Dilute Solution Properties of Water-Soluble Incompletely Substituted Cellulose Acetate

Kenji KAMIDE, Masatoshi SAITO, and Tatsuyuki ABE

Textile Research Laboratory, Asahi Chemical Industry Co., Ltd.,
Hachonawate, Takatsuki, Osaka 569, Japan.

ABSTRACT: Water-soluble incompletely substituted cellulose acetate (CA) was synthesized by the hydrolysis of cellulose diacetate with hydrochloric acid. CA having a degree of substitution DS between 0.39 and 0.81 was water-soluble. The CA ($DS=0.49$) whole polymer was fractionated into 15 parts, using water–methanol as the solvent–nonsolvent by the successive solution method. The CA ($DS=0.49$) polymer was soluble in highly polar organic solvents. Solution viscosity, light scattering, and membrane osmometry measurements were performed at 25°C on these fractions in N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), water, and formamide. The fractions had ratios of weight-to-number-average molecular weight M_w/M_n of approximately 1.3, independent of M_w. The following relations between limiting viscosity number $[\eta]$, z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ and M_w were obtained: $[\eta]=0.19\ M_w^{0.60}$ (cm^3 g^{-1}) and $\langle S^2 \rangle_z^{1/2}=0.50\times10^{-8}$ $M_w^{0.52}$ (cm) in DMAc at 25°C. Flory's viscosity parameter Φ in DMAc was $(1.82-2.18)\times10^{23}$, showing a small molecular weight dependence. The short-range interaction parameter A was estimated thermodynamically as 1.33×10^{-8} (cm) in DMAc and the conformation parameter σ found to be 2.29. The effect of DS on the molecular characteristics of cellulose acetate is discussed.
    KEY WORDS   Cellulose Acetate / Solution Property / Unperturbed Chain Dimension / Mark–Houwink–Sakurada Equation / Conformation Parameter /

For years the dilute solution properties of cellulose and its derivatives have been an important target of attention in polymer science. In spite of this, the effect of the degree of substitution (DS) on these properties has been studied only in part for cellulose nitrate and cellulose acetate, particularly in the limited range of higher DS. For example, Moore and his co-workers[1] established parameters in the Mark–Houwink–Sakurada (MHS) equation [eq 1] for cellulose nitrate with nitrogen content N%=12.4—13.8 in various solvents. Schulz and Penzel[2-4] measured the solution viscosity and light scattering of cellulose nitrates (N = 12.9 and 13.9%) in acetone and ethyl acetate and estimated the thermodynamic and hydrodynamic parameters. Recently, we determined the molecular parameters of cellulose acetate ($DS=2.46$ and 2.92) on the basis of solution viscosity, gel-permeation chromatography, sedimentation velocity, membrane osmometry, and light scattering.[5-8] We found the unperturbed chain dimension to be larger in cellulose acetate ($DS=2.46$) than in cellulose acetate ($DS=2.92$) and that A of cellulose acetate ($DS=2.46$) is markedly dependent on the solvent nature (*i.e.*, dielectric constant). These features were interpreted in terms of the polar character of cellulose acetate ($DS=2.46$). Unfortunately, no work has been carried out on cellulose acetate with a DS less than 2.4, probably because of its lesser industrial importance.

In order to understand the fundamental properties of their cellulose derivatives, it is important to investigate their solution properties over a wide range of DS. Cellulose acetate, of course, is not an exception. In this study, we synthesized water-soluble incompletely substituted cellulose acetate ($DS=0.49$) and performed solution viscosity, membrane osmometry, and light scattering measurements in a variety of solvents. The effect of DS and the solvent nature on the molecular charac-

teristics of cellulose acetate is discussed.

EXPERIMENTAL

Preparation of Water-Soluble Cellulose Acetate

Cellulose diacetate flakes ($DS = 2.46$, weight-average molecular weight $M_w = 1.2 \times 10^5$) synthesized in a previous paper[5] was crushed into a fine powder in a ball-mill and hydrolyzed using hydrochloric acid as catalyst, in a 77% aq acetic acid solution under nitrogen atomosphere at 40°C for various times of period. The incompletely substituted cellulose acetate thus hydrolyzed was recovered by precipitation with acetone, filtered, washed with acetone to remove all traces of acetic acid in the polymer, dried in vacuo at room temperature and finally stocked in a dark, cold place. Ten cellulose acetate whole polymers of various DS (polymer code MAW-1—MAW-10) were prepared in this manner.

The combined acetic acid content (AC) of the unfractionated and fractionated cellulose acetates was determined by back-titration, using sodium hydroxide and sulfulic acid. From C^{13}-NMR analysis of the CA whole polymer (sample code MAW-5, $DS = 0.49$) dissolved in deuterated dimethyl sulfoxide (DMSO-d_6), the probability of finding O-acetyl groups attached to the C_2, C_3, and C_6 atoms was estimated to be 0.10, 0.20, and 0.19, respectively.[9]

Molecular Weight Fractionation

The successive solutional fractionation (SSF) technique was applied. The original polymer (polymer code MAW-5; $AC = 16.1\%$, $DS = 0.49$) in water was fractionated at 25°C, using methanol, into 15 approximately equal fractions. The polymer volume fraction v_p^0 in the first fractionation step, from which a phase separation occurred, was 0.56%. In order to lessen the time necessary for the precipitate to settle completely in the bottom of the fractionation vessel, a small amount of sodium chloride was added to the aqueous solution. The supernatant phase was concentrated by evaporating off the water and methanol at 60°C, leaving a dry powder which was dissolved in water to make up a solution of 5 wt%. A large quantity of acetone was then added to completely precipitate the fraction, which was then filtered, washed with acetone and dried in vacuo.

Solution Viscosity

Solution viscosities of CA ($DS = 0.49$) fractions were measured in N,N-dimethylacetamide (DMAc), DMSO, water, and formamide (FA) using a modified Ubbelohde suspension-type viscometer at 25°C. The limiting viscosity number $[\eta]$ was determined from reduced viscosities η_{sp}/c (η_{sp}, specific viscosity; c, polymer mass concentration) at five concentrations by extrapolation to infinite dilution.

Membrane Osmometry

Osmotic measurements were carried out on solutions of CA in DMAc at 25°C with a Hewlett–Packard high-speed membrane osmometer model 502. The membrane was the Ultracella filter-type SH-11539 (regenerated cellulose, allerfeinst) manufactured by Sartorius-Membrane filter GMBH (West Germany).

Light Scattering

DMAc, water and FA were chosen as the solvents for the light-scattering measurements. CA ($DS = 0.49$) fractions were dissolved in freshly distilled solvents at 60°C to make 0.6 wt% solutions. The solutions were left standing for at least more than 16 h and then filtered with a sintered glass filter (2nd grade). The specific refractive index increments $\partial n/\partial c$ were determined by a Shimadzu differential refractiometer, model DR-4 at 25°C at a wavelength λ_0 of 436 nm to be 0.068, 0.131, and 0.069 (cm^3 g^{-1}) for CA fractions in DMAc, water, and FA, respectively. The stock solutions were centrifuged at 1.03×10^5 g for 2 h in a Hitachi model 55p-7 automatic preparative ultracentrifuge. The upper two-thirds of the supernatant phase was carefully filtered through a Sartorius membrane filter 0.15 μm and directly transferred into the light-scattering cylindrical cell. The light-scattering intensity was measured within an angle range from 30—150° using unpolarized incident light $\lambda_0 = 436$ nm at 25°C in a FICA model 42000 photogonio diffusiometer. The data obtained were analyzed according to Zimm's procedure.[10,11]

DISCUSSION

Solubility Behavior

Ten cellulose acetate samples with DS ranging from 0.10 to 1.96 were used in the water solubility test. Table I shows the results from this test. CA is

Table I. Degree of substitution (*DS*) dependence on water solubility of cellulose acetate[a]

Polymer	MAW-1	MAW-2	MAW-3	MAW-4	MAW-5	MAW-6	MAW-7	MAW-8	MAW-9	MAW-10
DS	1.96	0.98	0.81	0.65	0.49	0.39	0.34	0.33	0.16	0.10
Solubility	×	△	○	○	○	○	△	△	×	×

[a] ○, soluble; △, only swell; ×, insoluble.

water-soluble in a *DS* range of 0.39—0.81. It has for years been believed that CA is soluble in water in a *DS* range 0.6—0.8 at room temperature.[12] But, CA with a *DS* lower than 0.6 (in this case, 0.4) is evidently soluble in water at room temperature. The CA sample (polymer code MAW-5, *DS* = 0.49) was used for a further study.

In order to confirm the stability of aq CA solution, a 0.6 wt% solution of the CA whole polymer (*DS* = 0.49) in water was prepared and stocked in a dark place at 25°C. Figure 1 seems to indicate that although water is a poor solvent in light scattering measurements (see Table III) and CA molecules have a rather high tendency to crystallize when coagulated or precipitated as gels on heat-treatment, an aq solution of CA (*DS* = 0.49) is stable at least for several months at room temperature, with no indication of crystallization.

The solubility behavior of the CA whole polymer (*DS* = 0.49) in various organic solvents was examined. The polymer is found to be insoluble in less polar solvents such as hydrocarbons, chlorinated hydrocarbons, amines, esters, but soluble in very polar organic solvents such as formic acid (dielectric constant $\varepsilon = 58.5^{13}$), trifluoroacetic acid ($\varepsilon = 39.5^{13}$), dimethylacetamide ($\varepsilon = 37.8^{13}$), dimethyl sulfoxide ($\varepsilon = 46.6^{13}$), water ($\varepsilon = 78.3^{13}$), and formamide
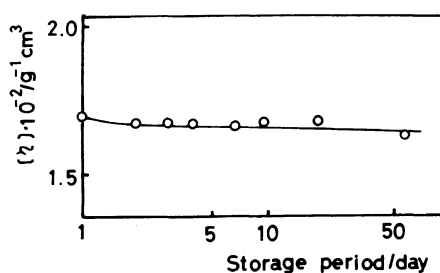

Figure 1. Limiting viscosity number [η] of cellulose acetate MAW-5 in water as a function of storage period of the original solution (0.6 wt%) at 25°C.

Table II. Results of successive fractionation run (water–methanol) and viscosity measurements on cellulose acetate (*DS* = 0.49) in various solvents

Sample code	v_m	ρ_s	[η]/cm³ g⁻¹ (at 25°C)				Huggins coefficient k'			
			DMAc	DMSO	H₂O	FA	DMAc	DMSO	H₂O	FA
MA-1	0.800	0.102	42	38	40	—	0.45	—	0.52	—
MA-2	0.755	0.085	—	79	80	87	—	0.39	0.62	0.46
MA-3	0.730	0.120	108*	106	118	124	0.43	0.53	0.52	0.49
MA-4	0.720	0.111	142	140	157	—	0.43	0.42	0.52	—
MA-5	0.715	0.044	133	132	151	156	0.38	0.45	0.47	0.57
MA-6	0.710	0.056	154	153	172	180	0.40	0.41	0.52	0.42
MA-7	0.707	0.027	167	167	172	180	0.34	0.39	0.52	0.49
MA-8	0.703	0.032	164	162	182	188	0.43	0.47	0.60	0.49
MA-9	0.699	0.020	185	178	193	198	0.35	0.40	0.59	0.60
MA-10	0.695	0.034	189	201	203	220	0.44	0.44	0.67	0.62
MA-11	0.691	0.018	200	—	215	230	0.48	—	0.69	0.68
MA-12	0.682	0.033	203	204	232	232	0.48	0.49	0.64	0.74
MA-13	0.671	0.054	235	235	259	257	0.57	0.56	0.78	0.74
MA-14	0.660	0.111	—	—	234	—	—	—	—	—
MAW-5	—	0.847	170	170	170	—	0.35	0.35	0.65	—
CMA-W1	—	—	452	—	—	—	0.46	—	—	—

$(\varepsilon = 111^{13})$. It should be noted that the solubility of CA ($DS = 0.49$) is controlled primarily by the dielectric constant of the solvent and the critical value of this constant above which the polymer dissolves is approximately 37.

Fractionation of CA (DS = 0.49)

The second and third columns of Table II give the composition of the methanol mixture, v_m, for each fractionation step and the fraction size ρ_s. v_m varies from 0.80 to 0.66. The total recovery of the polymer was 85%. The fourth to eleventh columns in the same table compile the limiting viscosity numbers $[\eta]$ and Huggins coefficients k' for CA in DMAc, DMSO, water, and FA. $[\eta]$ of the fractions in water covers a range from 40 to 259, indicating that fractionation according to molecular weight was performed successfully. The DS values for all the fractions are within 0.49 ± 0.01 and thus can be regarded as independent of M_w.

Molecular Weight and Molecular Weight Distribution of the Fractions

The Zimm plots for the CA ($DS = 0.49$) fraction MA-5 in DMAc and formamide are shown in Figures 2 and 3. No downward curvature can be seen in these plots.

Tables III and IV summarize the experimental results from light scattering (LS) and membrane osmometry (MO) on CA ($DS = 0.49$) solutions in DMAc, water, and formamide at 25°C. The maximum value of M_w for these fractions is a little below 15×10^4, which is an upper limit as long as the hydrolysis method is employed and a present there is no efficient method for preparing CA ($DS \leq 0.6$) with a higher M_w.

Excellent agreement of the M_w values of the fraction MA-5 in three different solvents confirms definitely the experimental reliability and also indicates that the CA ($DS = 0.49$) molecules dissolve molecularly in these solvents without association. The experimental error involved in the light-scattering measurement of M_w was estimated to be less than a few %.

The polydispersity parameter M_w/M_n, as determined by LS and MO, 1.30 ± 0.02 for the series of CA ($DS = 0.49$) fractions was used here.

The weight-average radius of gyration $\langle S^2 \rangle_w^{1/2}$ was calculated from the z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ and the M_w/M_n value, assuming the Schulz–
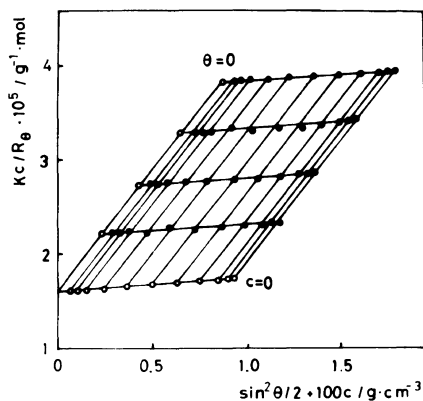

Figure 2. Zimm plot of a cellulose acetate ($DS = 0.49$) fraction MA-5 in DMAc at 25°C: unpolarized incident light wave length $\lambda_0 = 436$ nm; closed circles, measured points; open circles, points obtained by extrapolation.
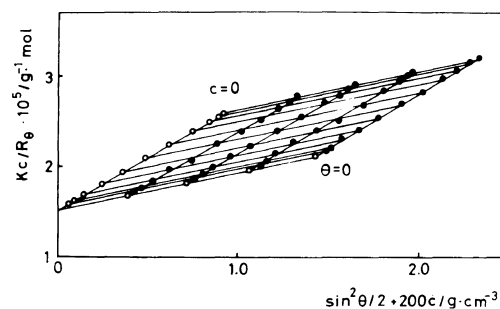

Figure 3. Zimm plot of a cellulose ($DS = 0.49$) fraction MA-5 in formamide at 25°C: unpolarized incident light wave length $\lambda_0 = 436$ nm.

Zimm molecular weight distribution.[6]

Mark–Houwink–Sakurada Equations

Figures 4a—d show the log-log plots of $[\eta]$ vs. M_w for CA ($DS = 0.49$) in DMAc, DMSO, water, and formamide at 25°C (open circles). From this figure the Mark–Houwink–Sakurada (MHS) equation,

$$[\eta] = K_m M_w{}^a \tag{1}$$

can be established by using the least-squares method. The results are as follows:

$$[\eta] = 0.19_1 \, M_w^{0.60} \quad \text{in} \quad \text{DMAc} \tag{a}$$

$$[\eta] = 0.17_1 \, M_w^{0.61} \quad \text{in} \quad \text{DMSO} \tag{b}$$

$$[\eta] = 0.20_9 \, M_w^{0.60} \quad \text{in} \quad \text{water} \tag{c}$$

and

Table III. Results of light-scattering, membrane-osmometry, and viscosity measurements on cellulose acetate ($DS=0.49$) in dimethylacetamide at 25°C

| Sample code | Light scattering | | | | Osmotic pressure | M_w/M_n | $\Phi \times 10^{-23}$ | α_s[b] | X[c] |
	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2} \times 10^8$ cm	$\langle S^2 \rangle_w^{1/2} \times 10^8$ cm	$A_2 \times 10^4$ cm³ mol g^{-2}	$M_n \times 10^{-4}$				
MA-1	—	—	—	—	0.97	—	—	—	—
MA-2	—	—	—	—	1.67	—	—	—	—
MA-3	4.55	137	123	4.80	—	—	1.85	1.03	4.3
MA-4	6.25	160	144	8.90	—	—	2.08	1.07	8.0
MA-5	6.32	164	148	7.50	—	—	1.82	1.05	4.2
MA-6	6.76	175	158	14.9	5.20	1.30	1.86	1.18	6.2
MA-7	7.25	184	166	13.8	—	—	1.86	1.18	6.2
MA-8	7.94	189	170	15.1	6.10	1.31	1.85	1.26	7.8
MA-9	8.00	191	172	15.0	—	—	2.01	1.24	10.5
MA-10	10.8	215	194	12.1	—	—	1.96	1.26	10.1
MA-11	11.1	223	201	10.2	—	—	1.92	1.13	6.6
MA-12	11.3	—	—	—	8.70	1.30	—	—	—
MA-13	14.5	253	223	3.1	11.3	1.28	2.18	1.03	9.0
MAW-5[a]	8.00	247	198	13.8	3.90	2.29	—	—	—

[a] Whole polymer.
[b] *via* penetration function.
[c] By method 1A.

Table IV. Results of solution-viscosity and light-scattering measurements on cellulose acetate ($DS=0.49$) fraction MA-5 in formamide, water, and DMAc at 25°C

Solvent	Dielectric constant ε	$[\eta]$[a] cm³ g^{-1}	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2} \times 10^8$ cm	$A_2 \times 10^4$ cm³ mol g^{-2}	$\Phi \times 10^{-23}$	$\Psi \times 10^3$	α_s	X
FA	111	156	6.30	349	8.4	0.22	8.7	1.01	0.14
Water	78.3	151	6.42	291	3.1	0.38	6.7	1.01	0.26
DMAc	37.8	133	6.32	164	7.5	1.82	4.9	1.05	4.2

$$[\eta]=0.20_9\, M_w^{0.60} \quad \text{in} \quad \text{FA} \tag{d}$$

The molecular weight range covered by eq a—d is $(4.55—14.5) \times 10^4$ (the ratio of the maximum to minimum M_w is 3.2). The MHS equations in water and in formamide coincide and the values for exponent a in the above equations range from 0.60 to 0.61 in these different solvents ($\varepsilon=37.8 \sim 111$). Thus, a is very insensitive to the solvent.

Equation a should be compared with those established for CA ($DS=2.92$) and CA ($DS=2.46$) in the same solvent at the same temperature.[5]

$$[\eta]=0.026_4\, M_w^{0.75} \quad \text{for} \quad \text{CA} \ (DS=2.92) \tag{e}$$

$$[\eta]=0.039_5\, M_w^{0.74} \quad \text{for} \quad \text{CA} \ (DS=2.46) \tag{f}$$

In Figure 4a, open rectangles represent CA ($DS=2.92$) and the open triangles stand for CA ($DS=2.46$), as reported in a previous paper.[6] In the lower M_w range, $[\eta]$ of CA ($DS=0.49$) is similar to that of CA ($DS=2.46$), but in the higher M_w range, $[\eta]$ for CA ($DS=0.49$) approaches that for CA ($DS=2.92$). The exponent a for CA ($DS=0.49$) is substantially smaller than the values obtained for CA ($DS=2.46$ and 2.92) in DMAc.

The limiting viscosity number $[\eta]$ of CA is a unique function of the dielectric constant ε of the solvent in which the polymer is dissolved. Figure 5 is
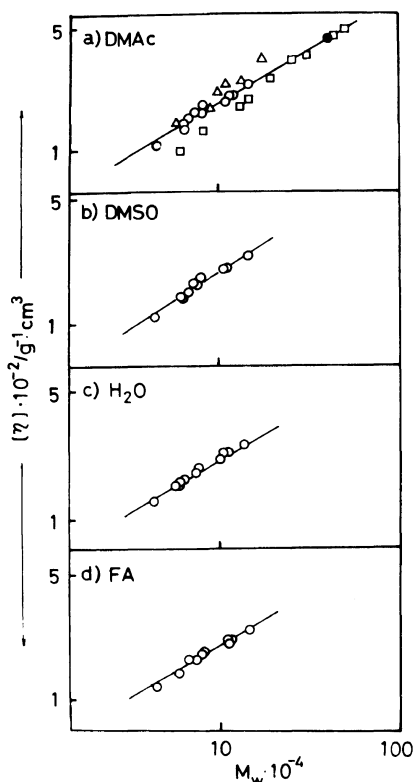
Figure 4. Log-log plot of limiting viscosity number $[\eta]$ against the weight-average molecular weight M_w for cellulose acetate $(DS=0.49)$ in dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), water, and formamide at 25°C. Straight lines represent the Mark–Houwink–Sakurada equations (eq a—d) determined by the least-squares method: ◯, CA $(DS=0.49)$ (this work); △, CA $(DS=2.46)$[5]; ☐, CA $(DS=2.92)$.[6]
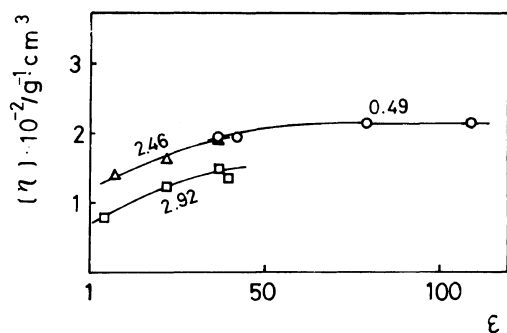
Figure 5. Limiting Viscosity number $[\eta]$ of three CA polymers having the dielectric constant ε of the solvent in which the polymers were dissolved: ◯, CA $(DS=0.49)$; △, CA $(DS=2.46)$[5,6]; ☐, CA $(DS=2.92)$[6]
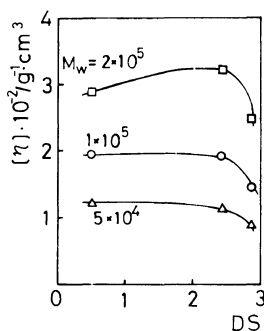

Figure 6. Effect of the degree of substitution (DS) on limiting viscosity number $[\eta]$ of cellulose acetate in DMAc at 25°C.

an example in which three kinds of CA fractions with the same molecular weight $(M_w=1 \times 10^5)$ and various DS (0.49, 2.46, 2.92) are shown. $[\eta]$ increases with an increase in ε, approaching an asymptotic value which depends on the DS value of the polymer. This phenomenon can not be interpreted in terms of the excluded volume effect (see, Table IV), but may be attributed to a significant change in the unperturbed chain dimensions with the solvent nature. Recently, we confirmed by nuclear magnetic resonance (NMR) that there exists a specific strong interaction between the O-acetyl proton or the hydroxyl proton of the CA molecule and the solvent and that the strength of this interaction depends on the solvent nature.[14]

The effect of the degree of substitution (DS) on the limiting viscosity number $[\eta]$ of CA in DMAc is illustrated in Figure 6, in which the value for CA $(DS=0.49)$ with $M_w=2 \times 10^5$ is calculated from eq a. Other points for CA $(DS=2.46)$ and CA $(DS=2.92)$ are calculated from eq d and a in ref 6. The DS dependence of $[\eta]$ varies with M_w of the polymer; for relatively small M_w, $[\eta]$ decreases monotonously with an increase in DS, but for large $M_w(M_w \gtrsim 2 \times 10^5)$, $[\eta]$ reveals a maximum at a DS value. In the DS range of 0.49—2.46, $[\eta]$ is not very sensitive to DS, slightly increasing or decreasing as DS gets large. In the comparatively narrow DS range from 2.46—2.92, $[\eta]$ decreases remarkably with an increase in DS. This seems to indicate that the interaction between the hydroxyl groups remaining on the CA molecule and the solvent plays an important role in the solution viscosity.

Radius of gyration and Second Virial Coefficient

The molecular weight dependence of the z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ in DMAc is shown in Figure 7 for CA ($DS=0.49$) in DMAc by open circles. In this figure, the data points for CA ($DS=2.92$) and CA ($DS=2.46$) are also included as open rectangles and an open triangle for comparison. Among these three kinds of CA with different DS, CA ($DS=0.49$) has the most compact form in DMAc.

$$\langle S^2 \rangle_z^{1/2} \quad \text{is related to } M_w \text{ by}$$

$$\langle S^2 \rangle_z^{1/2} = 0.50 \times 10^{-8} \, M_w^{0.52} \qquad \text{(cm)}$$

$$\text{for} \quad \text{CA } (DS=0.49) \quad \text{in DMAc at 25}^\circ\text{C} \qquad \text{(g)}$$

It is interesting that $\langle S^2 \rangle_z^{1/2}$ of the CA ($DS=0.49$) fraction in a given solution (closed circle in Figure 7) is approximately twice the value in DMAc. The CA ($DS=0.49$) polymer expands in the following order: DMAc < water < formamide.

The second virial coefficient A_2, determined for CA ($DS=0.49$) in DMAc at 25°C by membrane osmometry and light scattering shows that there is too much scatter around 1.1×10^{-3} (cm^3 g^{-2} mol) to allow a definite conclusion as to its molecular weight dependence.

The A_2 values of the CA ($DS=0.49$) fraction for the three solvents are of the order of 10^{-4} cm^3 mol g^{-2}, thus showing no systematic variation in the solvent (see the sixth column of Table IV).

Flory's viscosity parameter

$$\Phi[\equiv[\eta]M_w/(q_{w,z}^{-1}6^{3/2}\langle S^2\rangle_z^{3/2}), \, q_{w,z}$$
$$= \text{correction factor for polydispersity}]$$

for CA ($DS=0.49$) in DMAc is plotted against M_w as open circles in Figure 8. The corresponding values for aqueous and formamide solutions are shown in the seventh column of Table IV. Here, $q_{w,z}$ ($=1.41$) was calculated assuming the Schulz–Zimm distribution. The Φ for DMAc solution is smaller than that for CA ($DS=2.92$), in the same solvent (as denoted by the open rectangles), being 1.3—1.6 times smaller than the theoretical value (2.87×10^{23}) for a non-permeable polymer chain in the unperturbed state. The Φ values for CA ($DS=0.49$) in DMAc shows a significant molecular weight dependence which may be expressed by,

$$\Phi = K_\Phi M_\Phi^a \qquad (2)$$

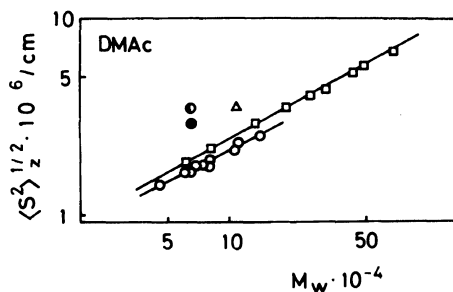where K_Φ and a_Φ are the parameters for a given

Figure 7. Molecular weight dependence of the radii of gyration $\langle S^2 \rangle_z^{1/2}$ for cellulose acetate in DMAc at 25°C: ○, CA ($DS=0.49$) (this work); △, CA ($DS=2.46$)[5]; □, CA ($DS=2.92$)[6]; ●, CA ($DS=0.49$) in water; ◐, CA ($DS=0.49$) in formamide.
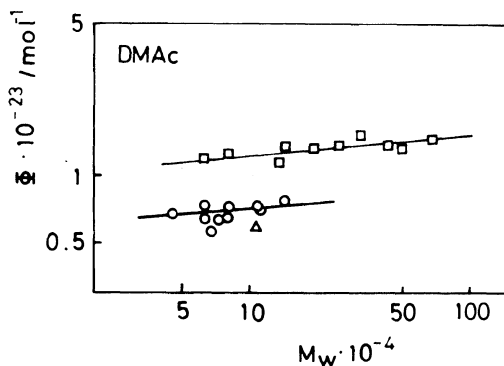

Figure 8. Molecular weight dependence of the Flory's viscosity parameter Φ for cellulose acetate in DMAc at 25°C: ○, CA ($DS=0.49$) (this work); △, CA ($DS=2.46$)[5]; □, CA ($DS=2.92$)[6].

polymer–solvent system. For CA ($DS=0.49$) in DMAc, we obtain $K_\Phi=0.61 \times 10^{23}$ and $a_\Phi=0.103$, which due to a relatively narrow range of M_w, are not accurate enough to estimating the unperturbed chain dimensions. The open triangle in Figure 8 denotes CA ($DS=2.46$) in DMAc.

The Φ value for CA in DMAc decrease in the order: CA ($DS=2.92$) > CA ($DS=0.49$) ⪼ CA ($DS=2.46$). The Φ values for CA ($DS=0.49$) in water and formamide are unexpectedly small, being approximately 1/16 and 1/30 the value in DMAc. This seems attributable to the large $\langle S^2 \rangle_z^{1/2}$ of CA in these solvents. Abnormally small values of Φ and its molecular dependence for cellulose acetate ($DS=0.49$—2.92) undoubtedly indicate a draining effect.

The expansion factor α_s in these solutions was calculated, according to the procedure described previously,[15] using the penetration function $\Psi(\equiv (4\pi^{3/2}N_a)^{-1}(A_2M^2/\langle S^2\rangle^{3/2})$. The results are listed in the ninth column of Table III and in the eighth column of Table IV. The α_s values obtained remain almost constant within experimental error, and are close to unity, suggesting that all the solvents exployed are thermodynamically poor solvents for CA. It should be remembered that any theory yields nearly the same relations between Ψ and the excluded volume parameter $\bar{z}$ for $\Psi \leq 0.1$ which is the range in the CA ($DS=0.49$)–solvent systems (the eighth column of Table IV). Using Φ and α_s, the draining parameter X, defined in the Kurata–Yamakawa theory,[16] was estimated (this method is referred to as the method 1A in the previous paper[15]), and is given in the last columns of Table III and IV. For the CA ($DS=0.49$)–DMAc system, the X values obtained in this narrow molecular weight range are too small to permit examination of their molecular dependence. These values were found to be from 4.2 to 10.5 (average 7.3), and are smaller than $X \gtrsim 10$ is the case for many vinyl-type polymers.

Figure 9 shows the variation in $[\eta]$, $\langle S^2\rangle_z^{1/2}$, Φ, α_s, and X for the CA ($DS=0.49$) fraction ($M_w=6.32\times 10^4$) with the dielectric constant ε of the solvent. Evidently, an increase in ε leads to larger values of $[\eta]$ and $\langle S^2\rangle_z^{1/2}$ and smaller values of Φ and X. α_s is nearly independent of ε. This strongly suggests that at least the observed marked variation in $[\eta]$, $\langle S^2\rangle_z^{1/2}$ and Φ does not arise from variation in the long-range interaction parameter.

Unperturbed Chain Dimension

The unperturbed chain dimension A is defined by,

$$A=(\langle R^2\rangle_0/M)^{1/2} \qquad (3)$$

with,

$$\langle R^2\rangle_0 = 6\langle S^2\rangle_0 \qquad (4)$$

($\langle R^2\rangle_0$ is the mean-square end-to-end distance of the polymer chain in the unperturbed state) was estimated by using the methods 2B, 2C 2E, and 2F, proposed in the previous paper.[15]
Method 2B:

$$\langle S^2\rangle_0^{1/2} = \langle S^2\rangle^{1/2}/\alpha_s \qquad (5)$$
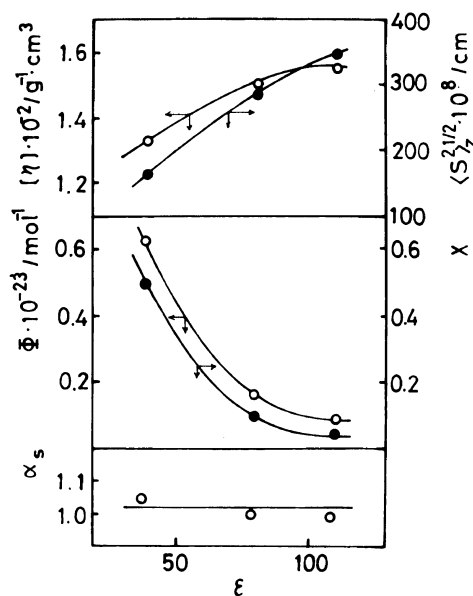
Method 2C: Baumann plot[17]

Figure 9. Dependence of limiting viscosity number $[\eta]$, radius of gyration $\langle S^2\rangle_z^{1/2}$, Flory's viscosity parameter Φ, expansion factor α_s and draining parameter X of CA ($DS=0.49$) fraction MW-5 on the dielectric constant of the solvent.

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

Method 2E: Stockmayer–Fixman plot[18]

$$[\eta]/M^{1/2} = K+2(3/2)^{3/2}\Phi_0(\infty)BM^{1/2} \qquad (7)$$

with

$$K=\Phi_0(X_0)A^3 \qquad (8)$$

Method 2F: Kamide *et al.* plot[19-24]

$$-\log K_m+\log[1+2\{(a-0.5)^{-1}-2\}^{-1}]$$
$$= -\log K+(a-0.5)\log M_0 \qquad (9)$$

$\Phi_0(X)$ denotes $\Phi(X)$ at $\alpha_s=1$, which is a function of the draining parameter X, and M_0 is the geometric mean of the upper and lower molecular weight limit for which eq 1 holds.

In Figure 10, the ratio $\langle S^2\rangle_{0,w}/M$ evaluated by the method 2B is plotted against M_w for CA ($DS=0.49$) in DMAc at 25°C. The plotted points scatter considerably around $\langle S^2\rangle_{0,w}/M_w=0.27\times 10^{-6}$ cm^2 g^{-1} mol (accordingly, A ($\equiv(6\langle S^2\rangle_0/M^{1/2})=1.28\times 10^{-8}$ cm) and the ratio $\langle S^2\rangle_{0,w}/M_w$ can be regarded as approximately constant (*i.e.*, $a_2 \equiv$ d ln $\langle S^2\rangle_{0,w}/M$/d ln $M_w \simeq 0$). The CA ($DS=0.49$) chain in the unperturbed state can be considered Gaussian to a first approximation. The same method was
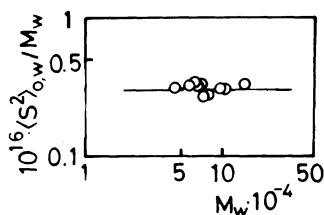
428

Figure 10. Unperturbed radius of gyration $\langle S^2 \rangle_{0,w}/M_w$ of cellulose acetate ($DS=0.49$) in DMAc at 25°C: full line, of $\langle S^2 \rangle_{0,w}/M_w=0.30\times10^{-16}$ cm^2 g^{-1} mol.

applied to the data of aqueous and formamide solutions in exactly the same manner, and A was found to be 2.42×10^{-8} cm and 2.97×10^{-8} cm in water and formamide, respectively, as indicated in the second column of Table VI.

In general, the radius of gyration $\langle S^2 \rangle^{1/2}$ can be expressed in terms of molecular weight by the relation

$$\langle S^2 \rangle^{1/2} = K_\lambda M^{(\lambda+1)/2} \tag{10}$$

where,

$$\lambda = a_2 + 2\varepsilon \tag{11}$$

$$\varepsilon = \mathrm{d}\ln\alpha_s/\mathrm{d}\ln M \tag{12}$$

$$a_2 = \mathrm{d}\ln\langle S^2 \rangle_0/M/\mathrm{d}\ln M \tag{13}$$

For the CA ($DS=0.49$)–DMAc system λ was estimated to be 0.04 from eq g. Putting $\lambda=0.04$ and $a_2=0$ into eq 11, we obtain $\varepsilon=0.02$, which is too small to detect experimentally from the molecular weight dependence of the expansion coefficient α_s. This means that the contribution of the excluded volume effect to the HMS exponent a is negligibly small, being consistent with $\alpha_s \lesssim 1.1$—1.2.

The exponent a in eq 1 is given by the relation

$$a = 0.5 + a_\Phi + 3\varepsilon + 1.5a_2 \tag{14}$$

Putting $a=0.60$, $a_\Phi=0.103$ and $\varepsilon=0.02$ for the CA ($DS=0.49$)–DMAc system into eq 14, we obtain $a_2 = -0.04$, which is too small to detect by experiment. The main factor contribution to the a value is the partially free draining effect; the volume effect is apparently minor.

Figure 11 shows the plots of Baumann, Stockmayer–Fixman, and Kamide et al. for CA ($DS=0.49$) in various solvents. The A and B values for CA ($DS=0.49$) solutions in DMAc, obtained from the intercepts and slopes of the above plots,
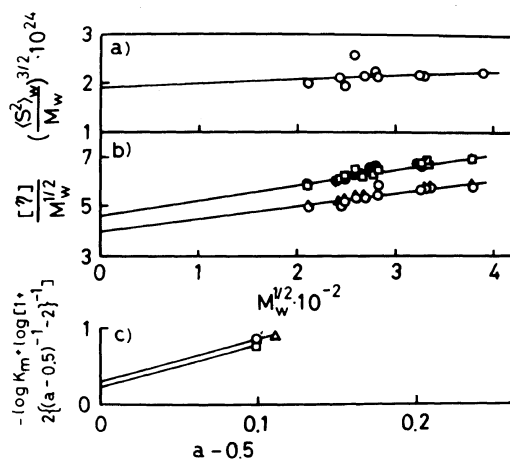

Figure 11. Baumann plot (a), Stockmayer–Fixman plot (b) and Kamide et al. plot (c) cellulose acetate ($DS=0.49$) in DMAc ($\bigcirc$), DMSO ($\triangle$), water ($\square$), and FA ($\bullet$) at 25°C.

Table V. Unperturbed chain dimension A, long-range interaction parameter B, conformation parameter σ, and characteristic ratio C_∞ of CA ($DS=0.49$) in DMAc at 25°C

Method	$A\times10^8$	$B\times10^{27}$	σ	C_∞
	cm	cm^3		
2B (α_s from Ψ)	1.28	—	2.23	10.0
2C ($a_2=0$)	1.38	0.79	2.35	11.4
2E ($a_2=a_\Phi=0$)	1.12	3.70	1.91	7.5
2F ($a_2=a_\Phi=0$)	1.14	—	1.94	7.8
Most probable	1.33	—	2.29	10.7

Table VI. Unperturbed-chain dimension A of cellulose acetate ($DS=0.49$) evaluated by method 2B, 2E, and 2F and conformation parameter σ and characteristic ratio C_∞, both estimated by method 2B

Solvents	$A\times10^8$/cm			σ	C_∞
	2B	2E	2F	2B	2B
DMAc	1.28	1.12	1.14	2.23	10.0
DMSO	—	1.12	1.14	—	—
Water	2.42	1.17	1.22	4.11	34.7
Formamide	2.97	1.19	1.22	5.06	52.5

are summarized in Table V. In Table VI, the A values in various other solvents, are tabulated. The prerequisites for the methods 2E and 2F are $a_2 = a_\Phi = 0$. The latter is evidently not acceptable from an experimental point of view (see Figure 8). The methods 2B and 2C are then preferred to methods 2E and 2F. The A values calculated from methods 2E and 2F are from some 20% (in DMAc) to 150% (in formamide) smaller than the most probable value, which is an average of the values obtained by the methods 2B and 2C. The large discrepancy in the A values derived by the thermo-dynamic (methods 2B and 2C) and hydrodynamic (methods 2E and 2F) approaches can be accounted for by taking the draining effect into consideration.

The conformation parameter σ and the characteristic ratio C_∞ were calculated from the A values in the conventional manner, and are given in Tables V and VI. $A = 1.33 \times 10^{-8}$ cm, $\sigma = 2.29$, and $C_\infty = 10.7$ were obtained as the most probable values for CA ($DS = 0.49$) in DMAc. The σ value obtained here for CA ($DS = 0.49$) in DMAc is the minimum of these values in 25 systems of cellulose, amylose and their derivatives in solvents,[5,6,15] and is not so different from those of the vinyl-type polymers.

The unperturbed-chain dimension A depends on the dielectric constant of the solvent as is evident for CA in Figure 12. This dependence is less remarkable for CA ($DS = 2.92$), probably due to its less polar character. It is interesting that the A value, extrapolated by $\varepsilon = 1$, is larger for larger DS.

The effect of the degree of substitution on A and σ for CA in DMAc is demonstrated in Figure 13. The cellulose chain becomes the most rigid at a certain specific degree of substitution ($DS = 2$—2.5). In other words, CA ($DS = 0.49$) is more flexible, as opposed to our preliminary prediction, than CA ($DS = 2.46$) at least in DMAc.

REFERENCES

1. G. P. Pearson and W. R. Moore, *Polymer*, **1**, 144 (1960).
2. G. V. Schulz and E. Penzel, *Makromol. Chem.*, **112**, 260 (1968).
3. E. Penzel and G. V. Schulz, *Makromol. Chem.*, **113**, 64 (1968).
4. E. Penzil and G. V. Schulz, *Makromol. Chem.*, **162**, 269 (1972).
5. K. Kamide, T. Terakawa, and Y. Miyazaki, *Polym. J.*, **11**, 285 (1979).

Figure 12. Dependence of the unperturbed chain dimensions A of cellulose acetate on the dielectric constant ε of the solvents: ○, CA ($DS = 0.49$) (this work); △, CA ($DS = 2.46$)[5]; □, CA ($DS = 2.92$).[6]

Figure 13. Effect of degree of substitution (DS) on the unperturbed chain dimension A, conformation parameter σ of cellulose acetate in DMAc at 25°C.

6. K. Kamide, Y. Miyazaki, and T. Abe, *Polym. J.*, **11**, 523 (1979).
7. S. Ishida, H. Komatsu, T. Terakawa, Y. Miyazaki, and K. Kamide, *Mem. Fac. Eng. Kanazawa Univ.*, **12**, 103 (1979).
8. K. Kamide, Y. Miyazaki, and T. Abe, *Makromol. Chem.*, **180**, 2801 (1979).
9. K. Kamide and K. Okajima, *Polym. J.*, **13**, 127 (1981).
10. B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).
11. B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
12. C. H. Malm, C. R. Tordyce, and H. A. Tanner, *Ind. Eng. Chem.*, **34**, 430 (1942).
13. J. A. Dean, Ed., "Lange's Handbook of Chemistry," twelfth ed, **10**, McGraw-Hill, New York, N.Y., 1979, p 103.
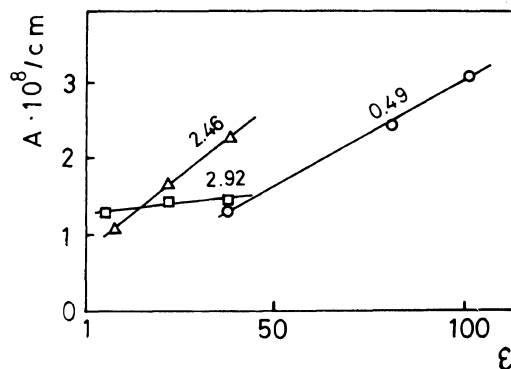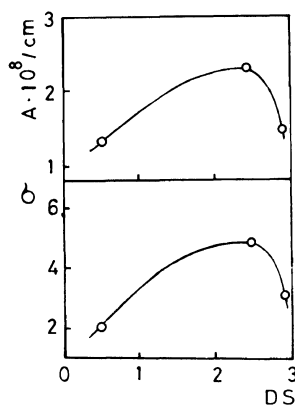14. K. Kamide, K. Okajima, and M. Saito, *Polym. J.*, **13**, 115 (1981).

15. K. Kamide and Y. Miyazaki, *Polym. J.*, **10**, 409 (1978).
16. M. Kurata and H. Yamakawa, *J. Chem. Phys.*, **29**, 311 (1958).
17. H. Baumann, *J. Polym. Sci., C,* **No. 3,** 1069 (1965).
18. W. H. Stockmayer and M. Fixman, *J. Polym. Sci., C,* **No. 1**, 137 (1963).
19. T. Kawai and K. Kamide, *J. Polym. Sci.,* **No. 54,** 343 (1961).
20. K. Kamide and T. Kawai, *Kobunshi Kagaku,* **19**, 441 (1962).
21. K. Kamide and T. Kawai, *Kobunshi Kagaku,* **20**, 512 (1963).
22. K. Kamide and W. R. Moore, *Kobunshi Kagaku,* **21**, 682 (1964).
23. K. Kamide and W. R. Moore, *J. Polym. Sci., B,* **2**, 1029 (1964).
24. K. Kamide, Y. Inamoto, and G. Livingstone, *Kobunshi Kagaku,* **23**, 1 (1966).