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Relationship between Intrinsic Viscosity and Molecular Weight for Fractionated Cellulose

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ABSTRACT

A relationship between intrinsic viscosity and molecular weight for fractionated cellulose is established. The exponent a of the Mark-Houwink equation is 0.80. The unperturbed dimensions of cellulose are discussed on the basis of the Stockmayer-Fixman and Kurata-Stockmayer viscometric theories, and it is determined that cellulose is not a very rigid macromolecule in nature. This conclusion disagrees with the results obtained by statistical mechanics procedures in which the restriction of β -glucose residues to the C1 conformation was kept. The steric hindrance factor, σ , is about 2, and it seems to be independent of the substituents in cellulose if it is evaluated in both cellulose and cellulose derivatives from viscometric data. From statistical mechanics data reported in the literature, σ is estimated as 4.4 for cellulose and cellulose derivatives, such as cellulose nitrate, and this means that the steric hindrances of the substituents have little influence on the rigidity of cellulose derivatives. This view disagrees with the results obtained from the non-Newtonian behavior of cellulose and cellulose nitrate in dilute solutions. By applying the Noda-Hearst theory, the conclusion is reached that cellulose nitrate is a more extended macromolecule than cellulose.

INTRODUCTION

Cellulose is not soluble in simple solvents but it is soluble in solvents of multicomponent composition where the active component is a metal chelate. Thus the dissolution probably involves a chemical reaction between the cellulose and the chelate so that the cellulose chains are dispersed in water and surrounded by excessive amounts of low molecular weight inorganic cosolute [1].

Much attention has been paid to the dependence of intrinsic viscosity on molecular weight for unfractionated cellulose. Relationships between intrinsic viscosity and molecular weight were established using the following solvents: cadoxene (ethylendiamine cadmium hydroxide), CED (cupriethylendiamine hydroxide), cuoxam (cupramonium hydroxide), EWNN (iron-tartaric acid sodium complex solution), and FeTNa (modification of EWNN).

Bolotnikova and Samsonova [2] and Valtasaari [1] found a change in the flexibility of cellulose chains at a degree of polymerization of 500. Vink [3] established that the exponent a in the Mark-Houwink equation approaches zero at the oligomer level and increases to exceed unity at levels below a degree of polymerization of about 100. Investigations of the same kind were carried out by Swenson et al [4].

From viscometric and light-scattering data, some authors have reached the conclusion that cellulose is not a very rigid macromolecule [5-8], a conclusion that has been challenged by Flory [9]. However, very few studies have been made [2] on fractionated cellulose. In the present paper a relationship between intrinsic viscosity and the number-average molecular weight for cellulose fractionated at a degree of polymerization range of 500 to 3000 is established using cadoxene diluted with water (1:1 by volume) as solvent.

The flexibility of cellulose is examined using viscometric theories and the results are compared with those obtained from the flow behavior of cellulose solutions.

EXPERIMENTAL

Solvent

Cadoxene was prepared by mixing in a 1:10 weight proportion of cadmium oxide and an aqueous solution of ethylendiamine (72% in water). Both the cadmium oxide and the ethylendiamine were reagent grade. The mixture was kept refrigerated (3°C) for several days with occasional shaking, and the liquid was separated by decantation and centrifugation. By addition of a sodium hydroxide-ethylendiamine-water solution, the final concentration was adjusted

to Cd5%, sodium hydroxide 0.36 M, and ethylenediamine:water (28:100).

Fractionation

Purified cellulose sulfite pulp was dissolved in cadoxene and the resulting solution was diluted 1:1 by volume with water added drop by drop under stirring. The solution was centrifugated to remove unsolved cellulose at temperatures below 25°C. Aqueous propanol (75% in propanol) was used as nonsolvent.

To avoid the precipitation of most of the sample in the first fraction, the addition of nonsolvent had to be done very slowly under strong stirring to allow equilibrium to be established after adding each drop. Once the proper cloudiness was reached, the solution stood for several hours in a thermostat at 7°C until the solution became clear. Then the solution was kept overnight in a bath at 25°C and the concentrated phase was separated by centrifugation. Each fraction was isolated by decomposing the cadoxene-cellulose complex with aqueous acetic acid (10%), and then it was washed several times with water until the acid was totally removed. After this, the cellulose fractions were washed with ethanol-water, ethanol, acetone, and benzene to improve their solubility. Finally it was dried under vacuum and weighed. An analysis of such a fractionation has been published elsewhere [10, 11].

Viscosities

The intrinsic viscosities have been measured in a Ubbelohde viscometer at shear stress $\tau = 8$ dynes/cm². Figure 1 shows that the dependence of intrinsic viscosity on shear stress for cellulose of $\bar{M}_n = 429,000$ is negligible for $\tau < 10$ dynes/cm² [12].

Number-Average Molecular Weights

Cadoxene-cellulose solutions diluted 1:1 with water were used in preliminary attempts of determining molecular weights. A stainless steel Fuoss-Mead block-type osmometer similar to that described by Henley [5] was used. Cellophane 300 membranes, kindly supplied to us by Papelera de Zicuñaga and La Cellophane Española, were conditioned according to the procedure of Henley [5]. These membranes, as well as Membranfilter membranes for osmometry, proved to be unsuitable for making osmotic measurements of cellulose solutions. Therefore, in order to determine the molecular weight, the cellulose fractions were nitrated.

The nitration of regenerated cellulose was carried out according to the procedure described by Bennet and Timell [13]. Acetic

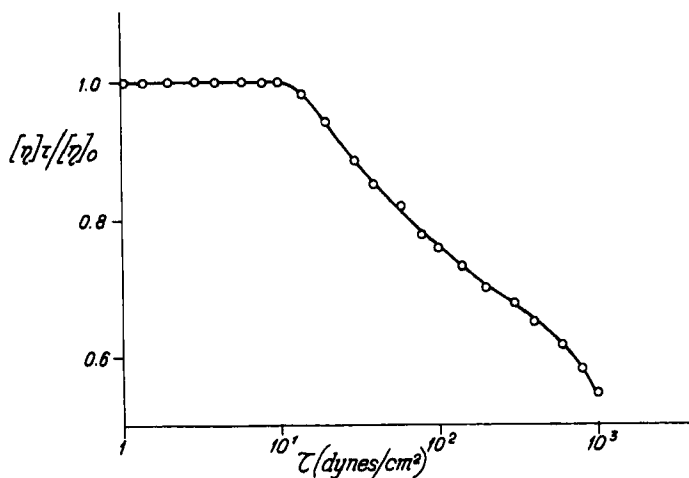


FIG. 1. Relative intrinsic viscosity vs shear stress for cellulose ($\bar{M}_n = 4.29 \times 10^5$) in cadoxene:water (1:1).

anhydride (100 ml) was slowly added to 67 ml of 90% nitric acid at -25°C . The cellulose fractions were added to portions of this mixture, after which the reaction mixture was transferred to an ice bath where it was kept for 3 hr. The product was poured into ice water, washed with large amounts of distilled water, and the nitrated samples were stabilized by extraction with methanol. The nitration occurred with no apparent degradation. The nitrogen content was determined by the Kjeldahl method.

Osmotic measurements of nitrated cellulose fractions dissolved in acetone were made in a Fuoss-Mead osmometer using cellophane 300 membranes. The molecular weights of the cellulose fractions were obtained from those of cellulose nitrate by the expression

$$\bar{M}_n (\text{cellulose}) = \bar{M}_n (\text{nitrate}) \times 162 / (162 + 45s)$$

where s is the degree of substitution of the cellulose nitrate.

RESULTS

The dependence of reduced viscosity (η_{sp}/C) on concentration showed an increasing upward curvature (Fig. 2) with increasing concentration and molecular weight. The data were extrapolated

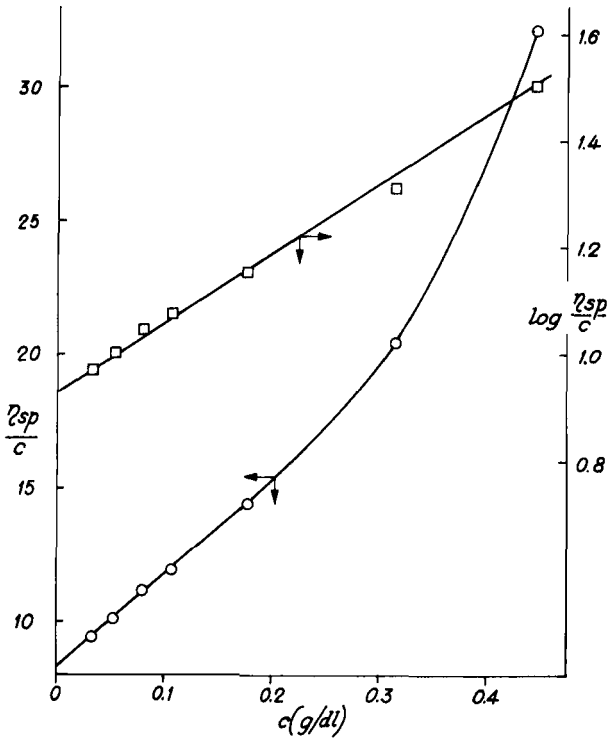


FIG. 2. Intrinsic viscosity of cellulose ($\bar{M}_n = 4.29 \times 10^5$) in cadoxene:water (1:1) at 2 dynes/cm². \circ and \square are extrapolations according to Huggins' and Martin's equations, respectively.

to infinite dilution by using the equations

$$\begin{aligned} \eta_{sp}/C &= [\eta] \left(1 + k'[\eta]C + k''[\eta]^2C^2 + O[\eta]^3C^3 \right) \\ \ln \eta_r/C &= [\eta] \left(1 - \beta'[\eta]C + \beta''[\eta]^2C^2 + O[\eta]^3C^3 \right) \end{aligned} \tag{1}$$

where

$$\begin{aligned} k' + \beta' &= 1/2 \\ \beta'' - k'' + k' &= 1/3 \end{aligned} \tag{2}$$

and by Martin's equation

$$\log(\eta_{sp}/C) = [\eta] + K[\eta]^2 C \quad (3)$$

which holds very well at moderate concentrations. Conditions given by Eq. (2) have been applied to estimate the intrinsic viscosities given in Table 1.

TABLE 1. Intrinsic Viscosities of Cellulose in Cadoxene:Water (1:1) and Number-Average Molecular Weights of Cellulose Nitrate and Cellulose

Fraction	[η] ^a Cellulose	$\bar{M}_n \times 10^{-5}$	
		Cellulose nitrate	Cellulose
2	8.43	6.40	4.13
5	5.90	4.73	2.73
7	5.00	3.72	2.27
9	3.28	2.12	1.38
10	2.70	1.64	1.02
11	2.08	1.13	0.73

^aIn deciliters/gram at 25°C.

The osmotic pressure of a solution of concentration C may be expressed as

$$\pi/C = RT/\bar{M}_n + AC + \dots \quad (4)$$

in which T is in °K and R is in (deciliters)(centimeters of water)/°K. Here π was measured in centimeters of water and C in grams/deciliter.

The data of Fig. 3 yield number-average molecular weights for cellulose nitrate, which together with those of cellulose are given in Table 1.

The dependence of $\log[\eta]$ on $\log M$ was found to be linear, as shown in Fig. 4. The computed values for the constants in the Mark-Houwink equation

$$[\eta] = KM^a \quad (5)$$

are $K = 2.63 \times 10^{-4}$ and $a = 0.80$ for the present system (Table 2).

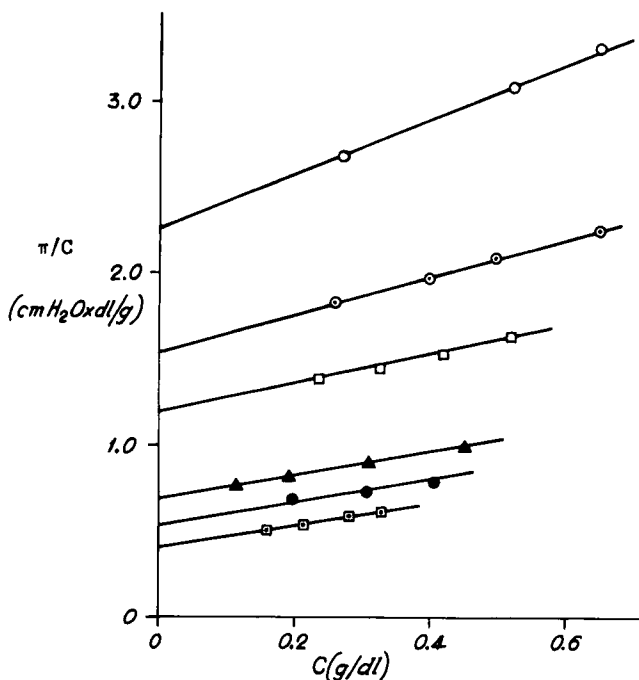


FIG. 3. Reduced osmotic pressures for the 2(■), 5(●), 7(▲), 9(□), 10(○), and 11(○) fractions of cellulose nitrate.

DISCUSSION

The exponent a of the Mark-Houwink equation is a commonly used index of the molecular expansion resulting from interaction with the solvent. The original Flory theory [14], which postulated that in the limiting case of an exceedingly good solvent $[\eta] \propto M^{0.8}$, has been challenged by a number of other theories [15-17], known as third power theories, which lead in the limit of a good solvent to a direct proportionality between the intrinsic viscosity and the molecular weight. On the other hand in a θ -solvent the polymer is tightly coiled and a is 0.5.

There are several relationships $[\eta] = f(M)$ for cellulose in various solvents, and a summary of them are given in Table 2. Although the intrinsic viscosities of cellulose in different solvents are higher in comparison with these of synthetic chain polymers, the exponent a

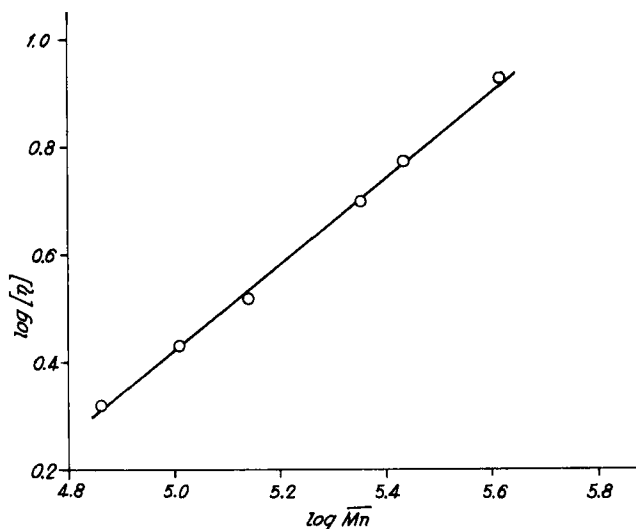


FIG. 4. Double logarithmic plot for intrinsic viscosity and number-average molecular weight at 25°C.

(≈ 0.8) is similar to those of flexible chains in good solvents. The Flory-Fox treatment of diluted solution properties of randomly coiled macromolecules establishes that [27]

$$[\eta] = K_{\theta} M^{1/2} \alpha^3 \quad (6)$$

where K_{θ} depends on the unperturbed dimensions of the dissolved molecules, and α , the linear expansion factor, depends on the solvent action. Introducing different expressions of α into Eq. (6) leads to several linear equations relating functions of $[\eta]$ with functions of M . A linear fit of the experimental data according to these equations means random coil behavior. Several equations have been examined by Cowie [28] who concluded that the most versatile remains the Stockmayer-Fixman relationship [15]:

$$[\eta]/M^{1/2} = K_{\theta} + 0.51 \phi B M^{1/2} \quad (7)$$

Another important relationship based on the Kurata-Stockmayer-Roig theory is [16]

$$[\eta]^{2/3}/M^{1/3} = K_{\theta}^{2/3} + 0.363 \phi B \{g(\alpha_{\eta}) M^{2/3} / [\eta]^{1/3}\} \quad (8)$$

where ϕ is the universal viscosity constant for chain polymers in solution, B is related to the Flory interaction parameter χ , and $g(\alpha_\eta)$ is given by

$$g(\alpha_\eta) = 8\alpha^3 / (3\alpha^2 + 1)^{3/2} \quad (9)$$

Viscosity data in good solvents should extrapolate to the same intercept K_θ when plotted by $[\eta]/M^{1/2}$ vs $M^{1/2}$ and $[\eta]^{2/3}/M^{1/3}$ vs $g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}$.

Flory [9] pointed out that the conclusions based on the application of Eqs. (7) and (8) were incorrect because all the premises of these theories break down in the low molecular weight region, and he further supported the earlier conclusion that the cellulose chains are stiff. However, Brown and Henley [8], with their data on hydroxyethylcellulose in water and in cadoxene, arrived at the conclusion that cellulose has relatively small unperturbed dimensions. The high extension of these molecules in solution has been attributed by Brown et al. [6-8] to the solvent effect rather than to short-range interactions.

Given the special nature of the cellulose solvents, we are conscious of the risks involved in calculating molecular parameters by extrapolation methods. However, with this reservation in mind, some of the basic molecular characteristics have been obtained using Eqs. (7) and (8) in order to compare them with those obtained by statistical mechanics procedures by Yathindra and Rao [29]. The data of Table 1 have been plotted according to the procedure of Stockmayer and Fixman, and Kurata and Stockmayer, as shown in Fig. 5. The values of K_θ

obtained by the successive approximation method suggested by Kurata and Stockmayer is 38×10^{-4} , which agrees very well with 37.6×10^{-4} obtained by equation (7). In the same figure are also plotted data of Henley [5] for unfractionated cellulose, and a value of 42×10^{-4} is obtained.

From

$$\langle r_o^2 \rangle / n\ell^2 = (M_o/\ell^2)(K/\phi)^{2/3} \quad (10)$$

the unperturbed dimensions were evaluated. Using $\phi = 2.5 \times 10^{21}$ and $\ell = 5.21 \text{ \AA}$, the resulting value of the unperturbed characteristic ratio is 7.9, considerably lower than 50, the value obtained by Yathindra and Rao. The theoretical free rotation ratio $(\langle r^2 \rangle / n\ell^2)_f$ depends on the

value to be assumed at the bridge oxygen atom, θ , which is not well known for these macromolecules. This ratio varies from 1.96 to 2.73 as θ varies from 110 to 119° [29]. The former value is in good agreement with the value of about 2.1 calculated by Benoit [30]. Taking $(\langle r^2 \rangle / n\ell^2)_f = 2$, the steric hindrance factor, σ , obtained is 2, which agrees with that calculated for vinyl polymers. This factor is something lower than for carboxymethylcellulose, hydroxyethylcellulose [6-8], and hylauronic acid [31, 32].

TABLE 2. Intrinsic Viscosity vs Molecular Weight Relations for Cellulose in Various Solvents

Solvent	Polydispersity	T (°C)	$[\eta] = \text{KM}^a$	Method* Ref.
Cuoxam	Unfractionated sample	25	$[\eta] = 0.77 \times 10^{-2} P_W^{0.81}$	NC, ls 18
		20	$[\eta] = 0.85 \times 10^{-4} M_V^{0.81}$	NC, os 19
	20	$[\eta] = 1.7 \times 10^{-4} M_V^{0.77}$	sd 20	
	20	$[\eta] = 6.8 \times 10^{-3} P_W^{0.9}$	NC, sd 21	
CED	Unfractionated sample	20	$[\eta] = 9.8 \times 10^{-2} P_W^{0.9}$	NC, sd 21
		25	$[\eta] = 1.33 \times 10^{-4} M_n^{0.9}$	NC, os 22
	25	$[\eta] = 1.7 \times 10^{-2} P_V^{0.8}$	os 23	
	25	$[\eta] = 2.2 \times 10^{-2} P_n^{0.78}$	24	
EWNN	Unfractionated sample	25	$[\eta] = 6.6 \times 10^{-3} P_W^{1.01}$	sd 25
FeTNa	Unfractionated sample	25	$[\eta] = 5.31 \times 10^{-4} M_W^{0.775}$	ls 1
Cadoxene:water (1:1)	Unfractionated cellulose	25	$[\eta] = 1.7 \times 10^{-2} P_W^{0.77}$	sd 5
		25	$[\eta] = 1.8 \times 10^{-2} P_W^{0.77}$	ls 5
	25	$[\eta] = 3.85 \times 10^{-4} M_W^{0.76}$	26	

	Fractionated cellulose	25	$[\eta] = 2.63 \times 10^{-4} M_n^{0.80}$	NC, os	This work	2
Cadoxene	Fractionated sample	25	$[\eta] = 5.93 \times 10^{-4} M^{0.94}$ ($M < 500,000$)	NC		2
		25	$[\eta] = 9.33 \times 10^{-4} M^{0.72}$ ($M > 300,000$)			2
	Unfractionated cellulose	25	$[\eta] = 5.10 \times 10^{-3} M^{0.94}$			2

*The last column shows the method by which the molecular weight of cellulose has been determined: sd, sedimentation and diffusion; ls, light scattering; os, osmometry; and NC, the molecular weight was determined by converting cellulose into nitrocellulose.

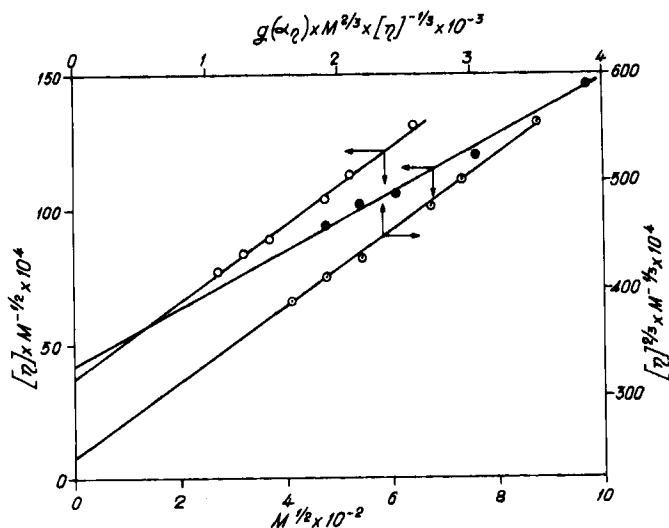


FIG. 5. Stockmayer-Fixman (\circ) and Kurata-Stockmayer (\odot) plots for fractionated cellulose in cadoxene:water (1:1), together with the data of Henley (\bullet) [5].

On the other hand, Yathindra and Rao [29] estimated σ at 4.4. This high value indicates that the preferred orientation of the glucose residues in cellulose chains gives rise to an extended conformation, in agreement with the conclusion of Flory [9, 14]. Furthermore, according to Yathindra and Rao, substituents such as nitrate have little effect on the unperturbed dimensions of cellulose chains.

Similar conclusions based on the small effect of steric hindrances on the flexibility of the cellulosic derivatives have been reached by Brown et al. [6-8], and their data indicate that the hindrances are higher in cellulose than in carboxymethylcellulose and hydroxyethylcellulose if σ for cellulose and both derivatives are obtained from light-scattering and viscometric data, respectively. However, the hindrances are almost the same if σ is evaluated from viscometric data in both cases. This view disagrees with the results obtained from the non-Newtonian behavior of cellulose solutions [12]. Noda and Hearst [33] recently presented a dynamic model for a polymer molecule with local stiffness that requires the introduction of a Lagrange multiplier whose magnitude is determined by the constraint that the contour length of the molecule has a fixed value L . This theory has proved to be useful in predicting the dependence of the relative intrinsic viscosity on the

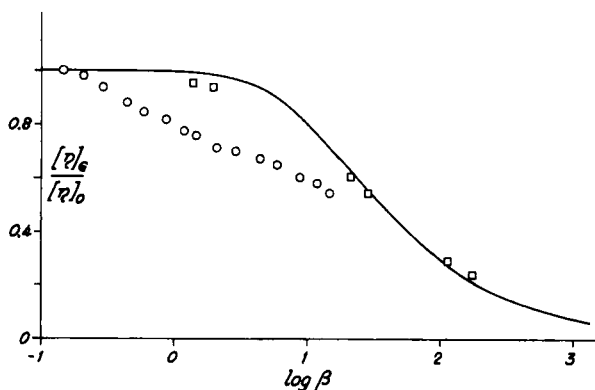


FIG. 6. Relative intrinsic viscosity as a function of the generalized shear rate, β . (\circ) Cellulose ($\bar{M}_n = 4.29 \times 10^5$) in cadoxene:water (1:1); (\square) cellulose trinitrate in ethyl acetate. Line, theoretical curve [12].

generalized shear rate, β , in those systems in which the excluded volume interactions can be ignored, e.g., cellulose nitrate in solution. The agreement between the experimental values and the theoretical ones for the non-Newtonian behavior of cellulose in solution are very poor, as can be seen in Fig. 6. The results show that the excluded volume effects for cellulose in solution are very important, and this polymer cannot be considered a very rigid macromolecule in nature. On the other hand, the experimental and theoretical values agree very well for cellulose nitrate, showing that the steric hindrances are very severe in this polymer.

Very recently Brant and Goebel [34] reported that an agreement between theoretical and experimental results concerning the unperturbed dimensions of cellulose can be achieved if the restriction of β -glucose residues to the C1 conformation is removed. The occasional occurrence of residues with a conformation belonging to the flexible cycle of conformations of the boat-skew class causes a dramatic reduction of the unperturbed dimensions of cellulose.

The behavior of cellulose in other solvents remains to be analyzed. Valtasaari [1] studied the configuration of cellulose dissolved in iron-sodium tartrate and obtained a value of 70×10^{-4} for K_θ . This means that the unperturbed dimension of cellulose is about 13 and the steric factor is about 2.5, both values lower than those obtained by statistics mechanics methods but higher than those obtained by us using cadoxene as solvent. Thus a striking difference appears in K_θ and σ when different solvents are used. If this lack of agreement is confirmed in further

experimental work, we dare to point out that one of the principal reasons for this failure may be, due to the solvent mechanism which is nowadays open to speculation. It has been suggested that Cd^{2+} and Fe^{3+} ions are capable of binding two and three successive glucosidic units, respectively. If this speculation is true, it is possible that the bond angles of cellulose in solution are distorted, and the viscometric as well other theories cannot be applied because such treatments imply that the bond angles are not affected by the solvent.

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