

Comparison of Various Solvents for Determination of Intrinsic Viscosity and Viscometric Constants for Cellulose

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ABSTRACT: Different solvents used to determine the intrinsic viscosity and the viscometric constants, a and K , published in the literature for cellulose, were compared. The various parameters affecting the viscometric constants were also evaluated. The main conclusions obtained from the experimental data available in the literature are that (1) the intrinsic viscosities in various solvents are ordered as follows: $[\eta]_{\text{LiCl/DMAc}} > [\eta]_{\text{NH}_3/\text{NH}_4\text{SCN}} \geq [\eta]_{\text{FeTNa}} > [\eta]_{\text{CED}} > [\eta]_{\text{Cadoxen}} > [\eta]_{\text{Cuoxam}}$; (2) the reported intrinsic viscosities and molecular weights for cellulose are lower than the true value due to degradation of cellulose in the solvents; (3) the rate of degradation was the smallest in LiCl/DMAc and

$\text{NH}_3/\text{NH}_4\text{SCN}$, moderate in cadoxen and FeTNa, and the highest in CED and cuoxam; (4) the plot of $\log K$ versus exponent a was linear and inversely related; (5) the curve was used for estimation of the constant K for cellulose in a solvent ($\text{NH}_3/\text{NH}_4\text{SCN}$) with a known exponent a ; and (6) among various reported solvents, LiCl/DMAc and $\text{NH}_3/\text{NH}_4\text{SCN}$ are advantageous over other solvents because of a complete dissolution of the polymer with a negligible reduction in its intrinsic viscosity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2189–2193, 2002

Key words: cellulose; intrinsic viscosity; viscometric constants

INTRODUCTION

Cellulose is considered the most plentiful organic resource on the Earth and is present in various plants as a principal component of cell walls, microorganisms, and animals. It consists of β -D-glucopyranosyl units with a (1–4)- β -D-linkage and forms a linear chain through many inter- and intramolecular hydrogen bondings. The linearity of cellulose makes it easy for the molecules to produce parallel arrays and cause a high degree of crystallinity.^{1,2}

Cellulose is produced from renewable resources and is a biodegradable polymer. Cellulose and its derivatives exhibit film- and fiber-forming properties.^{3,4} Enormous amounts of cellulose and its derivatives are consumed annually for a wide variety of products, for example, fiber, textile, paper, and membranes.^{3–5} They are also used for making copolymers, blends, and composites using other synthetic and natural polymers due to their various properties including fiber and film properties.^{3–6} Various properties of the polymer are closely related to its molecular weight. If the molecular weight is known along with a good understanding of the polymer conformation, many properties, such as mechanical and rheological properties, can be predicted.⁷ In addition, process conditions for cellulose and its conversions into its deriv-

atives, copolymers, blends, and composites can be also predicted. But the determination of average molecular weights (M_n , M_v , M_w , and M_z) of the polymer is time-consuming. Among them, the viscosity-average molecular weight, M_v , is a relatively quick and simple method and requires easy-to-use apparatus. The latter two are very important commercially. The determination of the viscosity-average molecular weight, M_v , requires measurement of the intrinsic viscosity of the polymer, $[\eta]$, in a solvent with known Mark–Houwink–Sakurada (MHS) equation constants, a and K .^{8,9} The value of $[\eta]$ varies with M_v (or DP_v , viscosity-average degree of polymerization) for a homologous series according to

$$[\eta] = KM_v^a = K_p DP_v^a \quad (1)$$

where K_p is a constant.

Accurate values for the constants can be determined when all parameters affecting them are taken into consideration. The correct values of the constants allow for an accurate estimation of the molecular weight. The objectives of this study were to compare various solvents used to determine the intrinsic viscosity and MHS equation constants published in the literature for cellulose and the parameters affecting the constants.

DISCUSSION

Comparison of various solvents used for intrinsic viscosity determination

The hydroxyl groups in cellulose contribute to strong intra- and intermolecular hydrogen bonding. These

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bonds reduce the solubility in water and other polar solvents. Cellulose cannot be dissolved completely in a poor solvent because of (i) its oriented and crystalline chemical structure and (ii) low-level polymer-solvent interactions and its possible precipitation even in dilute solutions. The presence of salts, alkalis, and acids in an aqueous solution weakens the bonds and allows solubility. However, in the presence of a larger quantity of salt, precipitation of the polymer is more possible. All the solvents used to determine the intrinsic viscosity of cellulose consisted of metal ions except for $\text{NH}_3/\text{NH}_4\text{SCN}$. Metal ions in an aqueous solution, either as impurities present in some origins or as added substances like metal oxides or salts, form a complex with cellulose. A chelate is formed between the metal ions and two hydroxyl groups on C-2 and C-3 of the glucopyranoside repeating units. This chelate is soluble in an aqueous solution.

Acids and alkalis, used as a component of the solvent or generated from salts in an aqueous solution, cause hydrolysis of the glucosidic bonds and lead to a decrease in the intrinsic viscosity of cellulose and its average molecular weight. However, the rate of degradation depends on the concentration of alkali, salt, and acid. Strong acids or bases are not appropriate solvents for determination of the hydrodynamic volume and molecular weight due to severe degradation of the cellulose chains.^{10,11} The viscosity of a dilute cellulose solution in 9% $\text{LiCl}/N,N$ -dimethylacetamide decreased slightly after storage for 30 days.^{12,13} The authors noted that the slight change in viscosity might be due to a change in inter- and intramolecular hydrogen bonding rather than to chain degradation. Brown and Wikström¹⁴ reported that the degradation of cellulose in cadoxen was small, in the range of 10–33 kDa, while Hudson and Cuculo¹⁵ pointed out that the reduced viscosity of cellulose in $\text{NH}_3/\text{NH}_4\text{SCN}$ slightly increased with time due to aggregation. In conclusion, the rate of degradation was the smallest in LiCl/DMAc and $\text{NH}_3/\text{NH}_4\text{SCN}$, moderate in cadoxen and FeTNa , and the highest in CED and cuoxam .^{10–17}

Different sources were used for preparation of cellulose samples. Cellulose is seldom found in a pure form. The level and nature of its impurity vary from one source to another and affect its solubility. The conformation of cellulose in a solution changes with the presence of impurities and is sensitive to the concentrations of these impurities. Some impurities induce degradation in cellulose. The percentage of purity and the nature and percentage of impurities affect the intrinsic viscosity and the constants, while, in the reports, unpurified cellulose was used for determination of the intrinsic viscosity and the constants.

Degradation may yield a change in the molecular weight distribution. Oxidative degradation of cellulose may also occur in some solvents such as

cuoxam .^{10,17} Oxygen in the air promotes oxidative degradation. If oxidative degradation of cellulose occurred, the end unit of the resulting macromolecules would not be the same as the cellulose unit due to the oxidation of the end unit. Thus, the chemical structure of the resulting polymer slightly changes and may cause a change in its solubility. Consequently, the intrinsic viscosity and molecular weight slightly change.

Among various reported solvents, LiCl/DMAc and $\text{NH}_3/\text{NH}_4\text{SCN}$ are advantageous over other solvents due to the following properties: (1) a great level of polymer-solvent interactions and complete dissolution of the polymer, and (2) a negligible reduction of the intrinsic viscosity of the polymer solution after a long period of storage.

The intrinsic viscosity (hydrodynamic volume/mass) is a measure of the dimension of macromolecules in solutions and polymer-solvent interactions. The greater value of the intrinsic viscosity in a solvent indicates a higher level of polymer-solvent interactions and a better solvent thermodynamically. The reported intrinsic viscosities in several solvents were evaluated quantitatively and are ordered as follows^{10,16–24}:

$$[\eta]_{\text{LiCl}/\text{DMAc}} > [\eta]_{\text{NH}_3/\text{NH}_4\text{SCN}} \geq [\eta]_{\text{FeTNa}} > [\eta]_{\text{CED}} \\ > [\eta]_{\text{Cadoxen}} > [\eta]_{\text{Cuoxam}}$$

Comparison of visometric constants available in the literature

The values of the MHS equation constants, a and K , published in the literature for cellulose, are presented in Table I. The values of a range from 0.66 to 1.19 and of K range from 1.278×10^{-4} to 1.128×10^{-1} . The smaller values of exponent a correspond to the greater values for K and vice versa. Exponent a represents the quality of the solvent. The greater the a , the larger interaction between the solvent and the polymer and the better the solvent. The large value of exponent a in LiCl/DMAc is due to the polyelectrolyte behavior of cellulose in the solvent, where Cl^- binds with the hydroxyl group of cellulose via formation of a complex ($-\text{OH Cl}^-\text{DMAc}^+$).¹² Figure 1 shows the reported values of $\log K$ versus a . An inverse linear relationship was observed. Rai and Rosen²⁷ obtained similar results for eight synthetic polymers. He and Wang²⁰ reported the values of the visometric constants for cellulose in paraformaldehyde/dimethylsulfoxide. Cellulose reacts with paraformaldehyde or formaldehyde and converts into methylolcellulose²⁸; thus, the reported values for a cellulose derivative cannot be used for cellulose.

The curve can be used to estimate the constant K in a solvent, if exponent a in a solvent is known. For

TABLE I
MHS Equation Constants for Cellulose for Different Solvents

Solvent	T (°C)	$K \times 10^3$ (cm ³ g ⁻¹)	$K_p \times 10^4$ (cm ³ g ⁻¹)	a	Molecular weight range (kDa)	No. samples	Method	Reference
Cadoxen ^a	25	38.5	18.4	0.76	10–943	9	SD	Brown and Wikström, 1965 ¹⁴
Cadoxen	25	55.1	25.0	0.75	225–945	6	SD	Henley, 1961 ¹⁶
Cadoxen	25	35.8	18.0	0.77	225–945	6	LS	Henley, 1961 ^{16,b}
Cuoxam ^c	20	112.8	31.9	0.657	20–250	9	OS	Harland, 1959 ²⁵
Cuoxam	25	6.98	6.80	0.90	194–1490	9	SD	Marx, 1955 ²⁴
0.5M CED ^d	25	10.1	9.84	0.90	194–1490	9	SD	Marx, 1955 ²⁴
CED	25	13.3	13.3	0.905	16–486	32	OS	Immergut et al., 1953 ²⁶
0.5M CED	25	29.0	17.0	0.80	20–120	14	OS	Vink, 1959 ^{17,b}
9% LiCl/DMAc ^e	30	0.1278	54.5	1.19	125–700	9	LS	McCormick et al., 1985 ¹²
NH ₃ /NH ₄ SCN	25	6.86	8.62	0.95	88–164	5	—	Hudson and Cuculo, 1980 ¹⁵
FeTNa ^f	25	53.1	27.4	0.775	33–560	10	LS	Valtasaari, 1965 ²¹

^a Triethylenediamine cadmium hydroxide.

^b Polydispersities of the polymer samples were taken into consideration.

^c Cuprammonium hydroxide.

^d Cupriethylenediamine hydroxide.

^e Lithium chloride/*N,N*-dimethylacetamide.

^f Iron–tartarate–sodium solution.

example, De Groot et al.²⁹ reported values of 0.74, 0.98, and 0.92 for exponent a in the solvent system of NH₃/NH₄SCN with three compositions of (27/73, w/w), (25.5/74.5, w/w), and (24.5/75.5, w/w), respectively. The corresponding values of K can be estimated to be 61.7×10^{-3} , 3.00×10^{-3} , and 6.38×10^{-3} , respectively.

Factors affecting the constants

The values of the constants, K and a , not only depend on the nature of the polymer and the quality of the solvent, but also on the polydispersity of the polymer samples, molecular weight range, and temperature.

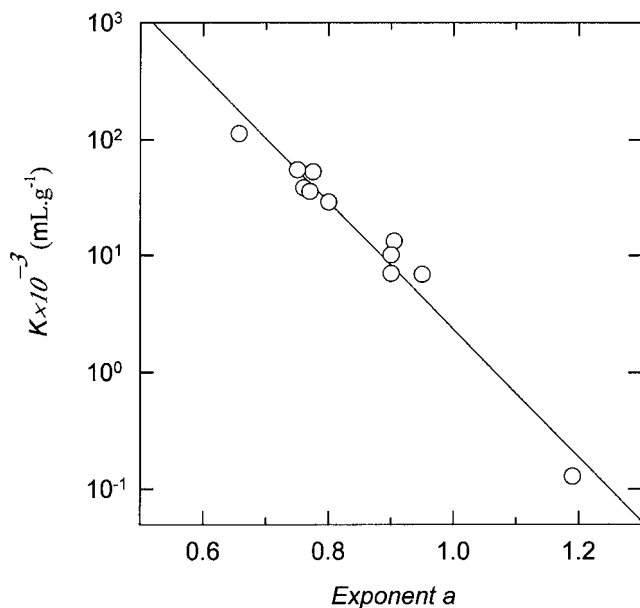


Figure 1 Relationship between $\log K$ and exponent a .

The authors used osmometry (OS), light-scattering (LS), and sedimentation (SD) methods for determination of the number-average (M_n), weight-average (M_w), and z-average (M_z) molecular weights, respectively. Various average-molecular weights (M_n , M_w , and M_z) other than M_v were substituted in the MHS equation, ignoring the effect of the polydispersity, while for a polydisperse polymer sample, the value of M_v is different from M_n , M_w , and M_z . In addition, for a particular polymer sample, the values of M_n , M_w , and M_z do not change in various solvents, while M_v is not unique and varies from one solvent to another, since it is a function of a , K , and $[\eta]$. A wrong substitution yields an error in the calculation of the constants. The error will be significant when the polymer samples have a broad molecular weight distribution and the value of M_n or M_z is substituted instead of M_v . The advantage of the light-scattering method is that it gives M_w , which is much closer to M_v than are M_n and M_z , because the value of exponent a falls in the range of 0.7 and 1.2 for cellulose. The closer a is to unity, the smaller the error for the constants. When the value of a is equal to unity, these values (M_v and M_w) are identical. There were two studies by Henley¹⁶ and Vink,¹⁷ where the polydispersity of the cellulose samples was taken into account. The authors determined the number-average or weight-average molecular weight by osmometry or the light-scattering method. They used a statistical function to describe the polydispersity, assuming that degradation of cellulose occurred by random scission. One way to calculate the constants with consideration of the polydispersity is to determine the weight-average molecular weight of the polymer samples by light scattering and their polydispersity correction factor, q_{MHS} , by size-exclusion chro-

matography. The correction factor has to satisfy the following equation³⁰:

$$[\eta] = Kq_{MHS} M_w^a \quad (2)$$

The values of K and a may vary with the molecular weight range, since the flexibility of the polymer conformation may change with its size. The range of molecular weight for a series of homologous polymers can be determined from the plot of $\log [\eta]$ versus $\log Mv$, where the plot is linear. If the molecular weight range is wide and deviation from linearity of the plot is high, the plot should be divided into smaller segments. Again, the smaller plot has to be linear. The upper and lower limits of the molecular weight are determined from the latter plot.

The constants vary with temperature because the hydrodynamic volume, $[\eta]M$, as well as the conformation of polymer depend on the solution temperature. Thus, the temperature correction factor, $d[\eta]/dT$ (change in intrinsic viscosity with temperature), should be determined for the correction of the temperature effect. Cellulose exhibits a negative dependence of the intrinsic viscosity with the temperature in the cadoxen solution.¹⁶ The average temperature correction factor in the range of 15–35°C was found to be 0.024 dL g⁻¹ deg⁻¹. Flory et al.,³¹ Moore and Brown,³² and Shabhag³³ found a negative dependence of the intrinsic viscosities of cellulose derivatives in various solvents with the temperature. These results suggest that the effective dimension of the macromolecules (hydrodynamic volume) decrease with an increase in the temperature via an increase in the chain flexibility. Since the applied range of temperature (20–30°C) was narrow, the thermal effect on the hydrodynamic volume should not be significant.

CONCLUSIONS

The overall conclusions obtained from the experimental data available in the literature are that (1) the intrinsic viscosities in various solvents are ordered as follows:

$$[\eta]_{\text{LiCl/DMAc}} > [\eta]_{\text{NH}_3/\text{NH}_4\text{SCN}} \geq [\eta]_{\text{FeTNa}} > [\eta]_{\text{CED}} \\ > [\eta]_{\text{Cadoxen}} > [\eta]_{\text{Cuoxam}}$$

(2) the reported intrinsic viscosities as well as the molecular weights for cellulose are lower than are the true values due to degradation of cellulose in the solvents; (3) the rate of degradation was the smallest in LiCl/DMAc and NH₃/NH₄SCN, moderate in cadoxen and FeTNa, and the highest in CED and cuoxam; (4) the plot of $\log K$ versus exponent a was linear and inversely related; (5) the curve was used to estimate the constants K for cellulose in a solvent (NH₃/

NH₄SCN) with a known exponent a ; (6) among various reported solvents, LiCl/DMAc and NH₃/NH₄SCN are advantageous over other solvents because of (i) a great level of polymer–solvent interactions and a complete dissolution and (ii) a negligible reduction of the intrinsic viscosity of the polymer in a solution after a long period of storage; (7) in most of the reports, (i) unpurified cellulose was used for determination of the intrinsic viscosity and the constants and (ii) the polydispersity of the polymer samples was not taken into account, while the intrinsic viscosity and the constants are sensitive to the level of purity of the cellulose, the nature and the level of impurities, and the polydispersity of the polymer samples; (8) the chemical structure of the cellulose in some solvents slightly changes due to oxidative degradation; consequently, its solubility and its intrinsic viscosity slightly change; and (9) the available information suggests that the flexibility of the polymer conformation in a solution increases with an increase in temperature.

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