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The Viscometric and Light-Scattering Determination of Dilute Solution Properties of Cellulose Diacetate

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ABSTRACT: Eleven cellulose diacetate (CDA) fractions each with a combined acetic acid content of 55.5 wt% and a ratio of weight- to number-average molecular weight $M_w/M_n=1.2-1.3$ were carefully prepared. These fractions were not contaminated by gel-like materials. Dilute solution properties were measured in acetone and tetrahydrofuran (THF) at 25°C by a light scattering method, membrane osmometry, viscometry and gel permeation chromatography. The following Mark–Houwink–Sakurada (MHS) equations were established for CDA : $[\eta]=0.133\ M_w{}^{0.616}$ in acetone and $[\eta]=0.0513\ M_w{}^{0.688}$ in THF. The draining parameter X, as determined by various methods, was found to be less than four in acetone, and less than eight in THF. The molecular weight dependence of Flory's viscosity parameters Φ, expressed as a_Φ $(=\mathrm{d}\ln\Phi/\mathrm{d}\ln M)$, was 0,716 and 0.105 in acetone and THF, respectively. The CDA polymer chain is gaussian in THF, but is not so in acetone. That is, a_2 $(=\mathrm{d}\ln(\langle S^2\rangle_0/M)/\mathrm{d}\ln M$, where $\langle S^2\rangle_0$ is the mean-square radius of gyration in the unperturbed state) was -0.471 in acetone. The unperturbed chain dimensions A $(=(6\langle S^2\rangle_0/M)^{1/2})$ obtained by methods in which a_2 and a_Φ (if necessary) were taken into account, agree well with each other, as the theory predicts. The value of A was 1.73 in acetone and 1.23 in THF. CDA is a typical semi-flexible polymer. The experimental second virial coefficient A_2 can be reasonably explained in terms of the theory, in which a_2 and a_Φ are considered.

KEY WORDS Cellulose Diacetate / Mark–Houwink–Sakurada Equation / Draining Parameter / Unperturbed Chain Dimension / Dilute Solution Property /

Cellulose diacetate (CDA) has a long history of research, corresponding to it's industrial importance. As far as dilute solution properties are concerned, the viscometric and membrane osmometric (MO) techniques have been predominantly used with very few exception.[1,2]

Numerous Mark–Houwink–Sakurada (MHS) equations between the limiting viscosity number $[\eta]$ and the molecular weight M, generally expressed as

$$[\eta]=K_{\mathrm{m}}M^{a} \tag{1}$$

have been proposed for CDA.[3] In eq 1, K_{m} and a are constants characteristic of a given polymer—solvent system at a given temperature and for a specific molecular weight range concerned. The number-average molecular weight M_n has been used in eq 1 for CDA fractions having rather wide molecular weight distribution (MWD), isolated by successive precipitational fractionation (SPF). Thus, no great confidence can be placed in the accuracy of the parameters K_{m} and a in eq 1 for CDA in solvents (especially, acetone).

The experimental difficulty was encountered for light scattering (LS) measurements of CDA even in a good solvent, owing to contamination by gel-like materials in the solutions.[4,5] Kamide and his coworkers have studied extensively the nature of prehump (*i.e.*, gel) in gel permeation chromatogram (GPC) obtained for CDA in acetone and tetrahydrofuran (THF)[4,5] and found the preparation procedure of CDA which produces no prehump when dissolved in the solvents.[5,6]

In this paper, we have attempted (1) to study, by viscometry, MO, GPC, and LS, the dilute solution properties of CDA fractions, fractionated from a carefully prepared original polymer, by successive solutional fractionation (SSF), which was experimentally and theoretically verified to give fractions with a very narrow MWD,[7–11] and (2) to evaluate the molecular parameters such as the partially free draining effect and unperturbed chain dimensions (UCD) from the dilute solution properties determined here.

EXPERIMENTAL

Polymer Sample and Solvents

High α-cellulose pulp, trade name Raycrod XG-LD, manufactured by ITT Rayonier Inc. (USA) (α-cellulose 95.4 wt%, β-cellulose 3.8 wt%, pentosan 1.0 wt%, ash 0.03 wt%, the viscosity-average degree of polymerization $P_v=1189$) was employed as a starting material. The cellulose pulp was converted into cellulose triacetate (CTA) by using the acetic anhydride—acetic acid—sulfuric acid system. CTA thus prepared was hydrolyzed with magnesium carbonate to yield CDA of 55.6-wt% combined acetic acid content (AAC).

According to the authors' more than twenty years of experience in the study of cellulose derivatives, in order to prepare CDA solution which is absolutely free from the gel-like materials, it is of prime importance to choose mild conditions of acetylation reaction, followed by a very careful hydrolysis reaction and to treat whole CDA polymers thus obtained with a weak acid, decomposing the cellulose acetate having a large weight-average molecular weight M_w, which contains a sulfuric acid group, sodium and calcium (particle size in acetone, 80—300 nm as determined by prehump II in GPC curve) and then to extract the component of cellulose diacetate with higher AAC (57—58 wt%) (partiale size, 150—450 nm in acetone, as detected by prehump I in GPC) with dichloromethane. It should be remembered that almost all previous investigators have used commercial products, which were not satisfactory for light scattering measurements.

Spectroscopy grade acetone and THF were further purified and distilled immediately before use. Tetrachloroethane (TCE) was reagent grade and used as received.

Fractionation

A solution of the original polymer in acetone was fractionated at 30°C by using ethanol as precipitant, according to SSF into 16 to 21 fractions. The polymer volume fraction $v_p{}^0$ of the solution at the first fractionation step, from which the phase separation occurs, was 2.1%. The detailed procedure of SSF experiments will be reported elsewhere.[12] The SSF run was duplicated to obtain enough fractions for further study (the first run was designated as EF-2 and the second run, EF-3). The combined acetic acid content of fractions was determined by infra-red spectroscopic method.[4] Of the resulting thirty seven fractions, eleven were chosen for further study, excluding GPC.

Light Scattering

The stock solution of CDA fractions was made by mechanical agitation at a concentration of approximately $5 \cdot 10^{-3}$ g/cm^3 with acetone or THF as solvent. The solutions of high molecular weight CDA fractions were cooled down below -70°C and subsequently warmed at 30°C in order to make dissolution complete. After these solutions were centrifuged at 29000 g for 1 h, the middle layer portions were collected by a microsyringe. The concentrations of the solutions were adjusted by adding pure solvent to the collected solutions which were then made to pass through a 200-nm Alpha metricel filter (Alpha −8), manufactured by Gelman Instrument Co. (GBR), directly into the cyclindrical light scattering cell. The solutions were allowed to stand at room temperature overnight. The solutions and solvents were thus free from dust and gels.

Light scattering measurements on CDA in acetone and in THF were carried out in a Shimadzu–Brice type light scattering photometer model PG-21 (for EF-2 series fractions) and in a FICA model 42000 photo gonio diffusiometer (for EF-3 series fractions).

Unpolarized light with wave length $\lambda=546$ and 436 nm were utilized in acetone and THF respectively. Cylindrical cells capped with a close fitting stainless stopper were employed in order to minimize evaporation of the solvent during measurements and were immersed in a bath containing benzene at 25±0.2°C. No scatter dissymmetry was observed; that is, in all cases, the dissymmetry factor was always less than 1.02. The concentration range was 1.25 to 0.5×10^{-3} g/cm^3. The apparatus were calibrated with benzene, using unpolarized 90° scattering light and taking the Rayleigh ratio $R_{90}=16.3\cdot10^{-6}$ cm^{-1} at $\lambda=$ 546 nm and $48.5\cdot10^{-6}$ cm^{-1} at 436 nm. Scattered intensities were measured at various angle from 37.5° to 142.5°.

The specific refractive index increment dn/dc on solutions of CDA in acetone and in THF was determined by a Shimadzu differential refractometer model DR-4 at 25 ± 0.2°C at a wave length of 546 and 436 nm. With this instrument, the refractive index increment measurements are accurate to $\pm1.3\times10^{-5}$ cm^3/g. The dn/dc value obtained for CDA solutions was 0.109 cm^3/g in acetone at $\lambda=546$ nm and 0.068 cm^3/g in THF at $\lambda=436$ nm. These values were found for three different fractions and two whole polymers with AAC=54.2–55.6 wt%. The dn/dc value for these systems are in fairly good agreement with the values found by Stein and Doty[1] (0.104—0.116 in acetone) and by Tanner and Berry[2] (*ca.* 0.11 (from Figure 2 of ref 2) in acetone and 0.0710 in THF). The refractive index of the solvents were measured on a Hitachi Abbe refractometer.

Zimm plots were made of Kc/R_θ against $\sin^2\theta/2+kc$ where symbols have their usual meaning. The second virial coefficient A_2, the z-average radius of gyration $\langle S^2\rangle_z^{1/2}$ and M_w were determined from the plots in the usual way.

Membrane Osmometer

The Hewlett Packard high-speed membrane osmometer model 502 was used for the osmometric measurement in THF and TCE. The membrane was a Selectron membrane filter type 0—8, manufactured by Schleicher and Schuell Inc. (DBR). M_n and A_2 were obtained from the linear part of a plot of π/c *vs.* c as intercept and slope, respectively. The diffusion of solute was not detected experimentally by comparing solvent reference values before and after the measurement.

Solution Viscosity

Viscosity measurements were made by a modified Ubbelohde suspension type viscometer in a constant bath controlled to ±0.01°C. $[\eta]$ was determined from the reduced viscosity at four or five concentrations by extrapolation of η_{sp}/c to infinite dilution. In this case, the kinetic energy correction was very small.

Gel-Permeation Chromatography

A Shimadzu gel-permeation chromatography model 1A was used. This instrument was filled with a five columns analytical set of cross-linked polystyrene gels: Toyo-soda G-2000S, G-3000S, G-4000S, G-6000S, and G-6000S. THF was used as the eluting solvent at a flow rate of 1 cm^3/min. The operating temperature was 25 ± 2°C. For the calibration of GPC, eleven well-defined CDA fractions were used.

RESULTS AND DISCUSSION

Molecular Weight and Molecular Weight Distribution of CDA Fractions

The acetic acid content for series of EF-2 and EF-3 fractions lies between 55.5 ± 1.0 wt%, independent of M_w, indicating that the fractionation with respect to the degree of substitution (DS) does not occur during the SSF run.

The prehump of the GPC curve, which was readily ovserved for CDA, prepared by the conventional manner, was not detected significantly in the present case. This strongly suggests that all the CDA molecule exist in a molecularly dispersed state in the solution, and this strongly supports the excellent agreement of M_w by LS in acetone with M_w by LS in THF and M_w by GPC, (THF).

In the evaluation of the molecular weight distribution of the CDA fractions, the plot of M_w (by LS in acetone) *vs.* eluent volume V_e was extrapolated linearly for both M_w sides. M_w and M_n as calculated from MWD curve thus obtained are tabulated in Table I.

The polydispersity parameter M_w/M_n, as determined by GPC, of the fractions is graphed in Figure 1 as open mark as a function of their M_w. The open circle and open triangle correspond to the first (EF-2) and second (EF-3) runs, respectively. Good reproducibility of SSF experiment is confirmed experimentally. Except for a few initial fractions M_w/M_n of the fractions can be considered as actually constant (1.2—1.3), independent of M_w. Figure 1 includes in a closed circles the data of Tanner and Berry,[2] who fractionated precipitationally commercial CDA (DS=

Table I. Results of light scattering, membrane osmometer, GPC, and viscosity measurements with cellulose diacetate in acetone and THF at 25°C

Sample code	Light scattering						Osmotic pressure		GPC		$[\eta]$, cm^3 g^{-1}	
	Acetone, 25°C			THF, 25°C			THF, 25°C		THF, 25±1°C			
	$M_w\times10^{-4}$	$A_2\times10^4$, cm^{3}mol g^{-2}	$\langle S^2\rangle_z^{1/2}\times10^8$, cm	$M_w\times10^{-4}$	$A_2\times10^4$, cm^3 mol g^{-2}	$\langle S^2\rangle_z^{1/2}\times10^8$	$M_n\times10^{-4}$	$A_2\times10^4$, cm^3 mol g^{-2}	$M_w\times10^{-4}$	$M_n\times10^{-4}$	Acetone	THF
EF 2–10	6.1	5.9	218	—	—		4.7	5.9	7.1	5.6	117	—
EF 3–6	—	—	—	7.4	4.4	160	4.8	5.2	7.5	6.0	—	113
EF 2–11–1	9.6	5.3	252	—	—	—	7.6	6.8	9.2	7.3	151	—
EF 3–8	—	—	—	10.0	4.9	181	—	—	9.8	7.5	—	138
EF 3–10	10.6	3.7	252	10.9	3.3	191	8.7	7.8	11.1	8.8	160	158
EF 2–14	11.5	3.7	280	—	—	—	10.8	6.0	11.4	9.0	187	—
EF 3–12	14.1	3.0	282	15.5	4.0	235	12.2	7.7	14.2	11.9	193	182
EF 2–15	15.4	5.2	310	—	—	—	12.0	5.4	14.9	11.5	218	—
EF 3–13	15.6	5.2	290	18.2	4.6	257	12.6	7.1	15.9	12.3	217	212
EF 3–14	18.5	4.3	310	20.0	2.5	277	14.0	5.0	17.5	12.7	241	230
EF 3–15	26.5	5.0	338	—	—	—	—	—	24.9	19.1	277	—

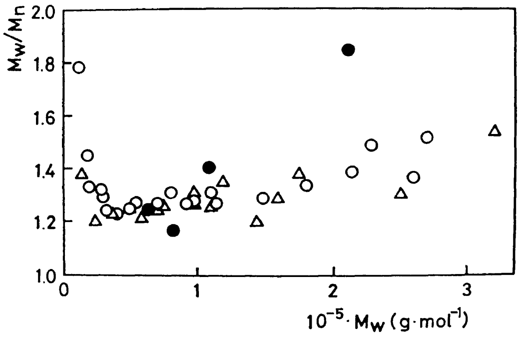

Figure 1. Variation of the ratio M_w/M_n of cellulose diacetate fractions with M_w: ○, successive solutional fractionation (SSF) run (EF-2), initial polymer volume fraction $v_p{}^0=2.1\,\%$, total number of fractions $n_t=21$; ,△ SSF run (EF-3), $v_p{}^0=2.1\,\%$, $n_t=16$; ●, successive precipitational fractionation (SPF) run by Tanner and Berry[2], $v_p{}^0=0.15\,\%$, $n_t=20$. M_w and M_n are determined by gel-permeation chromatography.

2.45) by using the same solvent—nonsolvent pair as that employed in this study. In spite of the very severe operating conditions used by them (*i.e.*, $v_p{}^0=0.3\,\%$ and total number of fractions in a run $n_t=19$), the polydispersity of the fractions isolated by SPF is larger than that of the fractions by SSF, showing a remarkable M_w dependence as the theory predicts. As a result, the fractions employed here have probably the narrowest MWD among cellulose derivative samples, which have been used before for the solution study.

A typical Zimm plot is demonstrated in Figure 2. The plot can be reasonably represented by non-distorted diamond shape, exhibiting no downward curvature. The double extrapolations $\lim_{c\to0} Kc/R_\theta$ and $\lim_{\theta\to0} Kc/R_\theta$ cut the ordinate axis at the same point. Although the highest fractions (EF-2-16 and EF-3-21) were completely soluble in acetone and THF, their Zimm plot revealed a downward curvature at lower angle and, so we discarded them.

The results of LS, MO, GPC (in part), and viscometry measurements are recorded in Table I. Two different LS apparatus always yielded consistent results (Compare the data between two fractions: EF-2-15 and EF-3-13). M_w as determined by LS in acetone is in good agreement with M_w by LS in THF and with M_w by GPC

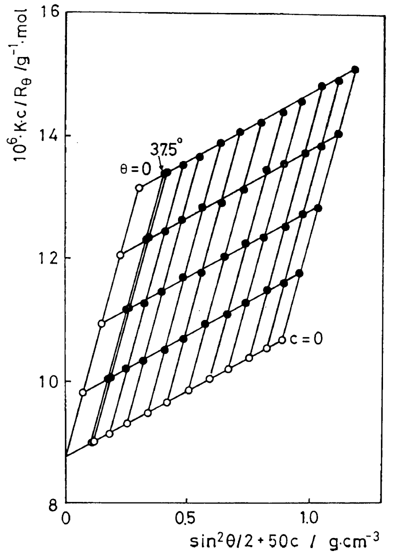

Figure 2. Zimm plot of a cellulose diacetate fraction EF 2–14 in acetone at 25°C; unpolarized incident light wave length $\lambda = 546$ nm. The symbols have their usual meaning.

in THF at least in the range of M_w from 6 to 26×10^4. M_n as determined by MO in THF agrees also with M_n by GPC in THF. The above coincidence definitely verifies the reliability of the methods adopted for the molecular weight determination and indicates that there is no association of CDA in acetone and THF, if the polymer samples are very carefully prepared. Tanner and Berry used for the light scattering measurements a mixed solvent, (THF—trifluoroethanol (TFE), 50: 50 volume ratio), which gave solutions as free from aggregation as any system they studied.[2] However it should be pointed out that the ratio of M_w as determined by LS in a mixed solvent to M_w by GPC in THF (M_{GPC} according to their notation) for the same polymer deviates very widely from unity in the range M_w by GPC$\geq 15.4 \times 10^4$. It seems to us that the disparity of M_w by LS/M_w by GPC from unity means some aggregation even in the mixed solvent.

The value of M_n determined by MO in TCE decreases with increasing temperature, approaching M_n by MO in THF as is shown in Figure 3. CDA molecule has considerable tendency to yield associated aggregates in poor solvents, like TCE below 70°C. Ikeda and Kawaguchi,[13] who overlooked this phenomena for CDA in TCE, insisted that TCE at 56.5°C acts as a Flory's theta solvent for CDA, in which A_2 by membrane osmometry vanishes.

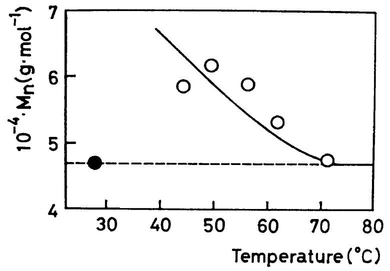

Figure 3. Plot of apparent number-average molecular weight M_n, as determined by membrane osmometry, for cellulose diacetate fraction EF 2–10 in tetrachloroethane (TCE) against the temperature of measurement: ○, M_n in TCE; ●, M_n in tetrahydrofuran (THF).

Mark–Houwink–Sakurada Equations

The Huggins constant k' increases continuously with M_w from 0.4 to 0.6 in acetone and THF. Log—log plots of $[\eta]$ *vs.* M_w for CDA in both solvents at 25°C are graphed in Figure 4, where M_w by LS in acetone is used for $[\eta]$ in acetone and M_w by LS in THF is employed for $[\eta]$ in THF. From this figure, the following MHS

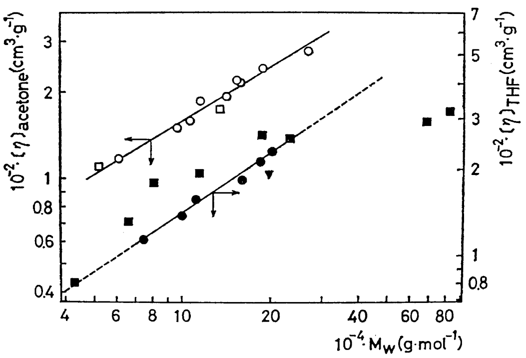

Figure 4. Log-log plot of limiting viscosity number $[\eta]$ against the weight-average molecular weight M_w for cellulose diacetate in acetone at 25°C (open mark) and in THF at 25°C (closed mark): ○; this work, □, data from Stein and Doty's work[1]; ■ and ▼, data from Tanner and Berry.[2] M_w is determined by light scattering method in acetone (○ and □), in THF (● and ▼) and in a mixed solvent (■).

equations are established by the least square methods

$$[\eta]=0.133\ M_w^{0.616} \text{ in acetone at 25°C} \quad \text{(a)}$$

$$(6.1\times10^4\leq M_w\leq 26.5\times10^4, \text{ sample number 9})$$

$$[\eta]=0.0513\ M_w^{0.688} \text{ in THF at 25°C} \quad \text{(b)}$$

$$(7.4\times10^4\leq M_w\leq 30.0\times10^4, \text{ sample number 6})$$

The value of a for acetone solution, as calculated from M_n, is 0.643. Among the five fractions employed for Stein and Doty's LS study,[1] two fractions (23B and 31B) were used for the viscosity measurements in acetone at 25°C by Badgley and Mark.[14] The data ($[\eta]$ and M_w) for these two fractions are plotted in Figure 4, for comparison as open rectangular. These data fall reasonably on the experimental line [eq a]. Also included are the data points obtained by Tanner and Berry for CDA (DS=2.45) in THF.[2] Here, M_w as determined by LS in a mixed solvent (closed rectangular) or in THF (closed triangle) is employed. Their data points scatter widely around eq b, indicating a large experimental error, particularly, in the higher M_w range.

The above equations (eq a and b) are obtained for the samples with $M_w/M_n=1.2-1.38$. Hence, equations can be readily converted into those for monodisperse samples. The results are

$$[\eta]=0.136\ M^{0.616} \text{ in acetone at 25°C} \quad \text{(a)}'$$

and

$$[\eta]=0.0524\ M^{0.688} \text{ in THF at 25°C} \quad \text{(b)}'$$

In deriving eq a′ and b′, the Schulz–Zimm distribution is assumed for the CDA fractions.

Up to now, numerous different MHS equations for CDA in acetone have been published by Kraemer,[15] Bartovics and Mark,[16] Sookne and Harris,[17] Badgley and Mark,[14] Philipp and Bjork,[18] Cumberbirch and Harland,[19] Moore and Tidswell,[20] and Ikeda and Kawaguchi,[13] who employed M_n except for Kraemer. All experimental equations lie to the left of eq a′, when $[\eta]$ and M are double-logarithmically plotted, and the wide variation of K_m and a of those equations can be reasonably explained by the polydispersity effect of the samples. It is noted that the molecular weight dependence of the polydispersity of the polymer samples utilized in literature made the exponent a large as compared with 0.616 obtained here.

Second Virial Coefficient and Radius of Gyration

The molecular weight dependence of A_2, as determined by LS, is plotted in Figure 5, where data of CDA (DS=2.43) in acetone from Stein and Doty's work[1] are also included as an open triangle. A_2 for CDA in acetone and in THF is of a magnitude order of 10^{-4} cm^3 mol g^{-2}, practically independent of M_w within a rather large experimental uncertainity as found for various cellulose, amylose and their derivatives. The value of A_2 as determined by LS in THF is somewhat (about 40—50%) larger than that by MO.

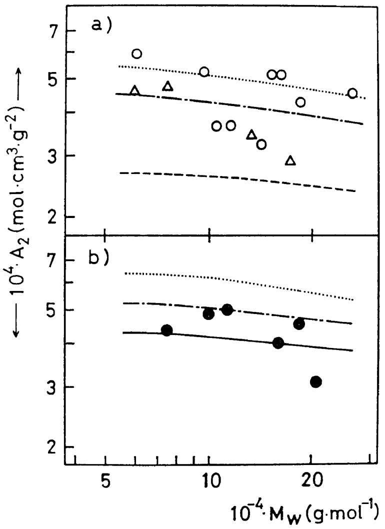

Figure 5. Molecular weight dependence of the second virial coefficient A_2 for cellulose diacetate solutions in acetone (a) and in tetrahydrofuran (b) at 25°C: ○, cellulose diacetate (degree of substitution DS=2.45) in acetone (this work); △, cellulose diacetate (DS=2.45) in acetone[1]; ●, cellulose diacetate (DS=2.45) in THF (this work). Lines are calculated by eq 32 and 5 from A (or K_0) and B, which are estimated by Methods 2C (full line), 2D (broken line), 2E (dotted line), and 2G (chain line), and the experimental $\langle S^2\rangle_w$ data.

Figure 6 displays the molecular weight dependence of $\langle S^2\rangle_z^{1/2}$ for CDA in acetone and THF. In the figure, the data of Stein and Doty[1] on CDA in acetone and of Tanner and Berry on CDA in THF at 25°C and TFE at 20°C are also included for the sake of comparison.

The molecular weight dependence of $\langle S^2\rangle_z^{1/2}$ of CDA in acetone from Stein and Doty's work

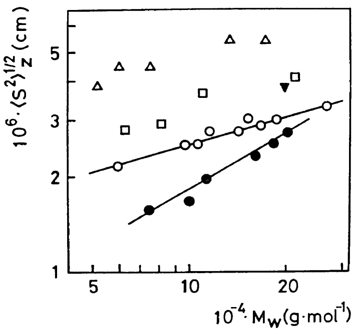

Figure 6. Molecular weight dependence of the radius of gyration $\langle S^2\rangle_z^{1/2}$ for cellulose diacetate solution: ○, acetone (this work); △, acetone (Stein and Doty)[1]; □, trifluoroethanol (Tanner and Berry)[2]; ●, tetrahydrofuran (THF) (this work); ▼, THF (Tanner and Berry).[2]

(see, λ' in eq 29) is of the same order as that obtained by us and the absolute magnitude of $[\eta]$ in acetone is almost the same as that in this paper (see, Figure 4), compared at the same molecular weight. However, the absolute magnitude of $\langle S^2\rangle_z^{1/2}$ by Stein and Doty is about two times larger than ours. The accuracy of Stein and Doty's work was pointed out by Doty, *et al.*,[21] to be in doubt due to colloidal contaminations. The value of $\langle S^2\rangle_z^{1/2}$ of CDA in THF from Tanner and Berry's work[2] (fraction 3;2) is about 50% larger than that obtained here of the polymer with the same M_w, but $[\eta]$ value of the fraction is about 20% smaller than $[\eta]$ calculated from eq a′. $\langle S^2\rangle_z^{1/2}$ is related to M_w by the relation

$$\langle S^2\rangle_z^{1/2}=7.39\times10^{-8}M_w^{0.308}\ \text{(cm)} \qquad \text{(c)}$$

in acetone at 25°C

and

$$\langle S^2\rangle_z^{1/2}=2.99\times10^{-9}M_w^{0.558}\ \text{(cm)} \qquad \text{(d)}$$

in THF at 25°C

Draining Effect Parameter

The draining effect parameter X, determined by eq 2[22]

$$X=(1/2)(6/\pi)^{1/2}(b/a')N^{1/2} \qquad (2)$$

was evaluated according to the methods used in previous papers[23,24] (b=diameter of hydrodynamic segment, a'=length of links connecting segments. $N+1$=number of links in a chain).

a. Method 1A.

Flory's viscosity parameters $\Phi(=[\eta]M_w/(q_{w,z}6^{3/2}\langle S^2\rangle_z^{3/2}$, $q_{w,z}$=correction factor of the polydispersity) for CDA solutions in acetone and THF at 25°C is listed in Table II and plotted against M_w in Figure 7. Here, $q_{w,z}$ was calculated by assuming the Schulz–Zimm distribution for the CDA fractions used. Obviously, Φ is smaller than the theoretical value for the nondraining limit in theta solvent ($\Phi_0(\infty)=2.87\times10^{23}$), having a positive molecular weight dependence, expressed by the relation of semiempirical nature

$$\Phi=K_\Phi M^{a_\Phi} \qquad (3)$$

For CDA, we obtain $a_\Phi=0.716$ in acetone and 0.105 in THF. The former is about three times larger than that theoretically calculated from $X=1.48$ and the excluded volume effect parameter a_1 ($\equiv 3\varepsilon$, where ε is defined by eq 13) $=0.10$ with an assumption of the gaussian chain (a_2 (see, eq 14) $=0$) and the latter is in good agreement with an expected value from X and a_1. The experimental fact of $a_\Phi>0$ has been investigated previously for various other cellulose derivatives.[24]

Next, we attempted an indirect estimation of the linear expansion factor $\alpha_s(=\langle S^2\rangle^{1/2}/\langle S^2\rangle_0^{1/2}$, $\langle S^2\rangle_0^{1/2}$=radius of gyration at unperturbed state) from M_w, A_2 and $\langle S^2\rangle_z^{1/2}$ data through use of a penetration function ψ due to Kurata–Fukatsu–Sotobayashi–Yamakawa (KFSY) theory[25] (here, $\langle S^2\rangle_z^{1/2}$ was converted to $\langle S^2\rangle_w^{1/2}$)

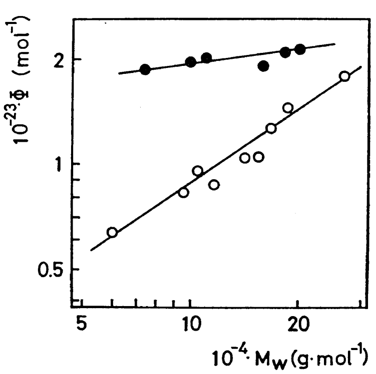

Figure 7. Molecular weight dependence of the Flory's viscosity parameter Φ for cellulose diacetate fractions in acetone (○) and in tetrahydrofuran (THF) (●) at 25°C.

Table II. Flory's viscosity parameter Φ, linear expansion factor α_s, and draining parameter X for cellulose diacetate in acetone and in THF at 25°C

	Acetone			THF		
Polymer code	$\Phi\times10^{-23}$	α_s[a]	X from eq 11	$\Phi\times10^{-23}$	α_s[a]	X from eq 11
EF 2–10	0.63_5	1.01	0.52	—	—	—
EF 3–6	—	—	—	1.87	1.05	4.6
EF 2–11–1	0.83_2	1.02 .	0.86	—	—	—
EF 3–8	—	—	—	1.98	1.08	6.4
EF 3–10	0.96_0	1.02	0.90	2.01	1.05	6.0
EF 2–14	0.89_3	1.01	0.88	—	—	—
EF 3–12	1.04	1.02	1.10	1.93	1.07	5.8
EF 2–15	1.04	1.03	1.10	—	—	—
EF 3–13	1.27	1.04	1.50	2.10	1.09	8.5
EF 3–14	1.45	1.04	2.25	2.13	1.04	8.2
EF 3–15	1.78	1.09	4.	—	—	—

[a] Trifluoroethanol.

$$\psi=0.746\times10^{-25}A_2M^2/\langle S^2\rangle^{3/2}=\bar{z}h_0(\bar{z}) \qquad (4)$$

where $$\bar{z}h_0(\bar{z})=(1/5.047)[1-(1+0.683\bar{z})^{-7.39}] \qquad (5)$$

$$\bar{z}=z/\alpha_s^3=(3/2\pi)^{3/2}(\alpha_s^{-3})BA^{-3}M^{1/2} \qquad (6)$$

$$\alpha_s^3=1+1.73z \qquad (7)$$

$$A=(6\langle S^2\rangle_0/M)^{1/2} \qquad (8)$$

A and B are the short- and long-range interaction parameters, respectively. The α_s value thus calculated is in the vicinity of unity, as tabulated in the third and sixth columns of Table II.

Using Φ and α_s data, X can be determined by eq 9

$$\Phi=\Phi_0(X)\alpha_s^{-[3-n(x)]} \qquad (9)$$

where $\Phi_0(X)$ and $n(X)$ have the usual meaning.[22] The X value for CDA fractions in acetone and in THF is given in the fourth and seventh columns of Table II. In acetone, X increases gradually with M_w from 0.52 to 4.2. $X=1.48$ and 6.6 are obtained as average for acetone and THF, respectively.

Stein and Doty[1] determined M_w, A_2 and $\langle S^2\rangle_z^{1/2}$ of the fractions in acetone, whose $[\eta]$ was also measured by Badgley and Mark.[14] By use of these data, we obtain $X=0.04$—0.07. Using data from Tanner and Berry's work[2] for CDA in THF and in TFE at 25°C, the X value as evaluated by Method 1A is found to be 0.70 in THF and 0.27—0.8 (average, 0.46) in TFE. It will be noted that contamination by gel-like materials leads to errorneously low X values.

b. Method 1B.

The exponent a in eq 1 and the expont a_s in the relation between the sedimentation coefficient at infinite dilution s_0 and M,

$$s_0=K_sM^{a_s} \qquad (10)$$

are related to X by the relation[23]

$$a=0.5+\nu(X)+n(X)\varepsilon+1.5a_2 \qquad (11)$$

and[23]

$$3a_s+a-2.0=\nu(X)-3\mu(X)+[n(X)-3m(X)]\varepsilon \qquad (12)$$

where

$$\varepsilon=\mathrm{d}\ln\alpha_s/\mathrm{d}\ln M \qquad (13)$$

$$a_2=\mathrm{d}\ln(\langle S^2\rangle_0/M)/\mathrm{d}\ln M \qquad (14)$$

$\nu(X)$, $\mu(X)$ and $m(X)$ are functions of X given by Kurata–Yamakawa (KY) theory.[22] X and ε can determined from a and a_s by use of eq 11 and 12, where a_2 is practically zero or known in advance. Assuming $a_2=0$, this method was applied to the data of Holmes and Smith (HS),[26] Golbev and Frenkel (GF),[27] and Ishida, *et al.* (I),[28] who employed the same fractions as those in this paper for sedimentation velocity measurement. The X value is evaluated as 0.75, 2.5, and 1.4 for HS, GF, and I works, respectively. If we put $a_2=-0.471$ (see Table IV) for the data from Ishida, *et al.*'s work on the CDA fractions in acetone ($a=0.616$ and $a_s=0.384$) into eq 11, we obtain $X=0.24$ in place of 1.4.

c. Method 1C.

The exponent a_η in the relation

$$D_0=K_d M^{a_d} \tag{15}$$

(D_0=diffusion coefficient at infinite dilution) is related to a and X by the formula[23]

$$a-3a_d+1=\nu(X)-3\mu(X)+(n(X)-3m(X))\varepsilon \tag{16}$$

Subsitution of numerical values for a and a_d into eq 11 and 16 enables us to determine X and ε if a_2 is predetermined. Holmes and Smith[26] carried out the diffusion measurement in acetone for the same CDA fractions as those cited in Method 1B. $a_d=0.70$ is obtained from their data. Using $a=0.98$ and $a_d=0.70$ and assuming $a_2=0$, we obtain $X=0.74$.

d. Method 1E

We can determine X from $[\eta]$ and the concentration dependence of sedimentation coefficient k_s by using the relation[29]

$$k_s/[\eta]=(55/8)N_A\Phi_0(X)^{1/3}P_0(X)^{-1}(16200\pi^2)^{-1} \tag{17}$$

where

$$k_s=\{(s_0/s)-1\}/c \tag{18}$$

s=sedimentation coefficient at concentration c, $P_0(X)$=function of X given by KY theory.[22] Equation 17 holds in the range $\alpha_s<2$.

Ishida and Kamide, *et al.*,[28] determined s for the same CDA fractions as those used here in acetone as a function of c. Using their data we obtain X=0.27—0.44 (average, 0.32).

The X values thus determined are in the range of 0.3∼7 as recorded in Table III, suggesting that the partially free draining effect on the viscosity, sedimentation and diffusion coefficients can never be ignored, particularly so in acetone. We have already demonstrated for cellulose and amylose and their derivatives that the X value is almost invariably less than 2.[24]

Unperturbed Chain Dimensions

Unperturbed chain dimensions (UCD), expressed by A in eq 8, can be determined from data on dilute solution properties in non-θ solvent by following methods.

a. Method 2B

$\langle S^2\rangle_0^{1/2}$ is calculated from the experimental $\langle S^2\rangle_w^{1/2}$ data and α_s, which is estimated from ϕ through use of eq 4—7. The value of A, that is $\langle S^2\rangle_{w0}/M$, thus obtained in acetone exhibits a

Table III. Draining parameter X of CDA

Solvent	DS	Temp, °C	X				Remarks
			Method 1A	Method 1B	Method 1C	Method 1E	
Acetone	2.45	25	0.52—4.2	—	—	—	This work
	—		(1.48)[b]	1.4[0.24][c]	—	0.27—0.44	Ishida–Kamide, *et al.*[28]
	—		—			(0.32)	
	2.43	25	0.04—0.07	—	—	—	Stein, *et al.*[1,14]
	—		(0.06)				
	2.33	20	—	0.74	0.74	—	Holmes–Smith[26]
	2.33—2.37	25	—	1.8	—	—	Golbev–Frenkel[27]
THF	2.45	25	4.6—8.5(6.6)	—	—	—	This work
			0.7	—	—	—	Tanner–Berry[2]
TFE[a]	2.45	20	0.27—0.8 (0.46)	—	—	—	Tanner–Berry[2]

[a] Trifluoroethanol. [b] Number in parenthesis means average. [c] Number in bracket denotes the value when a_2 is taken into account.

Table IV. Various parameters employed for evaluation of unperturbed chain dimensions of cellulose diacetate

Solvent	a in eq 1	a_Φ in eq 3	$K_\Phi\times10^{-24}$ in eq 3	a_2 in eq 14	a_1	
					eq 11′	eq 29
Acetone	0.61_6	0.71_6	$2.26\cdot10^{-5}$	−0.471	0.10_7	0.130
THF	0.68_8	0.10_5	0.0573	0	0.08_3	0.150

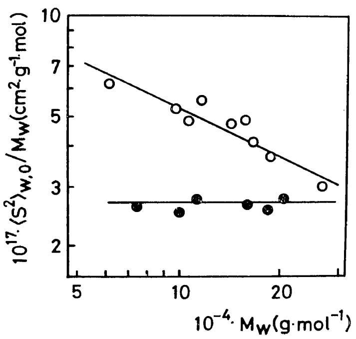

Figure 8. Molecular weight dependence of $\langle S^2\rangle_0/M_w$, as determined by method 2B, of cellulose diacetate in acetone (○) and in tetrahydrofuran (●) at 25°C.

rather striking molecular weight dependence as shown in Figure 8 and a_2, defined by eq 14, amounts to -0.471, $a_2<0$ is not unusual for cellulose derivatives.[24] The average value of A is found to be 1.68×10^{-8} cm. In contrast to this, the A value in THF 1.26×10^{-8} cm is almost independent of M_w (*i.e.*, $a_2=0$). The negative correlationships between a_Φ and a_2 have been demonstrated for numerous cellulose and amylose derivatives.[24]

b. Method 2C

Plot of $\langle S^2\rangle_w^{3/2}/M_w^{3/2}$ *vs.* $M_w^{1/2}$ (Baumann plot) according to eq 19[30]

$$\langle S^2\rangle^{3/2}/M^{3/2}=A^3/6^{3/2}+[1/(4\pi^{3/2})]BM^{1/2} \qquad (19)$$

yields $\langle S^2\rangle_{w,0}^{3/2}/M_w^{3/2}$ as an intercept at $M_w^{1/2}=0$ as shown in Figure 9a. A line can be drawn through all the data points and A value is found to be 2.14×10^{-8}cm in acetone and 1.24×10^{-8}cm in THF, respectively. The slope of the plot is theoretically expected to reflect the sign of the long-range interaction parameter B accordingly A_2, see eq 32, being negative when $A_2<0$. However, a large negative slope of the plot for CDA in acetone sharply contradicts with the experimental fact of $A_2>0$. This inconsistency can be ressolved only by taking into account $a_2\neq0$ in the original Baumann's equation [eq 19]. The A value thus estimated by this method for CDA in acetone is less accurate.

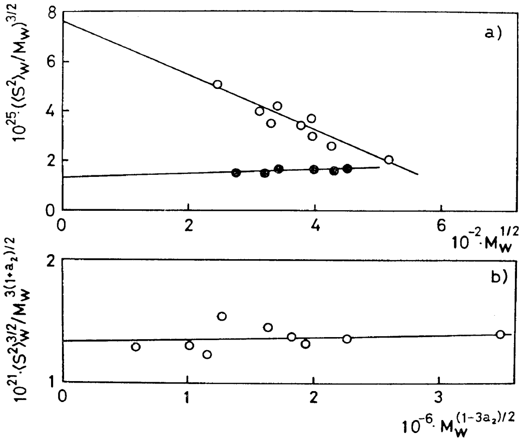

Figure 9. Baumann plot (a) and Baumann–Kamide–Miyazaki (BKM) plot (b) of cellulose diacetate (CDA) in acetone (○) and in tetrahydrofuran (●) at 25°C. In BKM plot $a_2=-0.471$ is used for in acetone.

c. Method 2D

When the polymer chain in the unperturbed state is nongaussian (*i.e.*, $a_2\neq0$) as in the case of CDA in acetone, eq 19 may be modified as[24]

$$\langle S^2\rangle^{3/2}/M^{3/2(1+a_2)}=K_0^{3/2}+\frac{1}{4\pi^{3/2}}BM^{(1-3a_2)/2} \qquad (20)$$

where

$$K_0=(\langle S^2\rangle_0/M)/M^{a_2}. \qquad (21)$$

Thus, from the graph of $\langle S^2\rangle_w^{3/2}/M_w^{3/2(1+a_2)}$ as a function of $M_w^{(1-3a_2)/2}=0$ (Baumann–Kamide–Miyazaki (BKM) plot), the parameter K_0 may be obtained as an intercept at $M_w^{(1-3a_2)/2}=0$. This plot is, of course, prerequisite a_2. Using $a_2=-0.471$, BKM plot for CDA in acetone is demonstrated in Figure 9b, from which $K_0=1.18\times10^{-14}$ cm^2 is estimated.

d. Method 2E

Stockmayer and Fixman (SF) plot according to eq 22[31]

$$[\eta]/M^{1/2}=K+2(3/2\pi)^{3/2}\Phi_0(\infty)BM^{1/2} \qquad (22)$$

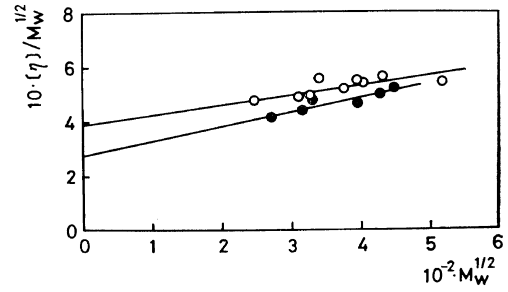

Figure 10. The Stockmayer–Fixman plot according to eq 22 for cellulose diacetate in acetone (○) and in tetrahydrofuran (●) at 25°C.

where

$$K=\Phi_0(\infty)(6\langle S^2\rangle_0/M)^{3/2} \qquad (23)$$

is applicable in the case of $a_\Phi=0$ and $a_2=0$. SF plots for CDA in acetone and THF are graphed in Figure 10. Resonable straight lines for each solution are obtainable. $A=1.10\times10^{-8}$ and 0.99×10^{-8} are evaluated in acetone and THF, respectively, where $\Phi_0(\infty)$ was assigned the value 2.87×10^{23}. These values are less reliable, because for the CDA solution $a_\Phi>0$ and $a_2\leq0$ are observed.

e. Method 2F

According to Kamide, Kawai, and their coworkers,[32,33] there exists a theoretical relationships between K_m and a in eq 1 in the case of $a_\Phi=0$ and $a_2=0$ as

$$-\log K_m+\log[1+2\{(a-0.5)^{-1}-2\}^{-1}]$$
$$=-\log K+(a-0.5)\log M_0 \qquad (24)$$

where M_0=the geometric mean of the upper and lower molecular weight limit $(M_1\cdot M_2)^{1/2}$, in which eq 1 holds. A plot of the left-hand side of eq 24 as a function of a -0.5 (Kamide plot) should be linear, with a slope equal to $\log M_0$. The Kamide plot for CDA in acetone and THF is illustrated in Figure 11. $K=0.399$ (*i.e.*, $A=1.2\times10^{-8}$ cm) in acetone and 0.289 ($A=1.00\times10^{-8}$ cm) in THF are determined by method 2F.

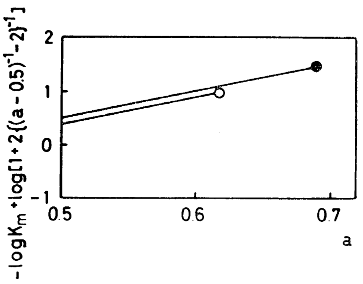

Figure 11. Kamide plot according to eq 24 for cellulose diacetate in acetone (○) and in tetrahydrofuran (●) at 25°C. The lines, which have slopes of 1/2 log (M_1M_2), are constructed to pass through each data point.

f. Method 2G

In the case of $a_\Phi\neq0$ and $a_2\neq0$, the well-known Flory–Fox viscosity equation can be rewritten in the form[24]

$$[\eta]/M^{0.5+a_\Phi+1.5a_2}$$
$$=6^{3/2}K_\Phi K_0^{3/2}+0.66K_\Phi BM^{0.5-1.5a_2} \qquad (25)$$

Evidently, eq 25 reduces to eq 22 when $a_\Phi=a_2=0$. It was found in a previous paper that the intrinsic viscosity of cellulose, amylose and their derivatives conforms very well to eq 25.[24] Plot of $[\eta]/M_w^{0.5+a_\Phi+1.5a_2}$ *vs.* $M_w^{0.5-1.5a_2}$ (Kamide–Miyazaki (KM) plot) for a given solvent results in a straight line and it is extrapolation to $M_w^{1/2}=0$ should give $6^{3/2}K_\Phi K_0^{3/2}$ (accordingly, K_0). By using the values of a_Φ and a_2 together with K_Φ summerized in Table VI, KM plot is constructed as shown in Figure 12, from which $K_0=1.16\times10^{-14}$ cm^2 in acetone and 2.50×10^{-17} cm^2 in THF are estimated.

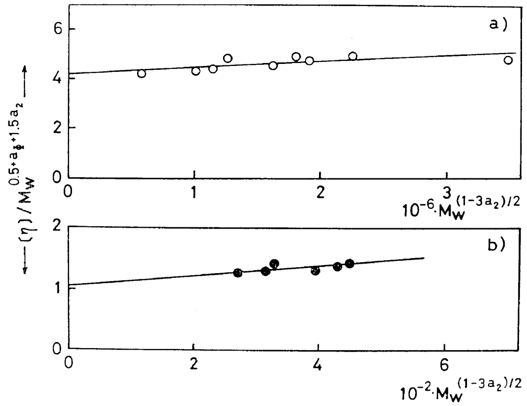

Figure 12. The Kamide–Miyazaki plot according to eq 25 for cellulose diacetate in acetone (○) and in tetrahydrofuran (THF) (●) at 25°C. The values of a_Φ and a_2 in Table VI are used.

g. Method 2H

Assuming $a_2=0$ and a_1 ($=3\text{d}\log\alpha_s/\text{d}\log M=3\varepsilon$)$=0$, Tanner and Berry derived eq 26[2]

$$M^{1/2}/[\eta]=(1+A'M^{-1/2})/(K'A^3) \qquad (26)$$

where K' and A' are parameters depending on the models used. The plot of $M_w^{1/2}[\eta]$ against $M_w^{-1/2}$ (Tanner–Berry plot) gives A from an ordinate at $M_w^{1/2}=0$. Figure 13 shows the Tanner–Berry plot for CDA in acetone and THF. We obtained $K'=(2.87/1.295)\times10^{23}$ for the former and $K'=2.87\times10^{23}$ for the latter from Table III in this paper and Table VIII of ref 2. A is found to be 1.45×10^{-8} cm in acetone and 1.37×10^{-8} cm in THF. For CDA in THF, Tanner and Berry have obtained $A=1.91\times10^{-8}$ cm this value is

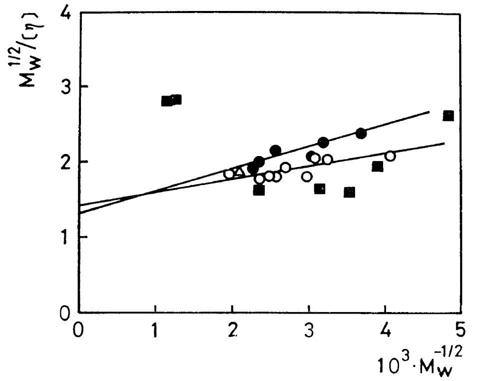

Figure 13. The Tanner–Berry plot according to eq 26 for cellulose diacetate in acetone (open mark) and in tetrahydrofuran (closed mark) at 25°C: ○ and ●, this work; ■, data from Tanner and Berry's workt.[2]

calculated from Table V of ref 2), which is about 40% larger than the value we obtained. The plot of their data scatters very much as shown in Figure 13 as closed rectangular, and it is extrapolation contains much uncertainity.

Table V summerizes the K_0, A values together with the B values as determined by Methods 2B—2H. In the case of $a_2 \neq 0$, the A value is calculated for $M_w = 1 \times 10^5$. Table V also includes the conformation parameter σ ($= A/A_f$, $A_f = A$ of a hypothetical chain with free internal rotation) and characteristic ratio C_∞.

If the A values estimated by Methods 2B, $\cdots$, 2H are designated as $A_{(2B)}$, $\cdots$, $A_{(2H)}$ for convenience, the following relations hold experimentally

$$A_{(2C)} > A_{(2B)} \simeq A_{(2D)} \simeq A_{(2G)} \gg A_{(2H)} > A_{(2E)} \simeq A_{(2F)} \quad \text{in acetone} \tag{27}$$

$$A_{(2H)} > A_{(2B)} \simeq A_{(2C)} \simeq A_{(2G)} \gg A_{(2E)} \simeq A_{(2F)} \quad \text{in THF} \tag{28}$$

From a theoretical view point, in the case of $a_2 \neq 0$ and $a_\Phi \neq 0$, methods 2B, 2D and 2G are expected to be the most reliable methods presently available for estimating the A value and in the case of $a_2 = 0$ and $a_\Phi \neq 0$, methods 2B, 2C, and 2G are recommended to employ.[24] The former corresponds to solution of CDA in acetone and the latter to CDA solution in THF. Agreement between methods 2E and 2F is excellent. However, the values estimated by these methods are 35% smaller than those by methods 2B, 2C (or 2D), and 2G, owing to the neglect of a_2 and a_Φ. Method 2H overestimates or underestimates the A value depending on the magnitude of $a_1 + 1.5a_2$.[34] In fact, in acetone $a_1 + 1.5a_2$ is negative (−0.6), and Method 2H is thus expected to underestimate A. In contrast to this, in THF $a_1 + 1.5a_2$ is positive (0.08) and so, Method 2H may overestimate the A value. It has been observed that when $a_2 < 0$ Method 2C has a tendency to overestimate A (see, Table 4a and b of ref 24). The relative order of the A value, as determined by the various

Table V. Unperturbed chain dimensions A, long-range interaction parameter B, conformation parameter σ and characteristic ratio C_∞ of cellulose diacetate in acetone and THF at 25°C

	Acetone					THF				
Method[a]	$K_0 \times 10^{16}$ cm^2	$A \times 10^8$, cm	$B \times 10^{27}$ cm^3	σ[c]	C_∞[d]	$K_0 \times 10^{16}$, cm^2	$A \times 10^8$, cm	$B \times 10^{27}$, cm^3	σ[c]	C_∞[d]
2B (α_s from ϕ)	—	1.66	—	3.44	24.7	—	1.23	—	2.56	14.1
2C ($a_2=0$)	—	2.14	−24.5	4.44	40.1	—	1.24	1.67	2.58	13.6
2D ($a_2 \neq 0$)	118	1.77[b]	0.90	3.69	27.7	—	—	—	—	—
2E ($a_2=a_\Phi=0$)	—	1.10	1.90	2.28	10.6	—	0.99	2.71	2.05	8.6
2F ($a_2=a_\Phi=0$)	—	1.12	—	2.32	10.9	—	1.00	—	2.08	8.9
2G ($a_2 \neq 0$, $a_\Phi \neq 0$)	116	1.75[b]	1.56	3.63	27.0	0.250	1.23[b]	2.11	2.55	13.2
2H ($a_1=a_2=0$, $a_\Phi \neq 0$)	—	1.45	—	3.00	18.4	—	1.37	—	2.85	16.6
Most probable value		1.73		3.59	26.3		1.23		2.56	13.5

[a] Same notations as those in ref 24 are used in order to avoid confusion.
[b] A value at $M_w = 1 \times 10^5$.
[c] C 1 chair conformation is assumed.
[d] The mean bond length $l = 5.47$ Å is used.

methods, agrees well with the results obtained for cellulose, amylose and their derivatives.[24] Therefore, the most reliable A value ($A_{(\mathrm{m})}$) can be defined as $(A_{(2\mathrm{B})}+A_{(2\mathrm{D})}+A_{(2\mathrm{G})})/3$ for CDA in acetone and $(A_{(2\mathrm{B})}+A_{(2\mathrm{C})}+A_{(2\mathrm{G})})/3$ for CDA in THF, respectively. $A_{(\mathrm{m})}$ values thus calculated are 1.73 in acetone and 1.23 in THF and are listed also in Table V. The value of σ corresponding to $A_{(\mathrm{m})}$ is not unusually high as compared with other cellulose derivatives.[24]

We thus conclude that cellulose acetate is a semi-flexible polymer, whose flexibility is remarkably influenced by the solvent nature, as was observed in cellulose, cellulose tricarbanilate and amylose tricarbanilate.[24] That is, CDA is considerably less flexible in acetone than in THF, suggesting that there is a specific solvent effect, like a temperature effect or solvation, on a short-range interaction.

The contribution of the excluded volume effect to the exponent a, a_1 ($\equiv 3\varepsilon$) can be roughly estimated from a, a_Φ, and a_2 by eq 11′

$$a=0.5+a_\Phi+a_1+1.5a_2 \qquad (11)'$$

The value of a_1 thus determined by eq 11′ is 0.107 in acetone and 0.083 in THF as summerized in the column of Table IV.

The a_1 value can be also estimated by using an alternative equation

$$\lambda'=a_2+2\varepsilon \qquad (29)$$

where

$$\lambda'=\mathrm{d}\ln(\langle S^2\rangle/M)/\mathrm{d}\ln M \qquad (30)$$

λ' is found to be -0.400 and 0.056 from eq c and d; thus, we obtain $a_1=0.130$ in acetone and 0.150 in THF. Both are slightly larger than those calculated from eq 11′. The fact that the exponent a_1 values are not as large as 0.2—0.3 confirms that acetone and THF are not good solvent.

Putting a_1 values obtained in this manner into the modified Voek's equation[35,36]

$$a_1+0.5=(4\alpha_s^2-3)/(5\alpha_s^2-3) \qquad (31)$$

$\alpha_s \simeq 1.1$ and 1.18 are calculated for CDA in acetone and THF, respectively. Those values are not so different from those estimated through use of the penetration function ϕ.

When the values of A and B are obtainable by Methods 2C, 2D, 2E, and 2G, we can calculate A_2 from A, B, and the experimental $\langle S^2\rangle_w$ value by using the relation.[37,38]

$$A_2=(N_A/2)Bh_0(z) \qquad (32)$$

In Figure 5, full (Method 2C), dotted (Method 2D), broken (Method 2E), and chain (Method 2G) lines are thus calculated by using eq 32 and 5 from A and B in Table V and $\langle S^2\rangle_z^{1/2}$ in Table I. The A_2 value calculated by Method 2C for acetone is a large negative value and is not shown in the figure. It is clear that Method 2G gives the best fit for the experimental data. Consequently, the methods used here prove highly satisfactory for interpreting the dilute solution properties of CDA.

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