

## VISCOSITY MEASUREMENTS. MARTIN EQUATION VERSUS MULTI-POINT METHODS

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### 1. General considerations

Chemists tend to regard viscosity as a specific property of fluids (both liquids and gases), but for a physicist viscosity is rather a coefficient used in the equations of flow.<sup>1,2</sup> This physical point of view explains why experimental determination of viscosity of cellulose solutions in organic solvents greatly depends on the applied method (equation, type and geometry of the viscometer), and a necessity of standardization of these measurements is obvious. At present, national standards require that the intrinsic viscosity of cellulose  $[\eta]$  is calculated according to one-point Martin equation from data obtained with a viscometer of strictly determined geometry.<sup>3,4</sup> This method is fast and sufficiently reliable but it is used only in paper industry and preservation science. Generally, the intrinsic viscosity of polymers should be determined by one of multi-point methods based directly on the following equation:<sup>5</sup>

$$[\eta] = \lim_{\substack{c \rightarrow 0 \\ D \rightarrow 0}} \left( \frac{\eta - \eta_0}{\frac{\eta_0}{c}} \right) \quad (1)$$

where:  $[\eta]$  – intrinsic viscosity of polymer,  $\eta_0$  – viscosity of solvent,  $\eta$  – viscosity of solution,  $c$  – concentration of solution,  $D$  – shear velocity.

Polymer handbooks give a general dependence of viscosity of a polymer solution on its concentration<sup>6</sup>:

$$\frac{\eta}{\eta_0} - 1 = [\eta] + k_1 [\eta]^2 c + k_2 [\eta]^3 c^2 + k_3 [\eta]^4 c^3 + \dots \quad (2)$$

From this equation the most commonly known multi-point equations can be derived – those of Huggins<sup>7</sup>, Kraemer<sup>8</sup>, and Schulz and Blaschke<sup>9</sup>. Practical application of these equations needs much tedious laboratory work and usage of series of viscometers of varying geometry in order to be in accordance with the requirement of shear velocity approaching zero.

### 2. One-point Martin method

In 1951 Martin<sup>10</sup> suggested the use of a much simpler one-point method, but no information about the origin of his equation was given in the paper. An attempt of reconstruction of the probable path of mathematical considerations, used in order to arrive at the final equation, will be presented below.

This seems to be very simple. When higher-order terms in equation (2) are neglected, one obtains the well known Huggins equation

$$\frac{\eta}{\eta_0} - 1 = [\eta] + k_1 [\eta]^2 c = [\eta] (1 + k_1 [\eta] c) \quad (3)$$

After applying logarithmic transformation to this equation one arrives at its other form

$$\ln \left( \frac{\eta}{\eta_0} - 1 \right) = \ln [\eta] + \ln (1 + k_1 [\eta] c) \quad (4)$$

and taking into account the approximation:

$$\ln(1 + x) \cong x \quad (5)$$

the final result is obtained:

$$\ln \left( \frac{\eta}{\eta_0} - 1 \right) = \ln [\eta] + k_1 [\eta] c \quad (6)$$

This is the logarithmic version of the Martin equation.

But there is a trap hidden in these calculations. One must remember that some numerical errors are generated through approximate formulae. For example, this specific approximation in eq. (5) generates a 10% relative error when  $-0.2 < x < +0.2$ . Let's have a closer look at the consequences. Both standard<sup>3</sup> and the second Martin publication<sup>11</sup> require fulfillment of the inequality  $2.5 < [\eta]c < 3.5$ . If we take into account only smaller of these limits and the value of Martin constant ( $K \equiv k_1$ ) equal to 0.3, it is easy to observe that the obtained value of the expression  $K[\eta]c = 0.75$  is much higher than the allowed value of  $x$  in the approximation (5). Therefore the generated numerical error greatly exceeds 10%. The conclusion seems to be obvious: though derived from the same basic equation (2), from which various multi-point equations are stemming, Martin equation cannot be treated as a basis for multi-point viscosity measurements.

Nevertheless, the Martin one-point method gives reproducible results when used in the case of cellulose solved in cupriethylenediamine. Therefore equation (6) must be regarded as an empirical equation of limited applicability. However, its unquestionable simplicity and strictly determined geometry of viscometer, as well

as strictly defined experimental conditions, make this method a perfect tool for rapid determination of intrinsic viscosity of cellulose<sup>3,4</sup>.

### 3. Experiments

Being fully aware that the Martin equation cannot be used for multi-point viscosity determination, we nevertheless tried to compare it with two other multi-point equations – that of Huggins, see eq. (3) and Kraemer:

$$\frac{\ln \frac{\eta}{\eta_0}}{c} = [\eta] - k'' [\eta]^2 c. \quad (7)$$

which can be also derived from equation (2) by applying the approximate formula (5). The measurements have been done on samples of two model papers P1 and P2 (described in publication<sup>12</sup>). The preliminary results, presented in Table 1, were both interesting and unexpected.

Table 1: Intrinsic viscosity of cellulose calculated by various equations. For multi-point methods correlation coefficients are given.

Type of paper	P1	P2
Huggins equation	233 ± 25 $r = 0.9976$	644 ± 12 $r = 0.9931$
Kraemer equation	354 ± 44 $r = 0.7169$	626 ± 5 $r = 0.9953$
Martin equation (multi-point)	331 ± 40 $r = 0.9725$	655 ± 13 $r = 0.9868$
Standard Martin equation	618	599

It seems that mutual accordance of the obtained values of intrinsic velocity depends on the type of paper being

studied. For paper P1 the results obtained by multi-point equations are much lower than the value calculated according to the standard<sup>3</sup>. This is not the case with paper P2, where, unexpectedly, all applied formulae lead to very similar values. This phenomenon undoubtedly deserves further studies – possibly not only on cellulose solutions in cupriethylenediamine, but also for other polymers.

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