry. All measurements were performed at 25°C.

## THEORY

The viscosity of solutions relative to the solvent viscosity,  $\eta_r$ , is measured and  $[\eta]$  calculated<sup>(1,2)</sup>. In the HK plot  $\eta_{sp}/c$  and  $\ln\eta_r/c$  are plotted against the pectin concentration ( $c$ ), where  $\eta_{sp} = \eta_r - 1$  is the specific viscosity. The intercept between the two straight lines is equivalent to  $[\eta]$ . This method is found well-suited for low polymer concentrations (typically below 2%)<sup>(2)</sup>. The HK method is time consuming, since it necessitates measurements at several concentrations. Therefore, another method based on a one-point determination of  $[\eta]$  has been developed, i.e. the SC equation<sup>(2)</sup>.

$$\text{Huggins: } \frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c$$

$$\text{Kraemer: } \frac{\ln\eta_r}{c} = [\eta] + k_2 [\eta]^2 c$$

$k_2$  is the Kraemer coefficient.

Solomon-Ciuta:

$$[\eta]_{SC} = \frac{1}{c} \sqrt{2(\eta_{sp} - \ln \eta_r)}$$

## RESULTS AND DISCUSSION

### Comparison between HK and SC methods

The HK plot for the GENU pectin type B (K-acetate buffer, pH 5.4) is shown in Fig. 1. From the intercept and the slopes an  $[\eta]$  of 5.46dl/g and a  $k_1$  of 0.35 are obtained. The same data were analyzed by the SC equation, as shown in Table 1. It is seen that  $[\eta]_{SC}$  is nearly constant with an average value of 5.46dl/g, in excellent agreement with the HK result.

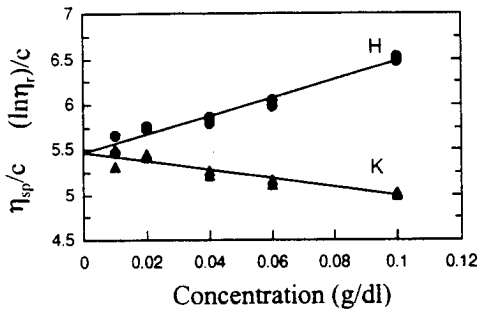


Figure 1. HK plot for GENU pectin type B rapid set in K-acetate buffer, pH 5.4. H and K are Huggins and Kraemer plots respectively.

Table 1.  $[\eta]_{SC}$  values determined by use of the SC equation (Pectin B in K-acetate buffer, pH 5.4).

Pectin concentration g/dl	0.01	0.02	0.04	0.06	0.1
$[\eta]_{SC}$ dl/g	5.46	5.54	5.43	5.42	5.47

Fig. 2 shows the same GENU pectin type B sample dissolved in K-acetate buffer with pH 4.4. In this solvent  $[\eta]$  is 5.30dl/g, close to the  $[\eta]$  of 5.46dl/g at pH 5.4, but with a rather different  $k_1$  value of 0.5. As seen in Table 2 it is no longer possible to obtain precise values of  $[\eta]$  by use of the SC-equation, since  $[\eta]_{SC}$  varies from 5.45 to 5.64dl/g. Even at the lowest concentration (0.04g/dl),  $[\eta]_{SC}$  deviates 3% from the  $[\eta]$  determined from HK plots.

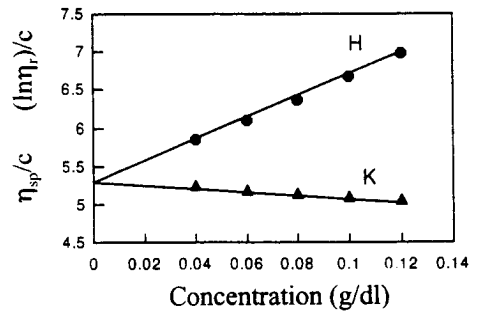


Figure 2. HK plot for GENU pectin type B rapid set in K-acetate buffer, pH 4.4. H and K are Huggins and Kraemer plots respectively.

Table 2.  $[\eta]_{SC}$  values determined by use of the SC equation (Pectin B in K-acetate buffer, pH 4.4).

Pectin concentration g/dl	0.04	0.06	0.08	0.10	0.12
$[\eta]_{SC}$ dl/g	5.45	5.47	5.53	5.58	5.64

The reason for the deviation between these estimates of  $[\eta]$  is due to the fact that the SC equation may either over- or under-estimate the  $[\eta]$  at finite concentration. Fig. 3 shows the SC determination of  $[\eta]_{SC}$  relative to the correct  $[\eta]$  value for different  $k_1$ -values. It is seen that only  $k_1$ -values 0.3 and 0.4 result in good agreement between  $[\eta]_{SC}$  and  $[\eta]$ .

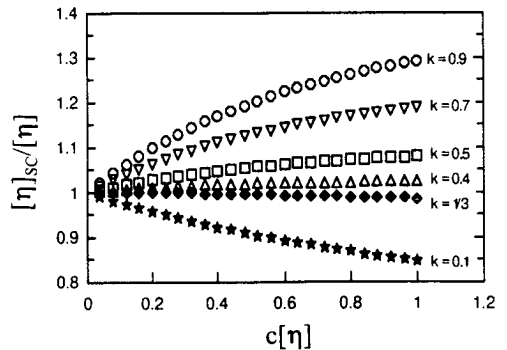


Figure 3. The deviation of  $[\eta]_{SC}/[\eta]$  vs  $c[\eta]$  for different  $k_1$ -values,  $k_1 = 1/3$  results in  $[\eta]_{SC}/[\eta] = 1$ .

A Taylor expansion confirms that the Solomon-Ciuta equation only gives correct estimates of  $[\eta]$  at low concentrations, when  $k_1 = 1/3$ . For systems with  $k_1 = 0$ , the Huggins equation will result in the best one-point determination of  $[\eta]$ . The Kraemer equation will be a more accurate one-point determination of  $[\eta]$  if  $k_1$  is close to 0.5. It is therefore concluded that the Solomon-Ciuta equation can only be used to obtain accurate estimates of  $[\eta]$  for  $k_1$  values close to 1/3. A given pectin sample will only under certain solvent condition give this  $k_1$  value, and it is therefore necessary to measure at several concentrations in order to estimate the value of  $k_1$ .

### The semi-dilute region

When entering the semi-dilute region the HK plot is no longer useful since the viscosity increases drastically with the concentration of pectin as seen in Fig. 4.

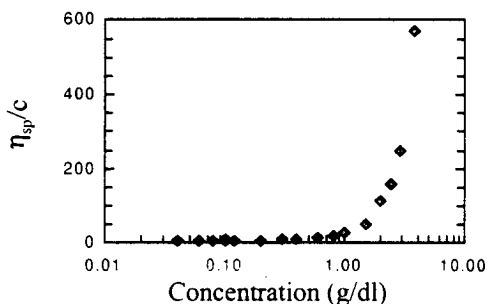


Figure 4. The reduced viscosity vs concentration for a GENU pectin type B (K-acetate buffer pH 4.4)

The critical concentration,  $c^*$ , characterizes the concentration, where the coils start to overlap. When entering the coil-overlap region the viscosity starts to increase in a non-linear fashion. The determination of  $c^*$  is illustrated in Fig 5. From such plots  $c^*$  is determined from the intercept of the two straight lines,  $c^*$  is approximately 0.7 g/dl. The slopes of the lines below and above  $c^*$  are 1.11 and 3.57 respectively. These values are in good agreement with results obtained by Axelos *et al.*<sup>(3)</sup>.

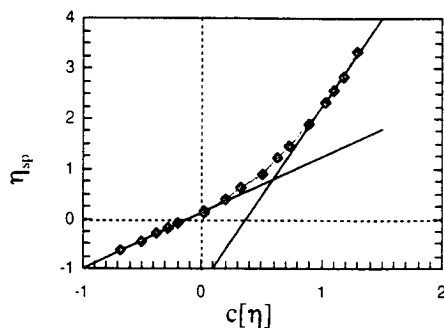


Figure 5. A log-log plot of  $\eta_{sp}$  vs the coil-overlap parameter ( $c[\eta]$ ) for a GENU pectin type B (K-acetate buffer pH 4.4).

### CONCLUSION

Provided a proper solvent is chosen for a given pectin such that  $k_1$  is close to 0.33, a one-point measurement allows a precise determination of  $[\eta]$ . However extrapolation techniques are preferred, since they are needed to determine the  $k_1$  value. In the present study good agreement was found between the HK and the SC determination of  $[\eta]$  giving an  $[\eta]$  value of 5.46dl/g for a high methoxyl pectin with DE 71.4% in one solvent whereas a shift of 1 pH unit resulted in a poor agreement. This is due to the fact that  $k_1$  changed from 0.35 to 0.5. The SC equation is therefore not a good method to estimate  $[\eta]$ . In the latter case viscosity measurements in the coil-overlap region resulted in a  $c^*$  of 0.7g/dl, and from a log-log plot of  $\eta_{sp}$  vs.  $c\eta$  the slopes resulted in 1.11 and 3.57 below and above  $c^*$ .

### REFERENCES

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