

Dilute Solution Properties and Unperturbed Chain Dimension of Cellulose Triacetate

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ABSTRACT: Cellulose triacetate (CTA, combined acetic acid content, 61.0 wt%) was successfully fractionated on the basis of molecular weight by successive solution fractionation using 1-chloro-2,3-epoxypropane as the solvent and hexane as the nonsolvent. The fractions cover a very wide range of molecular weights, having comparatively narrow molecular weight distribution ($M_w/M_n=1.4$, M_w = the weight-average molecular weight and M_n = the number-average molecular weight). To estimate molecular parameter viscosities, osmotic pressure, and light scattering measurements were carried out on twelve CTA fractions in various solvents. The following empirical relations were obtained for the limiting viscosity number $[\eta]$ and the radius of gyration $\langle S^2 \rangle_z^{1/2}$ in dimethylacetamide (DMAc) at 25°C: $[\eta]=2.64 \times 10^{-2} M_w^{0.75}$ ($\text{cm}^3 \text{g}^{-1}$), $\langle S^2 \rangle_z^{1/2}=0.463 \times 10^{-8} M_w^{0.55}$ (cm). For CTA/DMAc system, the CTA chain is gaussian in the unperturbed state and a_Φ ($=d \ln \Phi / d \ln M$, Φ = Flory's viscosity parameter) = 0.106 and the draining parameter $X=2$ were obtained. On the basis of the light scattering and viscosity data, the short-range interaction parameter $A=1.46 \times 10^{-8}$ cm, the conformation parameter $\sigma=3.14$, and the characteristic ratio $C_\infty=20.4$. These values were estimated by using method 2B, 2C, and 2G, proposed in the previous paper (This journal, 10, 409 (1978)). The A value in polar solvents (group I: DMAc, trifluoroacetic acid, and acetone) is significantly larger than that in non-polar solvents (group II: dichloromethane, tetrachloroethane, and trichloromethane). The effect of the degree of substitution on $[\eta]$ and σ for cellulose acetate in acetone is just the reverse of those for cellulose nitrate in the same solvent. The CTA chain is semiflexible and the contribution of the volume effect on $[\eta]$ is much smaller than that of the draining effect.

KEY WORDS Dilute Solution Property / Unperturbed Chain Dimension / Cellulose Triacetate / Cellulose Diacetate / Viscosity / Osmotic Pressure / Light Scattering / Draining Effect / Conformation Parameter / Characteristic Ratio /

Cellulose triacetate (we denote it by CTA hereafter) has held for many years, worldwide importance in industry as a staring polymeric material for fibers, plastics, films, and membranes. Nevertheless, very few comprehensive and reliable studies on its molecular characteristics have been reported up to now. Only the solubility behaviour of CTA in various solvents and their Mark-Houwink-Sakurada (MHS) equations (eq 6) have been the targets for studies in the past. In addition, all MHS equations, proposed hitherto, are less accurate¹ and are still not completely established. For instance, the Polymer Handbook compiles nine MHS equations for "CTA" solutions.² It is particularly noteworthy, however, that all these equations except for the Flory

et al.'s equation, are for cellulose diacetate (CDA) and not for CTA. More recently, during the course of our investigation, Nair *et al.*³ carried out light scattering measurements on CTA fractions in a mixed solvent [dichloromethane(DCM)/methanol = 1/1, v/v] and viscosity measurements in trichloromethane (TCM) over a very limited range of molecular weight (the ratio of the maximum to minimum weight-average molecular weight M_w , is only 1.72). As will be discussed later, their results are far beyond our understanding and in particular, the values of the radius of gyration $\langle S^2 \rangle_z^{1/2}$ are extraordinarily large. The main reason why the research of CTA dilute solution has been delayed and is still in a rather primitive state, although great advances have

made in elucidation of the molecular parameters for other cellulose derivatives, should be attributed exclusively to the great difficulty encountered in experiment on molecular weight fractionation. In fact from among a large number of studies of the molecular weight fractionation of CTA published since the mid-1930's, we can find very few successful examples.

In our earlier work,⁴ we determined the molecular properties of cellulose diacetate (CDA, combined acetic acid content (AC), 55.6 wt%) in solutions. In this work, we attempt to fractionate CTA efficiently by the solubility method and to measure, over a wide range of molecular weights, the dilute solution properties of CTA fractions, thus obtained, by viscometry, membrane osmometry (MO), and light scattering (LS) method and to determine in a general way the molecular parameters of CTA in comparison with CDA.

EXPERIMENTAL

Polymer Sample and Solvents

Purified cotton linter was acetylated by the standard method with an acetic anhydride-acetic acid-sulfuric acid mixture.^{5,6} The product was subjected to additional stabilization by an excess magnesium acetate. A proper amount of 35 wt% acetic acid was added to produce the precipitate completely which was filtered through filter paper and then washed with water. CTA, thus prepared (sample cord TA2), was dried *in vacuo* and had the number-average molecular weight $M_n = 5.85 \times 10^4$ by MO and the weight-average molecular weight $M_w = 2.35 \times 10^5$ by LS. The combined acetic acid content (AC) determination of the unfractionated CTA by the back-titration method using sodium hydroxide and sulfuric acid gave a value of 61.0 wt% (degree of substitution (DS) = 2.89).

1-chloro-2,3-epoxypropane, hexane, trifluoroacetic acid (TFA), acetone, dichloromethane (CDM), 1,1,2,2-tetrachloroethane (TCE), and trichloromethane (TCM) were of reagent grade and used as received. Dimethylacetamide (DMAc), used for light scattering method, was of guaranteed grade and was purified by drying over phosphorous pentoxide and distillation immediately prior to use.

Fractionation

Up to now, acetic acid and chlorinated hy-

drocarbons, which have the low dielectric constant ϵ , have been extensively employed as solvents for the molecular weight fractionation of CTA. The fractionation efficiency achieved by using the above-mentioned solvents was poor unfortunately and the numerous attempts made so far have met with very limited success.

In order to overcome the above-mentioned experimental difficulty, preliminary experiments on phase separation of CTA solution were performed for many solvent/nonsolvent combinations, including those employed in literature^{3,7-21}. Judging from the easiness of two liquid phase separation and of the solvent recovery, we chose 1-chloro-2,3-epoxypropane (epichlorohydrine) as solvent and hexane as precipitant.

Successive solution fractionation technique (SSF), originally advocated for use by Kamide and his coworkers,²² was applied. A 60 gram TA2 sample was dissolved in 1-chloro-2,3-epoxypropane (6000 cm³) and thermostated at 35°C. The requisite amount of hexane predetermined by a pilot fractionation, was added to the solution, resulting in phase separation. The supernatant phase was isolated by a vacuum line from the vessel and hexane and 1-chloro-2,3-epoxypropane in the phase were separated by step-wise evaporation in a rotary evaporator and re-used for further fractionation. The fractionation was carried out in a perfectly closed system. The fractionation apparatus was specially designed and is described elsewhere.²³ Finally, thirteen fractions were separated in a SSF run, in which the composition of the hexane at each step varied from 44.5 to 33.4 vol % at 35°C. Equilibrium between the two phases was not difficult to attain, so that the fractionation is efficient (see Table I). The polymer fractions prepared in this way were vacuum-dried at 60°C for one day. No hydrolysis of the acetyl group was detected.

Solution Viscosity

The CTA solutions for viscosity measurement were prepared at room temperature, excluding DMAc, in which the polymer was dissolved at 60°C. The CTA solution in acetone was prepared by the cooling method used in a previous paper.⁴ It has been known that CTA dissolves in acetone by cooling a slurry of CTA and acetone down to -40°C or below, followed by warming it to room temperature.^{21,24} As early as the late 1920s, Kita *et al.*²⁵ first pointed out

that the acetone solubility of CTA is mainly attributable not to the acetyl content, but to the "physical state" of polymer. Solution viscosity of CTA fractions was measured in DMAc, TFA, acetone, TCE, and TCM at 25°C and in DCM at 20°C, by using Ubbelohde-type capillary viscometers, specially designed so that no kinetic energy correction was necessary. The limiting viscosity number $[\eta]$, expressed in $\text{cm}^3 \text{g}^{-1}$, was determined as usual from Huggins plot (η_{sp}/c vs. c ; η_{sp} , specific viscosity and c , concentration). For the sake of comparison, $[\eta]$ of five CDA fractions prepared in the previous paper⁴ was measured in DMAc, TFA, and acetone at 25°C.

Membrane Osmometry

Osmotic pressure measurements were carried out with a Howlett Packard high speed membrane osmometer model 502 in DMAc, acetone, TCE, and TCM at 25°C. The membrane was a Sartorius allerfeinst membrane and no diffusing of the solute was observed.

The following relation holds between the osmotic pressure π and the concentration c (g cm^{-3})

$$\pi/c = RT\{1/M_n + A_{2,o}c + \dots\} \quad (1)$$

where R is the gas constant, T is temperature (K) and $A_{2,o}$ is the second virial coefficient obtained by membrane osmometry. M_n and $A_{2,o}$ were evaluated from the linear part of a plot of π/c vs. c as intercept and slope, respectively.

The polymer-solvent thermodynamic interaction parameter χ was calculated from the osmotic data using the relation

$$\chi = -\{\pi V_0/RT + \ln(1 - v_p) + (1 - 1/X_n^*)v_p\}/v_p^2 \quad (2)$$

where V_0 , solvent molar volume; v_p , volume fraction of polymer ($=V_0c/M$); X_n^* , the number-average molar volume ratio of polymer to solvent ($=M_n V_m/m$; V_m , molar volume of the monomer unit and m , molecular weight of the monomer unit).

Light Scattering

In preference to acetone DMAc was chosen as the solvent for the light scattering measurement, since it affords easy exclusion of the gel-like materials in solution. Two vacuum-dried CTA fractions (TA2-6 and TA2-13) and a CDA fraction (EF 3-11), obtained in the previous work,⁴ were dissolved in freshly distilled DMAc at 60°C. The specific re-

fractive index increment dn/dc of these solutions was determined in a Shimadzu differential refractometer model DR-4 at 25°C at a wave length λ_0 of 436 nm (4360 Å). Great care is required to ensure that DMAc is absolutely dry, since it is highly hygroscopic and will yield a high dn/dc value when wet. The dn/dc was found to be 0.0398 ($\text{cm}^3 \text{g}^{-1}$) for two CTA fractions, irrespective of their M_w values, and 0.0418 ($\text{cm}^3 \text{g}^{-1}$) for a CDA (AC=55.6 wt%) fraction.

The optical clarification procedure of the solution is similar to that used in the previous paper.⁴ After a 0.5% stock solution was centrifuged at $3 \times 10^4 \text{ g}$ for 90 min, the fresh solvent was added to the isolated upper layer, yielding the solutions with four different concentrations. The solutions prepared thus far were immediately followed again by centrifugation at $3 \times 10^4 \text{ g}$ for 90 min. The upper two-thirds of the supernatant phase was carefully filtered through a Sartorius membrane filter $0.2 \mu\text{m}$, directly into a light scattering cylindrical cell.

The light scattering measurements in the angle range 30–150° were made with vertically polarized incident light [$\lambda_0 = 436 \text{ nm}$ (4360 Å)] at 25°C in the Shimadzu-Brice type light scattering photometer model PG-21. The vertical component of the scattered light was measured. M_w and $A_{2,1}$ (the suffix 1 means light scattering) were determined from the Zimm plot. No distortion was observed in the Zimm plot for CTA solutions after ultracentrifugation for removing the gel particles attributable to non-CTA materials and in part to the associated CTA molecules.

RESULTS AND DISCUSSION

Molecular Weight and Molecular Weight Distribution of CTA Fraction

Table I gives a list of the experimental results by the membrane osmometry and light scattering for CTA solutions in DMAc, all evaluated at 25°C. In Table II are outlined the viscosity data obtained with solutions of the same CTA fractions in DMAc, TFA, acetone, DCM, TCE, and TCM. All measurements were made, with the exception of DCM, at 25°C. $\langle S^2 \rangle_z^{1/2}$ and $\langle S^2 \rangle_w^{1/2}$, tabulated in the fifth and sixth columns, represent the Z-average and weight-average radius of gyration, respectively. The $\langle S^2 \rangle_w^{1/2}$ values were converted from $\langle S^2 \rangle_z^{1/2}$ and the polydispersity (M_w/M_n) data through use of the

Table I. Results of membrane osmometer and light scattering measurements with cellulose triacetate in dimethylacetamide at 25°C

Sample code	Osmotic pressure			Light scattering					χ	$\Phi \times 10^{-23}$	α_s^d	X^e
	$M_n \times 10^{-4}$	$A_2 \times 10^{+b}$	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2} \times 10^{8c}$	$\langle S^2 \rangle_w^{1/2} \times 10^8$	$A_2 \times 10^4$	M_w/M_n					
TA2-1	—	—	—	—	—	—	—	—	—	—	—	—
TA2-2	1.96	13.2	—	—	—	—	—	—	0.29	—	—	—
TA2-3	2.71	13.1	—	—	—	—	—	—	0.30	—	—	—
TA2-4	4.11	12.2	6.36	180	159	13.6	1.54	1.15	0.31	1.10	1.4	1.4
TA2-5	5.60	11.8	8.22	214	186	13.4	1.46	1.19	0.32	1.10	1.5	1.5
TA2-6	9.78	11.4	13.7	287	253	15.1	1.40	1.09	0.32	1.16	1.4	1.4
TA2-7	11.4	11.4	14.9	277	249	12.5	1.30	1.32	0.33	1.17	2.1	2.1
TA2-8	14.6	11.7	20.0	342	303	12.1	1.37	1.29	0.32	1.16	2.0	2.0
TA2-9	20.2	11.4	26.2	395	356	11.3	1.30	1.33	0.33	1.15	2.2	2.2
TA2-10	21.9	10.6	30.8	421	371	9.5	1.40	1.49	0.34	1.16	2.9	2.9
TA2-11	31.7	10.8	44.4	531	468	9.9	1.40	1.38	0.32	1.19	2.5	2.5
TA2-12	35.7	10.7	50.0	565	503	10.8	1.40	1.36	0.34	1.12	2.3	2.3
TA2-13	47.8	10.4	69.0	671	587	10.4	1.44	1.47	0.33	1.15	2.6	2.6
TA2 ^a	5.85	9.12	23.5	467	353	7.8	4.02	1.12	0.36	—	—	—

^a Whole polymer. ^b $\text{cm}^3 \text{mol}^{-1} \text{g}^{-2}$. ^c cm^2 . ^d via penetration function ψ . ^e By method 1A.

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Table II. Results of viscosity measurements with cellulose triacetate in various solvents

Sample code	$M_w \times 10^{-4}$	$\text{cm}^3 \text{g}^{-1} \text{ (at } 25^\circ\text{C)}/[\eta]$					
		DMAc ^a	TFA ^b	Acetone	DCM ^{c,d}	TCE ^e	TCM ^f
TA2- 1	—	—	—	—	—	26	—
TA2- 2	—	59	—	—	—	38	—
TA2- 3	—	70	—	—	—	47	—
TA2- 4	6.36	102	96	—	59	60	(47) ^g
TA2- 5	8.22	131	118	110	71	73	69
TA2- 6	13.7	183	164	143	100	95	97
TA2- 7	14.9	195	—	154	—	98	—
TA2- 8	20.0	256	228	211	136	129	129
TA2- 9	26.2	327	—	265	—	163	—
TA2-10	30.8	350	286	282	184	168	171
TA2-11	44.4	451	385	357	—	214	210
TA2-12	50.0	490	434	398	260	243	228
TA2-13	69.0	607	508	480	306	270	272

^a Dimethylacetamide. ^b Trifluoroacetic acid. ^c Dichloromethane. ^d At 20°C. ^e Tetrachloroethane.

^f Trichloromethane. ^g Partially dissolved.

Table III. Results of osmotic pressure measurements with cellulose triacetate fractions in various solvents at 25°C

Sample code	$M_n \times 10^{-1}$				$A_2 \times 10^4 / \text{mol cm}^3 \text{g}^{-1}$				χ from eq 2			
	DMAc ^a	Acetone	TCE ^b	TCM ^c	DMAc ^a	Acetone	TCE ^b	TCM ^c	DMAc ^a	Acetone	TCE ^b	TCM ^c
TA2- 5	5.60	5.45	5.80	5.60	11.8	11.7	12.0	12.4	0.32	0.36	0.29	0.33
TA2-10	21.9	21.1	21.2	21.7	10.6	11.7	11.5	8.7	0.34	0.36	0.30	0.38

^a Dimethylacetamide. ^b Tetrachloroethane. ^c Trichloromethane.

relation

$$\langle S^2 \rangle_w^{1/2} = \left(\frac{h+1}{h+2} \right)^{1/2} \langle S^2 \rangle_z^{1/2} \quad (3)$$

with

$$h^{-1} = (M_w/M_n) - 1 \quad (4)$$

Equation 3 was derived for the case when the molecular weight distribution (MWD) of the polymer sample was represented by the Schulz–Zimm type distribution.

Flory's viscosity parameter Φ was calculated directly from eq 5 using the experimentally determined values

$$\Phi = [\eta] M_w / \langle S^2 \rangle_z^{3/2} 6^{3/2} q_{w,z} \quad (5)$$

with $q_{w,z}$ = the correction factor for the polymolecularity of the sample. The χ value, calculated by eq 2, showed no significant concentration dependence

within the concentration range studied; averaged values over the concentration covered here are shown in the Table I.

The CTA fractions separated in this work cover a wide molecular weight (M_w) range from 2.9×10^4 to 69.0×10^4 (*i.e.*, the ratio of the upper- to the lower-limited $M_w = 23.8$). The polydispersity, expressed in terms of M_w/M_n , of the CTA fractions lies between 1.30–1.54 and there is a reasonably constant M_w/M_n ratio of about 1.4 over the M_w range. Theoretical calculations^{26–29} as well as the actual experiments on polyethylene,²³ polystyrene,^{30–33} poly(α -methyl styrene),³⁴ and CDA,⁴ carried out at our laboratory, show that SSF always yields a series of fractions with nearly the same M_w/M_n , except for a few initial fractions. The results on CTA are in an excellent agreement with previous conclusions we reached, and these data do not seem to be the possibility of much further advance in preparing

CTA having very narrow MWD ($M_w/M_n \approx 1.1$), without finding of a new single solvent suitable for SSF. Molecules of cellulose derivatives have a peculiar tendency to associate in poor solvents. CDA in TCE below 70°C is just an example.⁴ For the purpose of clarifying this point to the case of CTA solutions in the solvents employed here, osmotic pressures of solutions of two CTA fractions, differing M_w (TA2-5 and TA2-10), in various solvents were measured. The results of these determinations are represented in Table III. Evidently, four solvents gave almost the same M_n value of CTA fraction, within the experimental error. This indicates directly that molecular association of CTA dose not occur in these solvents. As early as 1953, Staudinger and Eicher³⁵ found by the membrane osmometry a fairly good coincidence of M_n of a CDA (DS=2.37) sample in acetone with that in glacial acetic acid. After the measurement of M_n for a CTA (DS=2.88) whole polymer in nitromethane, TCM, and acetone, Cowie and Ranson²¹ concluded that neither degradation nor aggregation was apparent.

It has been generally believed that CTA is soluble only in acidic solvents.³⁶ But non-acidic solvents, such as DMAc, TFA, and acetone are also adequate solvents for CTA.

Mark-Houwink-Sakurada Equation

Figure 1a shows the log-log plot of $[\eta]$ vs. M_n or M_w for CTA solution in DMAc at 25°C. In this figure, the closed circle denotes M_n and the open circle is M_w . Both plots can be reasonably represented by straight lines, suggesting that the Mark-Houwink-Sakurada equation,

$$[\eta] = K_m M^a \quad (6)$$

or

$$[\eta] = K_m M_w^a \quad (6')$$

may be well established over the entire M_w range investigated.

The parameters K_m and a of MHS equations for six solvents were evaluated by using the least square method and MHS equations are represented, in Figure 1b-f, by straight lines through the observed points. MHS equations of this work are the most comprehensive correlations so far made between $[\eta]$ and the molecular weight. In general, $[\eta]$ values in CTA solution in chlorinated hydrocarbons are smaller than those of the same molecular weight in other

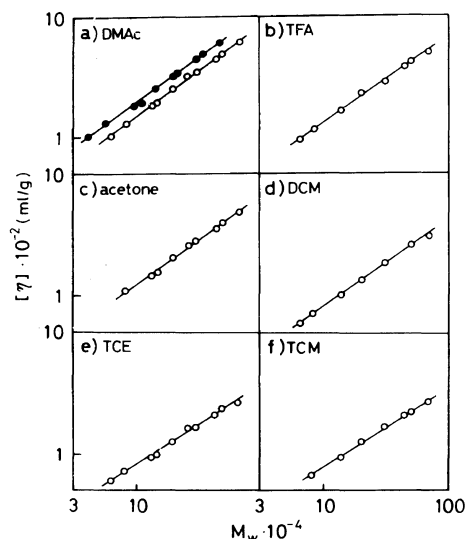


Figure 1. Log-log plot of limiting viscosity number $[\eta]$ against the weight-average molecular weight M_w (open mark) or the number-average molecular weight M_n (closed mark) for cellulose triacetate in dimethylacetamide (DMAc), trifluoroacetic acid (TFA), acetone, dichloromethane (DCM), tetrachloroethane (TCE), and trichloromethane (TCM). Straight lines represent the Mark-Houwink-Sakurada equations (eq a-g) determined by the least-squares method.

solvents by 50%.

The MHS equation corresponding to monodisperse CTA in DMAc can be readily derived from $[\eta]$ and M_w of CTA fractions, by taking into account the MWD of the fractions, as

$$[\eta] = 2.71 \times 10^{-2} M^{0.750} \quad (a)$$

In deriving eq a we assumed the Schulz-Zimm distribution with $M_w/M_n = 1.4$ for the samples. Almost the same equation as eq a can also be derived from $[\eta]$ and M_n of the fractions.

Table IV lists the MHS equations for CTA established in this work, together with those proposed hitherto. The exponent a values reported in the literature data for the systems studied here are generally in the range of 0.8~1.0, and are indeed markedly larger than our values (0.65~0.75). Notable differences in parameters in the MHS equations, as shown, are considered to have their origin in the considerable molecular weight dependence of the polydispersity of the samples used in literature, as demonstrated with CDA solutions.⁴ In particular, the systematic molecular weight depen-

Table IV. Mark-Houwink-Sakurada equations for cellulose triacetate in various solvents

Solvent	Temp °C	$K_m \times 10^2$	a	No. of sample		Mol wt range $M \times 10^{-4}$	Method	Acetyl content %	Ref
				Fr.	W.P.				
DCM ^a / ethanol (8/2, v/v)	25	1.41	0.834	24	—	2.15—20.4	vis ^f	60.9	14
	25	0.45	0.90	—	5	3.06—18.0	vis ^g	62	38, 39
TCM ^b	25	2.51	1.02	—	8	—	MO ^h	61.0	40
	25	4.54	0.649	7	—	8.22—69.0	LS ⁱ	61.0	this work
	20	0.22	0.95	13	—	1.36—13.0	MP	61	18
DCM	20	2.47	0.704	7	—	6.36—69.0	LS	61.0	} this work
DMAc ^c	25	2.64	0.750	10	—	6.36—69.0	LS	61.0	
TFA ^d	25	3.96	0.706	8	—	6.36—69.0	LS	61.0	
Acetone	25	2.89	0.725	9	—	8.22—69.0	LS	61.0	
TCE ^e	25	3.93	0.662	10	—	6.36—69.0	LS	61.0	

^a Dichloromethane. ^b Trichloromethane. ^c Dimethylacetamide. ^d Trifluoroacetic acid. ^e Tetrachloroethane.

^f Degree of acetylation was calculated from the cuprammonium limiting viscosity number of diacetylated fractions: $[\eta] = 0.0319 \times P_n^{0.657}$ (P_n , the number-average degree of polymerization was determined for CDA by osmometry).

^g M was calculated from the relationships for cellulose diacetate in acetone at 25°C: $[\eta] = 8.97 \times 10^{-3} M_n^{0.90}$, which is given by Phillips and Bjork.³⁹ ^h Membrane osmometry. ⁱ Light scattering.

dence of MWD of the samples will yield incorrectly high a values. Detailed discussions of the effect of MWD on MHS equation are presented elsewhere.³⁷

Radius of Gyration and Second Virial Coefficient

Figure 2 shows the radius of gyration $\langle S^2 \rangle_z^{1/2}$ plotted against the molecular weight for CTA solution in DMAc as open circle. From this figure, we obtain the following empirical relation.

$$\langle S^2 \rangle_z^{1/2} = 0.463 \times 10^{-8} M_w^{0.55} \quad (\text{cm}) \quad (\text{b})$$

In Figure 2 are also included the data from Nair *et al.*'s work³ on CTA in a mixed solvent (DCM/methanol, 1/1, v/v) as a closed circle, together with the point by Shakhparonov *et al.*⁴¹ on CTA in DCM (temperature was not described) as a closed rectangle. The Nair *et al.*'s value of $\langle S^2 \rangle_z^{1/2}$ is, indeed, larger by a factor of about 3.5 than the value obtained here for DMAc, compared at the same M_w . Thus, it is obvious that Nair *et al.*'s data of $\langle S^2 \rangle_z^{1/2}$ are the largest among all data available for cellulose derivatives.⁴² The data points obtained by Shakhparonov *et al.*⁴¹ for CTA in TCM is slightly smaller than those we obtained in DMAc. It is expected from the $[\eta]$ data in Table II that $\langle S^2 \rangle_z^{1/2}$ is smaller in TCM than in DMAc. An open triangle in the figure corresponds to CDA in DMAc (see Table VI).

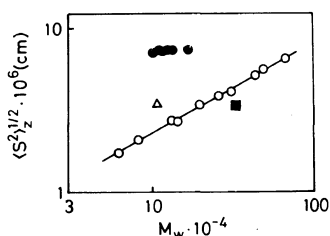


Figure 2. Molecular weight dependence of the radii of gyration $\langle S^2 \rangle_z^{1/2}$ for cellulose triacetate (CTA) and cellulose diacetate (CDA) solutions: \circ , CTA in dimethylacetamide (DMAc) (this work); \bullet , CTA in dichloromethane (DCM)/methanol (1/1, v/v) (Nair *et al.*'s work³); \blacksquare , CTA in DCM (Shakhparonov *et al.*'s work⁴¹); \triangle , CDA in DMAc (this work).

Figure 3 shows the log-log plot of the second virial coefficient A_2 against M_w for CTA solution in DMAc at 25°C. A_2 shows a small molecular weight dependence. In the lower M_w range, $A_{2,i}$ is slightly dependence. However, if we take into consideration the effect of MWD on A_2 and the experimental error involved, there is essentially no difference between $A_{2,i}$ and $A_{2,o}$. The polydispersity correction of the CTA samples, according to Casassa,⁴³ reduces the observed $A_{2,i}$ only by about 1% (and $A_{2,o}$ by about 9%). The second virial coefficient by membrane osmometry $A_{2,o}$ is related experimentally to its M_w through the equation:

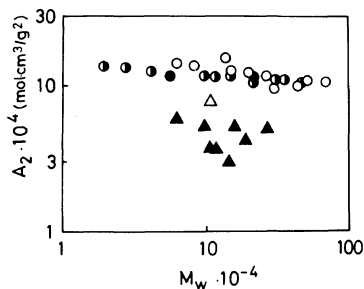


Figure 3. Molecular weight dependence of the second virial coefficient A_2 for cellulose triacetate (CTA) and cellulose diacetate (CDA) solutions: ○, CTA in dimethylacetamide (DMAc) by light scattering (LS); ●, CTA in DMAc by membrane osmometry (MO); ●, CTA in acetone by MO; △, CDA in DMAc by LS; ▲, CDA in acetone by LS.

$$A_{2,0} = 2.64 \times 10^{-3} M_w^{-0.071} \quad (c)$$

for a CTA solution in DMAc at 25°C. In Figure 3, the corresponding data for CDA solutions in DMAc and acetone are plotted for the sake of comparison. The A_2 values for CTA in DMAc are more than two times the values for CDA in acetone.

The $A_{2,0}$ values of CTA in DMAc and acetone are similar in magnitude, and slightly larger than those in the chlorinated solvents. The polymer-solvent interaction parameter χ for CTA is in the range 0.29–0.38 in DMAc, acetone, TCE, and TCM (Tables I and III). Howard and Parikh obtained $\chi = 0.38$ for an unfractionated CTA sample ($M_n = 3.82 \times 10^4$) solution in TCM.¹⁹ This value agrees fairly well, if the MWD of the sample is taken into account with those evaluated here. There is no obvious relation between $[\eta]$ and χ (or A_2) of a given sample dissolved in different solvents.

Flory's Viscosity Parameter and Excluded Volume Effect

Figure 4a illustrates the Flory's viscosity parameter Φ plotted as a function of the molecular weight for CTA solution in DMAc as open circle. As noted previously for other cellulose derivatives, the Φ value for CTA in DMAc reveals unquestionably a significant molecular weight dependence, which may be semiempirically expressed by

$$\Phi = K_\Phi M_w^a \quad (7)$$

with K_Φ and a_Φ the parameters for a given polymer/solvent system. For CTA in DMAc, we

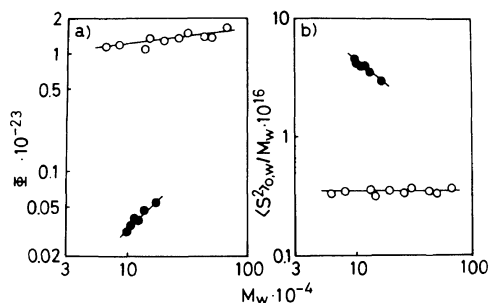


Figure 4. Molecular weight dependence of the Flory's viscosity parameter Φ (a) and of the ratio of the unperturbed radius of gyration $\langle S^2 \rangle_{0,w} / M_w$ to M_w for cellulose triacetate solutions (b): ○, CTA in dimethylacetamide (this work); ●, CTA in dichloromethane/methanol (1/1, v/v) (Nair *et al.*'s work³).

obtain $K_\Phi = 0.35 \times 10^{23}$ and $a_\Phi = 0.106$. In addition, the magnitude of Φ is less than 1.8–2.6 times the theoretical value (2.87×10^{23}) at the unperturbed state. These experimental facts show definitely that the draining effect may by no means be ignored, and that it plays an important role in the CTA/DMAc system at least over the entire molecular weight range in the experiment. The significant contribution of the draining effect has not really attracted very much attention, until similar results were reported very recently for CDA⁴ and other cellulose derivatives.⁴² It is of interest to note that the a_Φ value of CDA in acetone is known to be exceptionally large.⁴

According to the Kurata-Yamakawa (KY) theory,⁴⁴ Φ is a function of the draining parameter X in the form

$$\Phi = \Phi(X) \alpha_s^{-(3-n(X))} \quad (5')$$

where $\Phi(X)$ and $n(X)$ are functions of X , defined by KY theory.⁴⁴ Therefore, on the basis of eq 5 and 5' we can estimate X values from the data of $[\eta]$, M_w , $\langle S^2 \rangle_z$ and the expansion factor α_s , which was calculated from the penetration function ψ , to be described later. This method was referred to as the method 1A in the previous paper.⁴² The X values thus estimated are brought together in the last column of Table I, and from which the averaged X value was found to be 2.1.

To check the reliability of the values of Φ and a_Φ , which are very closely connected both with the draining parameter, the X value was also evaluated from the following equations

$$a_\Phi = \frac{1}{2} \frac{d \ln \Phi(X)}{d \ln X} - \{3 - n(X)\} a_1/3 \quad (8)$$

and

$$a_1 = a - 0.5 - a_\Phi - 1.5a_2 \quad (9)$$

where $n(X)$ is defined in the KY theory and a_2 is a parameter representing the non-gaussian nature of the chain in the unperturbed state, and is defined by $d \ln \langle S^2 \rangle_0 / M / d \ln M \langle S^2 \rangle_0^{1/2}$, the radius of gyration at unperturbed state). On substituting numerical values for the quantities a , a_Φ , and a_1 , obtained for CTA/DMAc system (*i.e.*, $a = 0.750$, $a_\Phi = 0.106$ and $a_2 = 0$ (see Figure 4b), into eq 8 and 9, X is found to be approximately 4. Therefore, the values of Φ and a_Φ are roughly concordant, although the values determined by method 1A are, beyond question, much more reliable.

The Φ values, calculated by using Nair *et al.*'s data, are represented in Figure 4a as closed circles. These values are, suprisingly, less than 10 times those we obtained and there are not examples of polymers, including cellulose derivatives/solvent system, showing such a small Φ values (for example, see Figure 5 of ref 42). Comparison of Figures 2 and 4, therefore, leads to the conclusion that Nair *et al.*'s data are not accurate enough to be analyzed, further for establishing empirically the dependence of Φ on M_w . Nair *et al.* estimated the short-range interaction parameter $A = (6 \langle S^2 \rangle_0 / M)^{1/2}$ according to the Stockmayer and Fisman plot (by our notation, method 2E), which retains its validity only in the case where both a_Φ and a_2 are concurrently zero.

The excluded volume parameter \bar{z} was estimated from the penetration function ψ , defined as $0.746 \times 10^{-25} A_2 M_w^2 / \langle S^2 \rangle_w^{3/2}$, and was calculated from the light scattering data in Table I, by the Kurata-Fukatsu-Sotobayashi-Yamakawa (KFSY-II) equation,⁴⁵

$$\psi = \bar{z} h_0(\bar{z}) = \frac{1 - (1 + 3.903\bar{z})^{-0.468}}{1.828} \quad (10)$$

For the CTA/DMAc system, KFSY-I⁴⁵ equation is not applicable, since the ψ values for this system frequently exceed the upper limit of KFSY-I⁴⁵ equation (0.198). The values of the linear expansion factor α_s given in Table I were calculated unambiguously from \bar{z} according to the procedure already described,^{4,42} using the relation

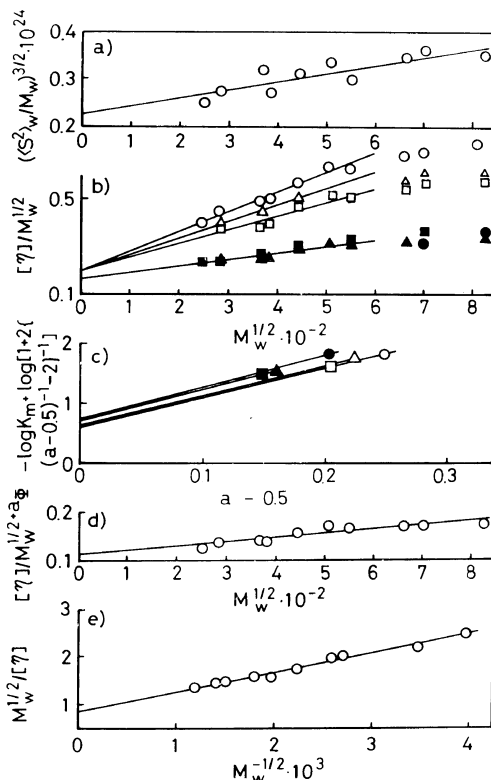


Figure 5. Baumann plot (a), Stockmayer-Fixman plot (b), Kamide *et al.* plot (c), Kamide-Miyazaki (I) plot (d) and Tanner-Berry plot (e) for cellulose triacetate in dimethylacetamide (O), trifluoroacetic acid (Δ), acetone (\square), dichloromethane (\bullet), tetrachloroethane (\blacksquare), and trichloromethane (\blacktriangle).

$$\alpha_s = (1 - 1.78 \bar{z})^{-1/3} \quad (11)$$

For CTA/DMAc system, $\alpha_s \leq 1.2$ was obtained and the excluded volume effect of this system is, as with other cellulose derivatives, small even at very high values of M_w .

Unperturbed Chain Dimension

The unperturbed chain dimension, A ($\equiv \langle R^2 \rangle_0 / M)^{1/2}$, $\langle R^2 \rangle_0$, the mean-square end-to-end distance in the unperturbed state) was estimated by using methods 2B, 2C, 2E, 2F, and 2H, proposed in the previous paper,⁴² for which the basic equations are as follows.

Method 2B:

$$\langle S^2 \rangle_0^{1/2} = \langle S^2 \rangle^{1/2} / \alpha_s \quad (12)$$

Method 2C:

$$\langle S^2 \rangle^{3/2} / M^{3/2} = A^{3/2} / 6^{3/2} + (1/4\pi^{3/2}) BM^{1/2} \quad (13)$$

(where B is long range interaction parameter.)

Method 2E:

$$[\eta] / M^{1/2} = K + 2(3/2\pi)^{3/2} \Phi_0(\infty) BM^{1/2} \quad (14)$$

(where $K = \Phi_0(\infty) A^3$, $\Phi_0(\infty) = 2.87 \times 10^{23}$.)

Method 2F:

$$-\log K_m + \log(1 + 2((a - 0.5)^{-1} - 2)^{-1}) \\ = -\log K + (a - 0.5) \log M_0 \quad (15)$$

(where M_0 is a parameter depending on the molecular weight rang, $M_1 - M_2$, and to which the MHS equation applies.)

Method 2G:

$$[\eta] / M^{0.5 + a_\phi + 1.5a_2} \\ = 6^{3/2} K_\phi K_0^{3/2} + 0.66 K_\phi BM^{(1 - 3a_2)/2} \quad (16)$$

(where $K_0 = (\langle S^2 \rangle_0 / M) / M_a^2$)

$$M^{1/2} / [\eta] = (K'(6 \langle S^2 \rangle / M)^{3/2})^{-1} (1 + A' M^{-1/2}) \quad (17)$$

(where K' and A' are parameters depending on the models used.)

Values of $\langle S^2 \rangle_z^{1/2}$ in Table I were converted to values of $\langle S^2 \rangle_{0,w} (= \langle S^2 \rangle_w / \alpha_s^2)$ using these α_s values (method 2B). The ratio $\langle S^2 \rangle_{0,w} / M_w$ plotted in Figure 4b as a function of molecular weight, as an open mark for CTA solution in DMAc, is almost independent of M_w and accordingly, the CTA chain can be reasonably treated as a gaussian chain, *i.e.*, $a_2 = 0$, and the same applies for the CDA solution in THF⁴. The closed mark in Figure 4b is the $\langle S^2 \rangle_{0,w} / M_w$ data point, calculated for a CTA/a mixture of DCM and methanol from Nair *et al.*'s

work³. In conclusion, for the CTA/DMAc system we obtain $a_\phi = 0.106$, $a_2 = 0$ and $a_1 (= a - 0.5 - a_\phi - 1.5a_2) = 0.144$. This latter value agrees well with an a value of 0.15 as calculated from eq b and $a_2 = 0$ by

$$a_1 = \frac{3}{2} \{ (d \ln \langle S^2 \rangle_w / M) / d \ln M - a_2 \} \quad (18)$$

For the CTA/DMAc system, the partially free draining effect is comparable to the excluded volume effect. It is therefore quite obvious that the dilute solution properties of CTA cannot be described adequately in terms of a simple two-parameters theory.

According to the methods (method 2C, 2E, 2F, 2G, and 2H),^{4,42} the short-range interaction parameter (*i.e.*, the unperturbed chain dimension) A was evaluated for the CTA/DMAc system. Figure 5 represents the Baumann plot (method 2C), Stockmayer-Fixman (SF) plot (method 2E), Kamide *et al.* plot (method 2F), Kamide-Miyazaki (I) plot (method 2G), and Tanner-Berry plot (method 2H). All these methods, except method 2E, gave a series of reasonably good straight lines. All plots based on the Stockmayer-Fixman relation showed downward curvature at high molecular weights. The A value and the long-range interaction parameter B (if possible), estimated from the intercepts and slopes of the above plots, are summarized in Table V. The results in Table V are in particularly good agreement with the theoretical predictions. Methods 2E and 2F considerably underestimate the A value due to $a_\phi \approx 0$ ⁴² and method 2H, on the contrary, overestimates the A value because $a_1 + 1.5a_2 > 0$.⁴⁶ Three methods (2E, 2F, and 2H) relating upon viscosity

Table V. Unperturbed chain dimensions A , long-range interaction parameter B , conformation parameter σ , and characteristic ratios C_∞ of cellulose triacetate in dimethylacetamide at 25°C

Method	$A \times 10^8$	$B \times 10^{27}$	σ	C_∞
	cm	cm ³		
2B (α_s from ψ)	1.43	—	3.07	19.4
2C ($a_2 = 0$)	1.49	3.9	3.20	21.1
2E ($a_2 = a_\phi = 0$)	0.887	4.3	1.91	7.49
2F ($a_2 = a_\phi = 0$)	0.995	—	2.14	9.43
2G ($a_\phi \approx 0$)	1.47	3.7	3.16	20.6
2H ($a_1 = a_2 = 0$, $a_\phi \approx 0$)	1.59	—	3.42	24.1
Most probable value	1.46	—	3.14	20.4

data are unlikely to provide values that are accurate in an absolute sense. As pointed out previously,^{4,42} the SF plot, observed to hold almost universally for vinyl-type polymers, does not hold for cellulose derivatives.

The method 2B, 2C, and 2G are the most reliable and promising in this respect. In fact, the A values determined by these three methods, within the limits of error are almost the same. Thus as the most probable value, we estimated a A of 1.46×10^{-8} cm.

The conformation parameter σ , defined by

$$\sigma = \langle S^2 \rangle_0^{1/2} / \langle S^2 \rangle_{0f}^{1/2} = A/A_f \quad (19)$$

and the characteristic ratio C_∞

$$C_\infty = A_\infty^2 M_b / l^2 \quad (20)$$

were calculated subsequently from the A value and tabulated in Table V, where $\langle S^2 \rangle_{0f}^{1/2}$ ($=6^{-1/2} \times A_f M^{1/2}$), the rootmean square radius of gyration of a hypothetical chain with free internal rotation, $A_f = 0.465 \times 10^{-8}$ for CTA and 0.481×10^{-8} for CDA; A_∞ , the asymptotic value of A at infinite molecular weight, M_b , mean molecular weight per skeletal bond and l , mean bond length. The most probable σ and C_∞ values are found to be 3.14 and 20.4, respectively for the CTA/DMAc system at 25°C. These values should be compared with $\sigma = 3.59$ ($C_\infty = 26.3$) for CDA in acetone and $\sigma = 2.56$ ($C_\infty = 13.5$) for the CDA/THF system.⁴

In order to understand this point better, viscometric and light scattering measurements were made on the solution of a fraction of CDA (AC = 55.6 wt%, sample code, EF 3-11), prepared by the procedure in

the previous paper,⁴ and dissolved in DMAc.

The results are given in Table VI, where the values for CDA/acetone, CDA/THF and CTA/DMAc systems, calculated from the molecular weight dependence of $[\eta]$, $\langle S^2 \rangle_z^{1/2}$, A_2 and Φ , are also shown in parentheses. The results given in the table show that CDA and CTA of the same M_w have a very different radius of gyration and limiting viscosity numbers even when determination is made in the same solvent, (DMAc). By use of method 2B, $A = 2.27 \times 10^{-8}$ cm and $\sigma = 4.88$ were evaluated for the CDA/DMAc system. These results indicate that in DMAc, the CTA molecule is much more flexible than the CDA molecule (see Figure 6).

Table V demonstrates that the A values, estimated by using only viscosity data ($[\eta]$ and M_w , or K_m and a), have a large error of \pm about 0.5×10^{-8} cm. Thus, if only the viscosity data are available, we can

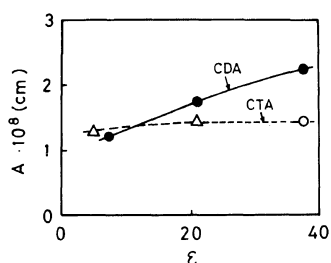


Figure 6. Dependence of the unperturbed chain dimensions A of cellulose triacetate (open mark) and cellulose diacetate (closed mark) on the dielectric constant ϵ of the solvents: circle, by method 2B, 2C (or 2D), and 2G; triangle, by method 2E and 2F, followed by the correction (see text).

Table VI. Light scattering data on cellulose diacetate in dimethylacetamide(DMAc) as compared with those of cellulose diacetate in acetone and tetrahydroforan(THF) and of cellulose triacetate in DMAc

Polymer	Sample	Solvent	Temp	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2}$	$\langle S^2 \rangle_w^{1/2}$	$A_2 \times 10^4$	$[\eta]$	$\Phi \times 10^{-23}$
			°C		10^{-8} cm	10^{-8} cm		$\text{mol cm}^{-3} \text{g}^{-2}$	
Cellulose diacetate (AC=55.6%)	EF3-11	DMAc	25	10.8	344	310	0.77 ₅	227	0.58
		Acetone	25	10.8	(262) ^a	(234)	—	(168)	(1.00)
		THF	25	10.8	(192)	(173)	—	(149)	(2.16)
Cellulose triacetate (AC=61.0%)	—	DMAc	25	10.8	(272)	(240)	(1.25)	(157)	(0.85)

^a The values in parantheses are calculated from the molecular weight dependence of $\langle S^2 \rangle_z^{1/2}$ (or $\langle S^2 \rangle_w^{1/2}$, or $[\eta]$ or Φ) experimentally determined.

Table VII. Unperturbed chain dimensions A of cellulose triacetate, evaluated by method 2E and 2F

Method	$A \times 10^8/\text{cm}$					
	DMAc ^a	TFA ^b	Acetone	DCM ^c	TCE ^d	TCM ^e
2E	0.995	0.995	0.995	0.823	0.823	0.823
2F	0.995	1.00	0.995	0.853	0.876	0.884
Most probable value	1.46	—	—	—	—	—

^a Dimethylacetamide. ^b Trifluoroacetic acid. ^c Dichloromethane. ^d Tetrachloroethane. ^e Trichloromethane.

estimate, by methods 2E and 2F, only the comparable variation of the A value with the solvent nature. In Figures 5b and 5c the data points other than those for DMAc are plotted. Table VII shows the A values, estimated by methods 2E and 2F, of CTA in various solvents.

From Table VII, it is clear that DMAc, TFA, and acetone give almost the same A values and on the other hand, chlorinated hydrocarbons, like DCM, TCE and TCM, yield slightly smaller A values. Comparison of Tables V and VII thus allow us a rough estimation of the true A value which is found to be 1.46×10^{-8} for the former solvents (group I) and $A \approx 0.87 \times 10^{-8} \times 1.46/0.977 = 1.27 \times 10^{-8}$ (Here, 0.87 is an average value of A estimated by method 2F for solutions in solvents of group II (DCM, TCE, and TCM) and 0.977 is a corresponding value for group I (DMAc, TFA, and acetone), respectively) for the latter group of solvents (group II), respectively. Here these values were obtained on

the usual assumption that the importance of the draining effect (*i.e.*, a_ϕ value) is independent of the solvent nature, but this is not necessarily so. The former is *ca.* 15% larger than the latter. The unperturbed chain dimension of CTA, like a variety of other cellulose derivatives differing in chemical composition (for example, cellulose tricaproate and cellulose tricarbonylate), varies with the nature of the solvent.⁴²

In Table VIII are compiled the molar volume, dipole moment μ , dielectric constant ϵ , electric negativity and solubility parameter δ of the solvents employed in this work. Many of the best solvents for CTA have estimated values of δ in the range 9–11 (cal cm^{-3})^{1/2}. Evidently, all solvents belonging to group I are highly polar (or high dissociable character), capable of displaying a basic or amphoteric nature toward CTA molecules. In contrast to this, the solvents of group II are chlorinated nonpolar hydrocarbons, acting as a weak acids toward CTA

Table VIII. Some physical properties of solvents employed in this study

Solvent	Molar volume	Dipole moment	Dielectric constant	Electric negativity ⁵²		Solubility parameter ⁵³
	V_0	μ				
	cm^3/mol	10^{-18} c.u.s	ϵ	by IR	by NMR	$(\text{cal cm}^{-3})^{1/2}$
DMAc ^a	92.3	3.79 ⁴⁷	37.8 ⁴⁷	118	—	10.8
TFA ^b	Ca. 100	2.30 ⁴⁸	39.5 ⁴⁸	—	—	—
Acetone	73.3	2.75 ⁴⁹	21.4 ⁴⁹	55	-0.94	9.8
		2.90 ⁴⁸	20.7 ⁵⁰			
1-chloro-2,3-epoxypropane	78.2	—	22.6 ⁴⁸	—	—	—
			23 ⁵¹			
DCM ^c	64.1	1.89 ⁴⁹	7.77 ⁴⁸	0	—	9.95
		1.62 ⁴⁸	9.08 ⁵⁰			
TCE ^d	104.6	—	7.29 ⁴⁷	0	—	9.67
			8.20 ⁴⁹			
TCM ^e	80.0	1.18 ⁴⁹	5.05 ⁴⁹	0	0	9.30
			4.806 ⁵⁰			

^a Dimethylacetamide. ^b Trifluoroacetic acid. ^c Dichloromethane. ^d Tetrachloroethane. ^e Trichloromethane.

molecules. This distinct difference in the solvent nature between groups I and II can be considered to be closely related to the significant change in the A value. We have found, in the study of CDA,⁴ that the A value in acetone is larger than that in THF. Apparently, the former solvent has a higher polarity than the latter. Figure 6 shows the plots of the A values of CTA and CDA against the dielectric constants of the solvents, in which the polymers are dissolved. Actually, an increase in the dielectric constant invariably accompanies an increase in the A value, particularly for CDA, which is considered to be much more polar than CTA. In other words, both CTA and CDA molecules increase their rigidity as the solvents become polar. Therefore, the polarity of the solvents seems to provide a good key for correlating the A value with the solvent nature. This kind of study is only at its beginning stage. Further experimental work is highly desirable before the detailed mechanism, at the molecular level, of the interaction between the solvent and the specific polar group in the cellulosic chain, which is responsible for causing the profound solvent dependence of the short-range interaction parameter, can be well understood.

Moore and Russell³⁷ considered that basic solvents (like group I) may interact with hydroxyl group and break the assumed intramolecular hydrogen bonding between the hydroxyl and acetyl groups existing in CDA molecules and the change in $[\eta]$ with the solvent can be interpreted in terms of the intramolecular hydrogen bonding. If Moore and Russell's hypothesis is justified even for not fully substituted CTA (in this study, $DS=2.89$), then it follows that group I should give lower $[\eta]$ than group II. The experimental results, showing just the reverse

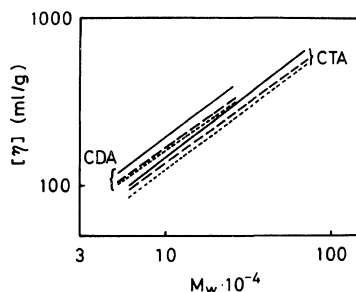


Figure 7. Typical Mark-Houwink-Sakurada relations for cellulose triacetate (CTA) and cellulose diacetate (CDA) in dimethylacetamide (full line), trifluoroacetic acid (broken line), and acetone (dotted line).

of this prediction, indicates that this hypothesis is not valid.

As noted before, the χ value, and accordingly the B value, are almost independent of the solvent nature. However, $[\eta]$ increases in the order: TCM < TCE < acetone < DMAc, since $[\eta]$ depends not only on the solvent power, but also on A , the draining effect and the non-gaussian nature. In summary, the effect of the solvent on the dilute solution properties is shown not by B but by A . This conclusion is generally accepted for cellulose derivatives.

Effect of the Degree of Substitution of Cellulose Acetate on $[\eta]$ and the Unperturbed Chain Dimension

Table IX summarizes the viscosity data on solutions of five CDA ($DS=2.46$) fractions, employed in the previous paper,⁴ in DMAc and TFA at 25°C. The table includes also the literature data (M_w by LS and $[\eta]$) in acetone.⁴

The following MHS equations were established from these $[\eta]$ - M_w data by the least square(s) method for CDA in DMAc and TFA, respectively

$$[\eta] = 3.95 \times 10^{-2} M_w^{0.738} \quad \text{in DMAc} \quad (d)$$

and

$$[\eta] = 5.27 \times 10^{-2} M_w^{0.696} \quad \text{in TFA} \quad (e)$$

We have already obtained the MHS equation for CDA in acetone.⁴

$$[\eta] = 0.133 M_w^{0.616} \quad \text{in acetone} \quad (f)$$

Figure 7 depicts the MHS equations established for CTA and CDA in DMAc, TFA, and acetone by straight lines. As far as DMAc, TFA, and acetone

Table IX. Intrinsic viscosity number of cellulose diacetate in various solvents

Sample code	$M_w \times 10^{-4}$ ^a	$[\eta]$ at 25°C/cm ³ g ⁻¹		
		DMAc ^b	TFA ^c	Acetone ^d
EF 2-10	6.1	140	113	117
EF 2-11-1	9.6	170	145	151
EF 3-10	10.6	205	178	160
EF 3-12	14.1	243	193	193
EF 3-14	18.5	315	247	241

^a By LS in acetone solution. ^b Dimethylacetamide.

^c Trifluoroacetic acid. ^d Ref 4.

Table X. $[\eta]$, Φ , A , and α_s data for cellulose triacetate(CTA) and cellulose diacetate(CDA) as compared with polychloroprene(PCP) and poly(α -methylstyrene) (P α -MS) for $M_w = 1 \times 10^5$

Polymer/Solvent	$[\eta]$	$\Phi \times 10^{-23}$	$A_{(m)} \times 10^8$	α_s
	$\text{cm}^3 \text{g}^{-1}$		cm	
CTA/DMAc ^a	148 ^d (156) ^e	1.19	1.46	1.10
CDA/acetone	160 (156)	0.90	1.73	1.02
CDA/THF ^b	141 (141)	1.97	1.23	1.07
CDA/DMAc	193 (—)	0.58	2.27	1.02
PCP/MEK ^c	35 (35)	2.9	0.72	1.0
P(α -MS)/ <i>t</i> -decane ^{54,55}	21 (21)	2.3	0.67	1.0
P(α -MS)/cyclohexane ^{56,57}	23 (26)	2.3	0.71	1.0

^a Dimethyl acetamide. ^b Tetrahydrofuran. ^c Methyl ethyl ketone. ^d Calculated from MHS equations. ^e Calculated by eq 18 from Φ , A , and α_s data.

are concerned, in a given solvent $[\eta]$ is about 20–30% smaller for CTA than it is for CDA of the same M_w .

The limiting viscosity number $[\eta]$ can be calculated from Φ , A , M_w , and α_s through use of the well-known Flory–Fox equation:

$$[\eta] = \Phi A^3 M_w^{1/2} \alpha_s^3 \quad (21)$$

In Table X are listed the values of $[\eta]$, Φ , A , α_s for CTA and CDA with $M_w = 1 \times 10^5$. In this case, $[\eta]$, Φ and α_s are interpolated from their molecular weight dependence experimentally determined and can be approximately considered as the experimental values. The parenthesis in the table means the $[\eta]$ value calculated from eq 21. The calculated values are roughly in agreement with the experimental ones. Small Φ , small α_s near to unity, and large A are the features of cellulose acetate solutions.⁴² For the sake of comparison, the corresponding data⁴² obtained for polychloroprene,^{54,55} and poly(α -methylstyrene)^{56,57} in the solvents are included in Table X. The experimental results indicating that the $[\eta]$ value of cellulose acetate (and probably other cellulose derivatives) solutions is about 3 to 10 times greater than that of the flexible, less polar polymer of an equivalent molecular weight, may be clearly ascribed to the large unperturbed chain dimensions due to the rigidity of the cellulosic chains.

Figure 8 shows the effect of the degree of substitution (DS) of cellulose acetate and cellulose nitrate (CN) with $M_w = 1 \times 10^5$ on their $[\eta]$ and σ in acetone and DMAc. Here the data points of CN are the results in the previous paper,⁴² analyzed from

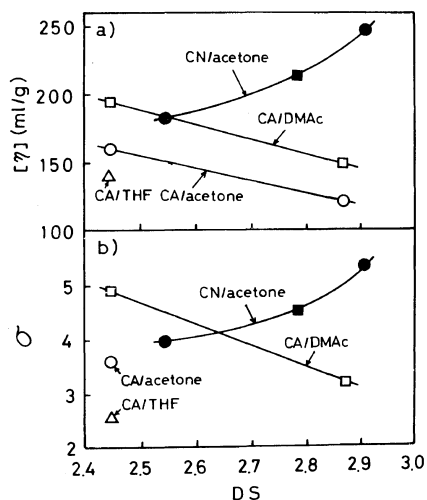


Figure 8. Effect of the degree of substitution (DS) on the limiting viscosity number $[\eta]$ of cellulose acetate (CA) and cellulose nitrate (CN) with $M_w = 1 \times 10^5$ in acetone, dimethylacetamide (DMAc) and tetrahydrofuran (THF) and their conformation parameter σ : \square , CA in DMAc (this work); \circ , CA in acetone (this work and Kamide *et al.*'s work⁴); \triangle , CA in THF (Kamide *et al.*'s work⁴); \bullet , CN in acetone (data from Schulz and Penzel's work^{58,59}); \blacksquare , CN in acetone (data by Huque *et al.*⁶⁰).

works by Schulz and Penzel,^{58,59} and by Huque *et al.*⁶⁰ $[\eta]$ as well as σ increases with DS in CN solutions, but decreases in CA solutions. A similar tendency for $[\eta]$ were observed by Howlette *et al.*⁶¹, Moore and Russel,^{62,63} and Ueda⁶⁴ for CA and Warrow,⁶⁵ and Linsley and Frank⁶⁶ for CN. These truly remarkable differences between CA and CN,

with respect to the effect of DS, may be attributable to the fact that the CA molecule acts as proton acceptor to the solvents in question and the CN molecules act as electron acceptors.

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