

Cellulose Molecular Weights Determined by Viscometry

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Synopsis

The equation suggested in the standard method SCAN C15:62 for the estimation of the degree of polymerization (DP) of a cellulose sample from its intrinsic viscosity ($[\eta]$) in cupriethylenediamine hydroxide (cuene) solution, $\bar{P}^{0.905} = 0.75 [\eta]/\text{mL g}^{-1}$, where \bar{P} is an indeterminate average DP, is incorrect. Although differences between the experimental results from several laboratories need to be resolved, a tentative replacement ($\bar{P}_v^{0.90} = 1.65 [\eta]$) is suggested, based upon the pooled data and a conversion from the intrinsic viscosity of cellulose tricarballylate (CTC) in tetrahydrofuran (THF) to that of cellulose in cuene. The treatment of statistical errors in Mark-Houwink-Sakurada parameters, and the nonlinearity of the $\log[\eta]$ - $\log \bar{P}_v$ correlation are discussed.

INTRODUCTION

The viscosity average DP (degree of polymerization), \bar{P}_v , of a cellulose sample is conveniently estimated from the intrinsic viscosity of its solution in 0.5M cupriethylenediamine hydroxide (cuene)¹⁻³ by application of the Mark-Houwink-Sakurada (MHS) equation $[\eta] = K\bar{M}_v^a = K'\bar{P}_v^a$, where $[\eta]$ is the weight average intrinsic viscosity, \bar{M}_v is the viscosity average molecular weight, and K , K' , and a are empirical constants. In practice, cellulose solution intrinsic viscosity is often estimated from a single viscosity measurement.¹

It is a very common misconception that if the average DP of a polymer is measured by viscometry, then that DP must always be \bar{P}_v , and, as \bar{P}_v is generally close to \bar{P}_w (weight average DP), viscosity measurements should give an approximate \bar{P}_w . In fact, the DP average obtained by viscometry may be very far from both \bar{P}_v and \bar{P}_w , depending on the method of determination of the MHS parameters and on the molecular weight distributions (MWDs) of the sample and standards. In spite of several published warnings (e.g., Refs. 4-7), it is not always appreciated that, for general applicability, \bar{P}_v must be used in the MHS correlation. If the polymer standards are almost monodisperse, then \bar{P}_n (number average) or, preferably, \bar{P}_w may be used as an approximation to \bar{P}_v . If only polydisperse samples are available (as is generally the case), \bar{P}_v should be estimated, for example, by means of polydispersity correction factors,^{5,8} before the MHS correlation is made. Such a correction can only be carried out when the MWD is simple, e.g., log-normal. Once the values of K' and a have been correctly determined, the MHS equation may be used within the limitations of the concept to estimate the *viscosity average* DP for samples of arbitrary MWD.

During our work on the characterization of cellulose samples, we noted that the MHS parameters suggested in the standard methods and elsewhere¹⁻³ for the cellulose/cuene system gave incorrect results. The ASTM method² states that a good approximation for degree of polymerization is given by $\bar{P} = 1.9 [\eta]$, without referring to the origin of the formula. This equation also greatly underestimates \bar{P}_v if it is assumed that $\bar{P} = \bar{P}_v$. The recommended constants for the cellulose/cuene system were originally derived⁹ from osmometric measurements of cellulose trinitrate samples in acetone. The DP of samples calculated from this correlation, on the assumption that the result is a viscosity average, would be too low by a factor of $\sim \bar{P}_w/\bar{P}_n$ (simple distributions). The polydispersity indices (\bar{P}_w/\bar{P}_n) were not reported, but they may have been in the range 1.5-3. To obtain a valid equation, the viscosity average molecular weight for each sample should have been estimated (using a measured polydispersity index and a reasonable approximation for a) before the correlation with intrinsic viscosity was made. Of the many published formulae, it is unfortunate that the one chosen as an example in the standard method¹ is probably the most misleading. It should be noted that a correlation between \bar{P}_n and $[\eta]$ cannot generally be used to predict even \bar{P}_n from the intrinsic viscosity of samples with arbitrary polydispersity and MWD because there is no unique relationship between \bar{P}_n and $[\eta]$.

Although others have commented on this matter with reference to cellulose nitrate solutions (e.g., Ref. 6), there is still evidence of misunderstanding (e.g., Refs. 10-12), and considerable potential for misinterpretation of experimental results. In this paper we discuss recent published work on cellulose DP determination and present some of the results of our investigations.

EXPERIMENTAL

Cellulose tricarbaniolate (CTC) samples were prepared from cotton linters, hydrolyzed cotton linters, and Avicel PH101, and characterized by high performance size exclusion chromatography (HPSEC) and low angle laser light scattering (LALLS) photometry.¹³ Nitrogen contents of the six CTC samples used in this study were 8.04% with standard deviation 0.09% (theoret. 8.09%). The intrinsic viscosities in tetrahydrofuran (THF) were determined at 25°C using a modified Ubbelohde viscometer with four timing bulbs.¹⁴ Extrapolation to zero shear rate could not be achieved because the data could not be satisfactorily linearized. Instead, a reference value of 500 s⁻¹ was chosen. Lower shear rates have been shown¹⁵ to have little effect. Intrinsic viscosities in cuene solution of the original cellulose samples were estimated from single point viscosities by application of the Martin equation:¹

$$\log \eta_{sp} = \log(c[\eta]) + kc[\eta]$$

where $\eta_{sp} = \eta/\eta_0 - 1$, η_0 = viscosity of medium [the viscosity of 0.5M cuene solution at 25°C is 1.144 mPa s, calculated from the relative efflux times of 0.5M cuene solution and water (1.285)¹ and the viscosity of water at 25°C (0.8904 mPa s)], η = measured viscosity of polymer solution at known concentration c , and $k = 0.13$ for this system.

$[\eta]$ is the only unknown; therefore, only one measurement is necessary. Tables for this single point determination of intrinsic viscosity are given in the SCAN Standard C15:62.¹ In this paper, the units of $[\eta]$ and K' are mL g⁻¹.

RESULTS AND DISCUSSION

Recently,¹⁰ the intrinsic viscosity/DP relationships of the tricarbonyls and trinitrates of cellulose were compared, and an apparent discrepancy was found between the two correlations. At a given cuene viscosity, the "DP_w" (Ref. 10 notation) of the nitrate appeared to be very much lower than that of the tricarbonyl. Random chain degradation during the nitration process was considered an unlikely explanation in view of the consistency of the data with those from several investigations in other laboratories. The MHS formula used¹⁰ for cellulose trinitrate in acetone was that published by Sihtola et al.,³ who had used the formula originally derived by Immergut et al.⁹ from osmotic pressure data. As mentioned above, that formula greatly underestimates \bar{P}_v . This misinterpretation accounts for most of the apparent discrepancy.

Cael et al.¹⁰ compared their MHS correlation for CTC in THF (based on a universal calibration procedure rather than on their measured intrinsic viscosities) with those obtained by Danhelka et al.,¹⁶ El Ashmawy et al.,¹⁷ and Valtasaari and Saarela.¹⁸ Their Figure 5¹⁰ depicts the various data in relation to the predicted MHS plot. Although the implication is that the predicted line is compatible with the published data, we make the following comments:

1. The data of El Ashmawy et al.¹⁷ are not comparable because very impure cellulose was used (α -cellulose content 78–80%) and because derivatization was not complete. Although their higher DP fractions may have been free from hemicellulose carbanilate, the degree of substitution (DS) was erroneously obtained from the relationship $DS = 3N/8.09$, where N is the percent nitrogen content of the derivative. The correct relationship is $DS = 162N/(1400-119N)$, giving a mean DS of only 2.6 for their five original samples.

2. One of the two sets of data taken from Danhelka et al.¹⁶ is not for CTC in THF but for CTC in acetone. Danhelka et al. did publish two sets of CTC/THF data, but Cael et al. inadvertently plotted the CTC/acetone data instead of the first set of CTC/THF data.

3. Valtasaari and Saarela¹⁸ reported a set of results obtained privately from Burchard and Keilich and used those data to calibrate their HPSEC by the "universal" method. The Burchard and Keilich data should have been included, as the CTC samples were probably well fractionated¹⁹ and, in any case, must be more comprehensive and accurate than the indirectly measured HPSEC results.

We have redrawn Figure 5 from Ref. 10 (see our Fig. 1), including our own data and those of Valtasaari and Saarela¹⁸ (direct measurements), Cael et al.¹⁰ (direct measurements), Danhelka et al.,¹⁶ and Burchard and Keilich (reported in Ref. 18). A similar figure, relating $[\eta]_{\text{CTC}}$ and weight average molecular weight has been published recently.²⁰ (*Note:* The subscript CTC denotes the CTC/THF system; no subscript implies the cellulose/cuene system or polymer/solvent systems in general.) All the DP values shown in our Figure 1

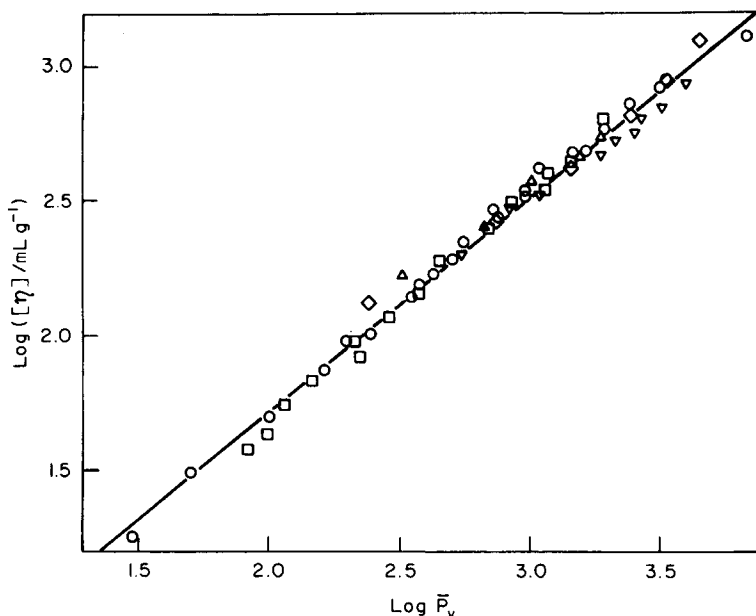


Fig. 1. Mark-Houwink-Sakurada plot for CTC in THF: (◇) \bar{P}_v data from this work; (□) \bar{P}_w data from Burchard and Kielich, reported in Ref. 18 corrected to 25°C; (○) calculated \bar{P}_v data from Ref. 16; (Δ) calculated \bar{P}_v data from Ref. 18; (▽) calculated \bar{P}_v data from Ref. 10.

approximate the viscosity average. Polydispersity corrections were made to our data and to those of Danhelka et al., Cael et al., and Valtasaari and Saarela. Although no polydispersity correction was made to the data of Burchard and Keilich, a temperature correction, estimated from one of our samples in THF and from published intrinsic viscosity data for CTC in dioxane,^{21,22} was applied. The quantitative effect of temperature is not well defined in the literature, but appears to increase with increasing DP²²; we applied a conservative negative correction ranging from zero at $[\eta]_{\text{CTC}} = 70 \text{ mL g}^{-1}$, to 5% at $[\eta]_{\text{CTC}} = 700 \text{ mL g}^{-1}$. One of the Burchard and Keilich data (the lowest DP result) (reported in Ref. 18) was rejected as an outlier.

Table I contains the five sets of data used in our analyses (corrected as indicated above). The results of linear regression analysis are given in Table II. Note that the errors in K' and a are strongly correlated^{23,24} because the mean position of the data points in the MHS plot is far from the origin of the graph. Neither parameter can be considered in isolation because positive deviations in a are largely balanced by negative deviations in K' . The effect of errors in K' and a are greatly overestimated^{10,25} if their correlation is neglected.

The joint 95% confidence ellipses for the linear regression constants from the individual data sets are presented in Figure 2. These regressions were calculated with the origin moved to the centroid of the pooled data to minimise the correlation between regression constants. The abscissa in Figure 2 represents the MHS exponent a , but the ordinate does not represent $\log K'$ because of the change in the origin of the coordinates. The large variation in ellipse size is due mainly to the variation in the number of data points. It

TABLE I
Corrected Viscosity and Molecular Weight Data for CTC in THF at 25°C

Ref. 16		Burchard and Keilich reported in Ref. 18		Ref. 10		This work		Ref. 18	
$[\eta]_{\text{CTC}}$ (mL g ⁻¹)	\bar{P}_v	$[\eta]_{\text{CTC}}$ (mL g ⁻¹)	\bar{P}_v	$[\eta]_{\text{CTC}}$ (mL g ⁻¹)	\bar{P}_v	$[\eta]_{\text{CTC}}$ (mL g ⁻¹)	\bar{P}_v	$[\eta]_{\text{CTC}}$ (mL g ⁻¹)	\bar{P}_v
31	51	36	85	203	457	133	247	169	345
97	198	44	100	304	840	269	746	253	682
156	382	56	118	340	1090	420	1450	379	1040
226	561	69	148	474	1820	660	2490	461	1500
295	732	85	225	537	2120	890	3390	542	1900
347	963	96	218	577	2500	1249	4550		
422	1090	119	293	652	2660				
485	1470	145	380	716	3200				
590	1950	190	457	881	3930				
730	2450	253	703						
900	3350	316	863						
1300	6820	351	1160						
		412	1190						
18	30	449	1470						
50	101	642	1960						
74	164								
102	245								
139	355								
172	430								
193	511								
276	763								
335	969								
487	1640								
845	3180								

appears from the generally low overlap area that there is little agreement between laboratories, as a result of differences in the number and molecular weight range of CTC samples, of curvature in the true $\log[\eta]_{\text{CTC}}-\log \bar{P}_v$ relationship and of differences in experimental technique. The areas of these confidence ellipses are underestimated owing to omission of the variance associated with individual points. As there is no obvious physical justification for the exclusion of any of the data sets (that of Ref. 10 appears to conform least), we have chosen to retain all of the results in Figure 1. The values of a

TABLE II
Results of Linear Regression Analysis on the Data in Table I

Ref. no.:	16	18 ^a	10	This work	18	Pooled data
Number of points	23	15	9	6	5	58
a	0.814	0.871	0.704	0.755	0.672	0.806
K' (mL g ⁻¹)	1.23	0.84	2.46	1.92	3.35	1.26
$\log K'$	0.091	-0.076	0.391	0.283	0.525	0.100
r^2	0.996	0.995	0.992	0.989	0.990	0.991

^aBurchard and Keilich, reported in Ref. 18.

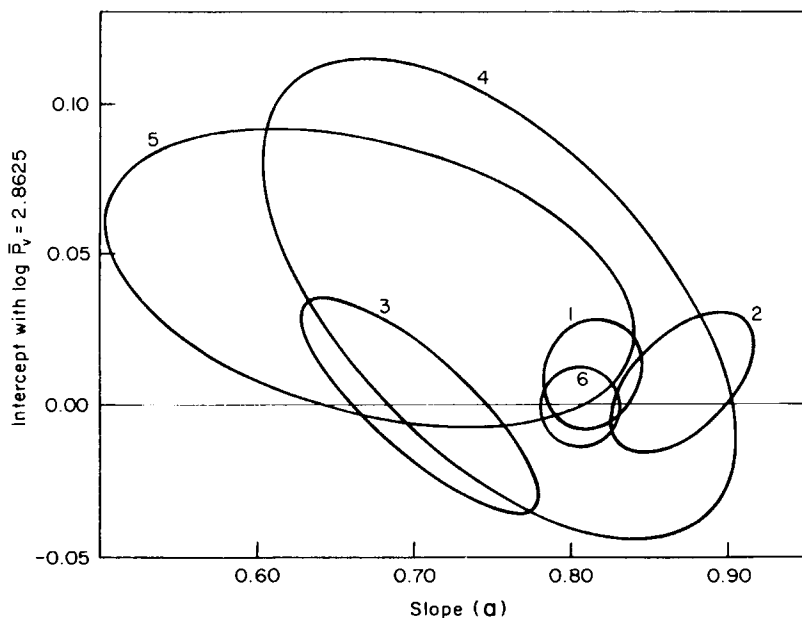


Fig. 2. Joint 95% confidence ellipses for the linear regression coefficients obtained from each of the data sets with the coordinate origin at the centroid of the pooled data: (1) Ref. 16; (2) Burchard and Kielich, reported in Ref. 18; (3) Ref. 10; (4) this work, (5) Ref. 18; (6) pooled data.

and $\log K'$ obtained are 0.806 and 0.100, respectively, with 58 points ($r^2 = 0.991$); thus,

$$\bar{P}_v^{0.806} = 0.794 [\eta]_{\text{CTC}}$$

The joint 95% confidence ellipse is given in Figures 2 and 3. The confidence region in Figure 2, for the pooled data, is circular owing to the absence of correlation between regression constants when the centroid of the data is chosen as the origin, and to a deliberate choice of scaling factors. Figure 3 demonstrates the correlation between a and $\log K'$ errors.

The MHS parameters from these five investigations appear to be excessively variable, such that K' ranges from 0.84 to 3.35 mL g⁻¹ and a ranges from 0.87 to 0.67. It has been implied¹⁰ that if other work had produced new K' and a values in the above ranges, then the new result would have been consistent with the old. Draper and Smith²⁴ discuss the fallacy in this argument. As a further demonstration of the correlation between the MHS parameters, the $\log K'$ and a pairs from each of the data sets in Table II are shown in Figure 4, with the weighted regression line. Similar correlations apply to experimental results for all other polymer/solvent systems. Thus, the apparently high variability found in the literature for the value of K' is actually an artifact produced by the plotting technique and, in isolation, should be regarded neither as an indicator of data variability nor as an exceptional problem in the determination of MHS parameters.

The relationship between the intrinsic viscosity of cellulose in cuene and that of CTC in THF is shown in Figure 5 where the regression line is

$$[\eta] = 0.471 [\eta]_{\text{CTC}}^{1.114}$$

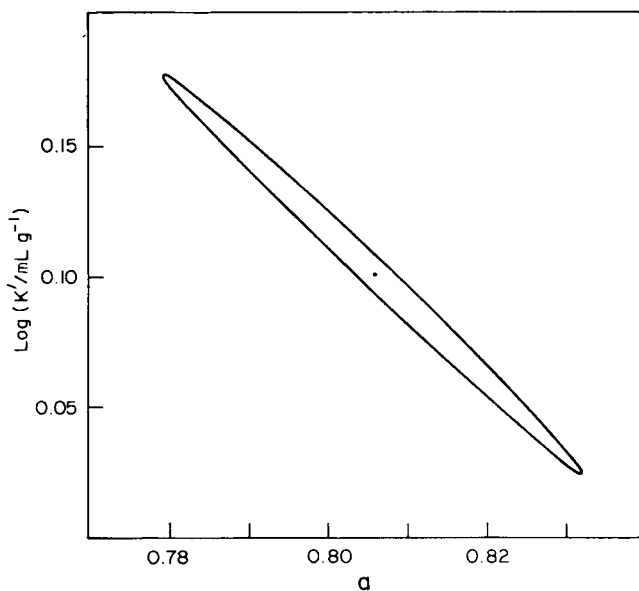


Fig. 3. 95% confidence region for the MHS parameters calculated from the pooled data.

Combining this result with the MHS equation for CTC in THF, we can determine an approximate relationship between cuene intrinsic viscosity and \bar{P}_v for the range $700 < \bar{P}_v < 5000$:

$$\bar{P}_v^{0.90} = 1.65 [\eta].$$

This equation should be considered as a temporary solution because of the indirect methods used to obtain the coefficients, including the use of a single point viscosity method to estimate $[\eta]$, and because of the many corrections

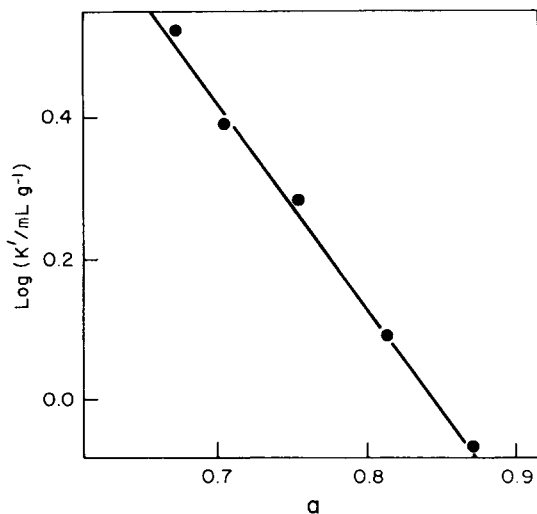


Fig. 4. Correlation between the MHS parameter pairs listed in Table II.

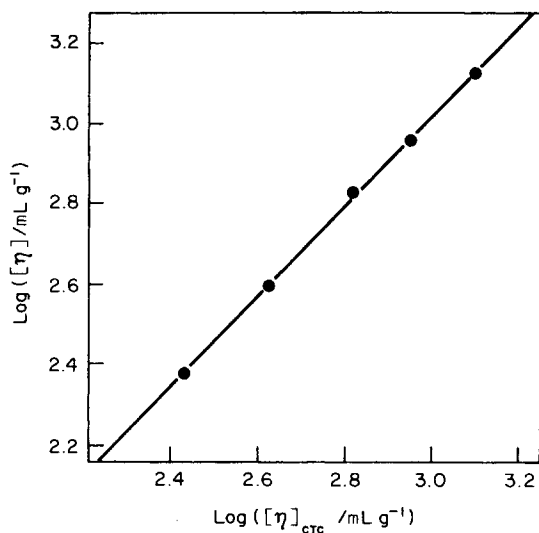


Fig. 5. Correlation between the intrinsic viscosity of cellulose in cuene and that between CTC in THF.

applied to the published data. However, it gives much more accurate values for \bar{P}_v than does the equation suggested in the standard.¹

Curvature is often evident in a $\log[\eta]$ - $\log \bar{P}_v$ plot (e.g., Refs. 19 and 22). Although it is standard practice to use straight lines to fit the data, there is no theoretical justification for the linearity of the relationship between $\log[\eta]$ and $\log \bar{P}_v$. Figure 6 shows the least-squares second-order fit to the pooled data; the first derivative (equivalent to the MHS exponent α) and correspond-

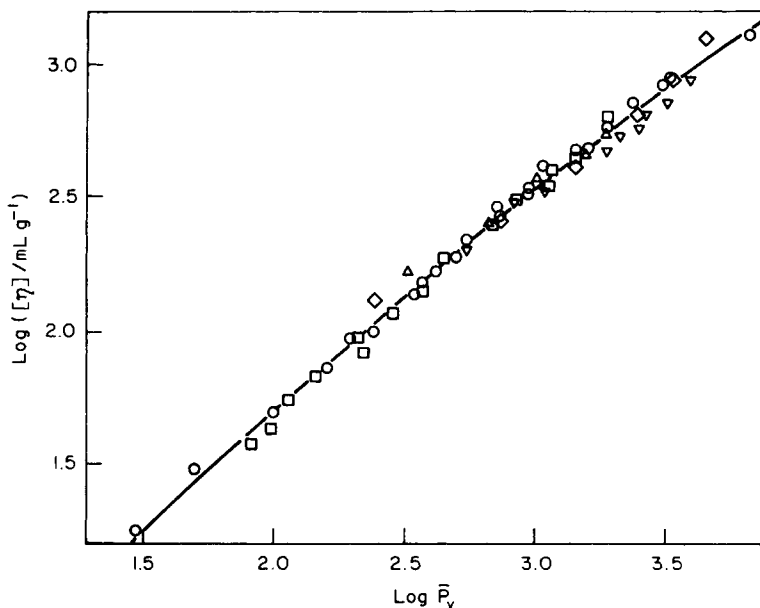


Fig. 6. Second order fit to pooled data from Table I. Symbols are as for Figure 1.

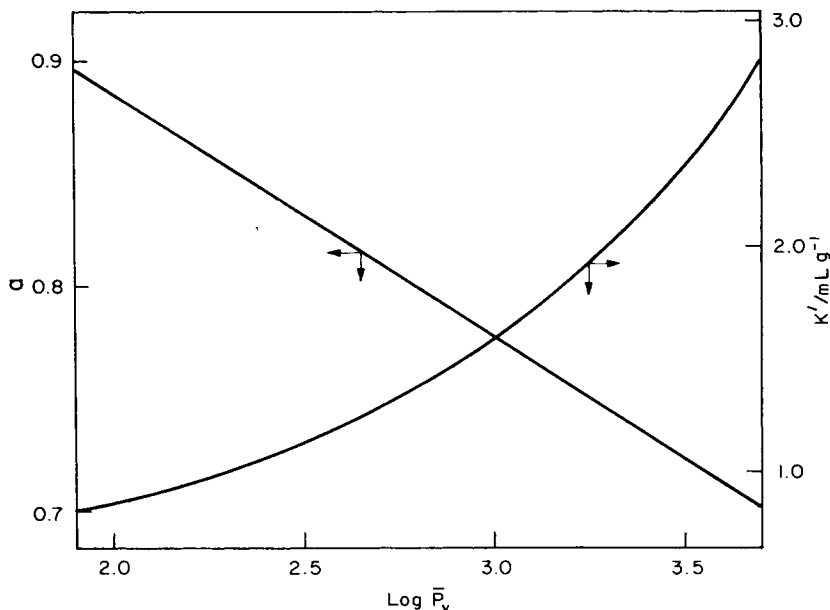


Fig. 7. Slope of regression line (MHS parameter a) in Figure 6, and corresponding K' as functions of \bar{P}_v .

ing K' are shown in Figure 7. The improvement in fit over the linear model is significant at the 1% level. From this regression,

$$\log[\eta]_{\text{CTC}} = -0.288 + 1.102 \log \bar{P}_v - 0.0541(\log \bar{P}_v)^2$$

$$\log K' = -0.288 + 0.0541(\log \bar{P}_v)^2$$

$$a = 1.102 - 0.1082 \log \bar{P}_v$$

The MHS exponent a is now a function of DP and covers a similar range to that in Table I. In general, nonlinear correlations should be used judiciously when curvature is significant. However, pending resolution of the discrepancies between the results from different laboratories, evident in Figure 2, we recommend using the linear model in this case, despite the slightly lower apparent precision.

CONCLUSIONS

Suppliers and consumers of cellulosic products have been using, for many years, relationships between degree of polymerization and intrinsic viscosity in cuene which give very misleading results, particularly when the polydispersity is high, as is very often the case for commercial samples. The relationships referred to in the standards are the most misleading and should be replaced. A more accurate equation is suggested which is based on data from several sources. Further adjustment of this equation will require direct correlation of cuene intrinsic viscosity with \bar{P}_v over a wide range. The interpreta-

tion of errors in the MHS parameters must take into account their strong correlation. If the relationship between $\log[\eta]_{\text{CTC}}$ and $\log \bar{P}_v$ is confirmed to be nonlinear, then for accurate work the traditional MHS correlation should be abandoned in favor of one in which K' and a are functions of \bar{P}_v .

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References

1. SCAN Standard C15:62, Viscosity of cellulose in cupriethylenediamine solution (CED).
2. ASTM Standard D1795-62, Standard test method for intrinsic viscosity of cellulose.
3. H. Sihtola, B. Kyrklund, L. Laamanen, and I. Palenius, *Pap. Puu*, **45**, 225 (1963).
4. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, Chap. VII, p. 313.
5. R. E. Bareiss, *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, Part IV, p. 115.
6. A. M. Holtzer, H. Benoit, and P. Doty, *J. Phys. Chem.*, **58**, 624 (1954).
7. H.-G. Elias, *Macromolecules*, Plenum, New York, 1977, Vol. 1, Chap. 9.
8. L. H. Peebles, *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, Part II, p. 405.
9. E. H. Immergut, J. Schurz, and H. Mark, *Monatsh. Chem.*, **84**, 219 (1953).
10. J. J. Cael, D. J. Cietek, and F. J. Kolpak, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **37**, 509 (1983).
11. J.-M. Lauriol, P. Froment, F. Pla, and A. Robert, *Holzforschung*, **41**, 109 (1987).
12. J.-M. Lauriol, J. Comtat, P. Froment, F. Pla, and A. Robert, *Holzforschung*, **41**, 165 (1987).
13. R. Evans, R. H. Wearne and A. F. A. Wallis, *J. Appl. Polym. Sci.*, in press.
14. J. Schurz and E. H. Immergut, *J. Polym. Sci.*, **4**, 279 (1952).
15. I. Kössler, J. Danhelka and M. Netopilik, *Polym. Bull. (Berlin)*, **3**, 559 (1980).
16. J. Danhelka, I. Kössler, and V. Bohackova, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 287 (1976).
17. A. E. El Ashmawy, J. Danhelka, and I. Kössler, *Sven. Papperstidn.*, **77**, 603 (1974).
18. L. Valtasaari and K. Saarela, *Pap. Puu*, **57**, 5 (1975).
19. W. Sutter and W. Burchard, *Makromol. Chem.*, **179**, 1961 (1978).
20. J. Danhelka, M. Netopilik and M. Bohdanecky, *J. Polym. Sci. Polym. Phys. Ed.*, **25**, 1801 (1987).
21. V. P. Shanbhag, *Arkiv Kemi*, **29**, 1 (1968).
22. P. Maissa, M. J. Seurin and P. Sixou, *Polym. Bull. (Berlin)*, **15**, 257 (1986).
23. U. K. O. Schroder and K. H. Ebert, *Makromol. Chem.*, **188**, 1415 (1987).
24. N. R. Draper and H. Smith, *Applied Regression Analysis*, 2nd ed., Wiley, New York, 1981, Chap. 2.
25. V. Deniz and O. Guven, in *Polymer '85 Preprints*, IUPAC, AAS, RACI International Polymer Symposium, Melbourne, Australia, 1985.

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