Temperature Dependence of Limiting Viscosity Number and Radius of Gyration for Cellulose Dissolved in Aqueous 8% Sodium Hydroxide Solution

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ABSTRACT: A regenerated cellulose with a weight-average molecular weight $\bar{M}_w$ of 8.0×10^4 was dissolved in 8 wt% aq sodium hydroxide (NaOH) solution under adequately chosen conditions. The solution viscosity and light scattering measurements were carried out over a wide range of temperature T ranging 0.6 to 46°C and 3.5 to 45°C, respectively. The apparent $\bar{M}_w$ of the sample, determined by the light scattering in aq NaOH, remained practically constant (7.9×10^4) at $10 \leq T \leq 45°C$, being in good agreement with the true $\bar{M}_w$ (8.0×10^4), evaluated by the light scattering method in cadoxen. This means that cellulose dissolves molecularly in 8 wt% aq NaOH. This solution was found to be a Flory theta solvent at about 40°C, at which the second virial coefficient A_2 vanishes. The Flory viscosity parameter Φ was *ca.* 1/5 the theoretical value (2.87×10^{23}) of the unperturbed undraining chain, indicating that cellulose is a partially free draining chain when dissolved in aq NaOH. The unperturbed chain dimension A decreased with T. The flexibility of the cellulose chain in aq NaOH lies between those in cadoxen and iron sodium tartarate and all of them are classified as semi-flexible. The negative temperature dependence of the limiting viscosity number $[\eta]$ was explained as mainly due to a large negative $\partial A / \partial T$.

KEY WORDS Cellulose / Aqueous Alkali Solution / Light Scattering / Viscosity / Temperature Dependence / Unperturbed Chain Dimension / Flory's Theta Temperature /

Recently Kamide and his collaborators[1-3] analysed in a very systematic manner the experimental data of solution viscosity, light scattering, sedimentation and diffusion for cellulose and its derivative (CD) solutions, concluding for the molecular properties of these polymers that the excluded volume effect is extremely small and the unperturbed chain dimension A varies depending on the polarity of the solvent, but in common solvents cellulose chain behaves semiflexibly. However, as far as CD solutions are concerned, the above conclusions were derived at a constant temperature, near room temperature and only fragmental knowledge of the temperature dependence of the molecular characteristics is obtained up to now. For example only a few theta solvents were determined for CD as the solvent, in which A_2 becomes zero; cellulose tricarbanirate (CTC)–anisole ($\Theta = 94°C$),[4] CTC–hexanol (73°C), and cellulose diacetate (CDA)–2-butanone (50°C).[5,6] Another example is two conflicting molecular explanations for a significantly negative temperature coefficient of the limiting viscosity number of CD solutions around room temperature.[7-21] Suzuki *et al.*[21] determined directly by experiments the temperature dependences of $[\eta]$, z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ and A_2 for CDA-acetone system, concluding that the temperature coefficient of A is a predominant factor controlling $d[\eta]/dT$ (T, temperature).

Whether their conclusion for a specific CD solution can be applicable to other CD systems or not remains unsolved.

There are very few solvents suitable for molecular characterization of cellulose and then, studies on cellulose dilute solutions have been carried out at constant temperature only in cadoxen[16,22] and iron sodium tartarate (FeTNa).[23] After finding the experimental fact that cellulose can be dissolved molecularly in aq lithium hydroxide[24] (LiOH) and NaOH[25] at around 4°C when cellulose has a proper supermolecular structure and an adequate dissolving procedure is employed, we[24] investigated the dilute solution properties of a cellulose–6 wt% aq LiOH solution system by viscometry and the light scattering method. In that study, a significant negative coefficient of $[\eta]$, $d\ln[\eta]/dT < 0$, for the above system was also observed over the temperature range -5—$45°C$ as was the case of numerous CD solutions.

This article investigates the dilute solution properties, including $[\eta]$, $\langle S^2\rangle_z^{1/2}$, A_2 and the weight-average molecular weight $\bar{M}_w$, of cellulose–8 wt% aq NaOH solution as function of temperature over a range of ca. 0—45°C.

EXPERIMENTAL

Preparation of Cellulose Sample and Its Solutions

The regenerated cellulose sample used in a previous paper[24] (sample code SA3, $\bar{M}_w = 8.0 \times 10^4$) was utilized for in this study. One gram of sample was dried at room temperature in vacuo for one day and immersed in 10 gram of water, stood at a temperature below $-10°C$ for one day to freeze the water. Then, the above mixture solid was defreezed and the cellulose suspended in water was obtained. This pretreatment which promotes the swelling of cellulose was very helpful to make a gel free cellulose solution. On the other hand, 15.92 gram of NaOH (guaranteed reagent) were mixed with 173.08 gram of distilled water to

give aq NaOH solution, maintained at $-6°C$, to which the cellulose–water suspension was added carefully. The mixture was agitated mechanically for 5 min and finally a clear and transparent 0.5 wt% ($5.45 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$) cellulose solution in 8 wt% aq NaOH solution was prepared. The solution was filtered through a sintered glass filter (grade 1) and used for the viscosity and light scattering measurements.

Solution Viscosity

The filtered cellulose solution was diluted with 8.04 wt% aq NaOH solution to give four solutions with different cellulose concentrations.

Solution viscosity was measured in a modified Ubbelohde suspension type viscometer at temperature ranging from 0.6—46°C. The temperature was controlled to $\pm 0.01°C$. $[\eta]$ was determined using a Huggins plot.

Light Scattering

The refractive index of 8% aq NaOH solution n_0 was determined on a Hitachi refractometer PRA-B with an unpolarized light of wave length 633 nm at temperatures from 3.5 to 45°C. For the same reason as described in the previous paper[24] for cellulose–6 wt% aq LiOH solution, the specific refractive index increment under constant chemical potential μ of NaOH in the solutions $(\partial n/\partial c)_\mu$ (c, concentration of polymer, $\mathrm{g\,cm^{-3}}$) could not be evaluated. Then, $(\partial n/\partial c)$ at constant NaOH fraction in aq NaOH, designated as $(\partial n/\partial c)_{\phi N}$, was determined by a Shimadzu differential refractometer type DR-4 with an incident light of wave length λ_0 of 633 nm at temperatures in the range 10—45°C.

Eight % aq NaOH solution (simply referred to as aq NaOH) was filtered through a poly(tetrafluoroethylene) (PTFE) membrane FP series (pore diameter 0.1 μm), manufactured by Sumitomo Denko Co. (Osaka) in a circulating filtration apparatus for 24 h and filtered three times through a PTFE membrane

FP series (pore diameter 0.1 μm) installed in a Millipore pressure holder under atomospheric pressure.

The cellulose solution with $c = 0.545$ g cm^{-3} was centrifuged at 1×10^5 g for 60 minutes at 10°C in a Hitachi model 55p-7 automatic preparative ultracentrifuge. The upper two-thirds of the supernatant phase were carefully sucked up with a microsyringe and filtered through a PTFE membrane (pore diameter 0.45 μm) installed in a Millipore pressure holder. Then the aq NaOH, purified as described before, was added to give cellulose solutions of five different cellulose concentrations. Each solution was filtered under atmospheric pressure at 20—27°C through PTFE membranes (pore diameter 0.1, 0.22, 0.3, 0.45 μm) and the last filtrate was directly transferred a cylindrical light scattering cell, which was then sealed with Parafilm "M" (manufactured by American Can Co. (U.S.A.)) in order to avoid absorption of carbondioxide from the air. The light scattering measurements for each solution were carried out successively at six different temperatures of 3.5, 10, 26, 35, 41, and 45°C (controlled to ± 0.1°C). After the experiments at a given temperature and when measurements had to be intercepted temporarily, the solution was once cooled to 4°C and stocked. In order to avoid gelation, all measurements were designed in the direction of rising temperature. A light scattering apparutus, DLS-700 manufactured by Otsuka Electronics (Osaka), was utilized with an incident light (vertically polarized light) of $\lambda_0 = 633$ nm. The calibration of the apparatus was done with the literature value[26] (1.184×10^{-6} cm^{-1}) of reduced Rayleigh ratio of benzene. The following operating conditions were employed: Gate time 160 second, accumulation 100 times, the measuring angle 20—150° (10° each). The data were analyzed according to Zimm's procedure to evaluate apparent $\bar{M}_w^*$, $\langle S^2 \rangle_z^{1/2}$ and the apparent second virial coefficient A_2^*.

RESULTS AND DISCUSSION

Figure 1 shows the plots of η_{sp}/c (η_{sp}, specific viscosity) against c for a cellulose sample code SA3–8 wt% NaOH solution over a wide temperature range. At each temperature the plot can be accurately represented by a straight line. $[\eta]$, evaluated by extrapolating η_{sp}/c to $c = 0$, and Huggins coefficient k', determined from
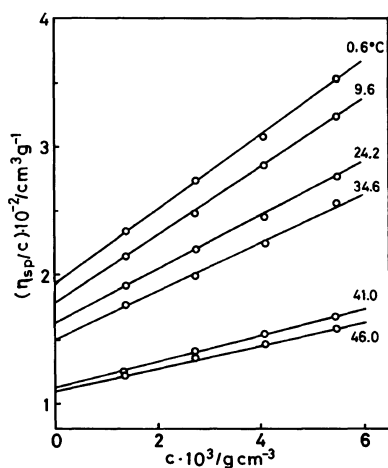

Figure 1. Plots of the ratio η_{sp}/c (η_{sp}, specific viscosity; c, concentration) against c at various temperatures ranging from 0.6 to 46°C.
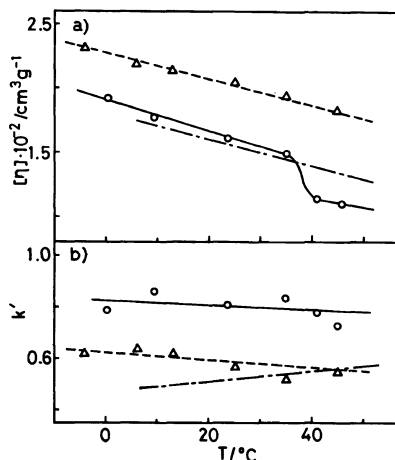

Figure 2. Plots of limiting viscosity number $[\eta]$ (a) and Huggins' constant k' (b) against temperature T. ○, cellulose–8% NaOH aq solution (solid line) (this work); △, cellulose–6% LiOH aq solution[24] (broken line); chain line, cellulose diacetate–acetone system.[21]

the slope of the plot, are plotted as a function of temperature in Figure 2. Here, in the figure, the literature data on cellulose (sample code SA3)–6 wt% aq LiOH solution[24] (triangle) and CDA ($\bar{M}_w = 9.4 \times 10^4$)–acetone[21] (chain line) systems are included for comparison. Inspection of Figure 2 leads to the conclusion that [η] of cellulose–8 wt% aq NaOH is smaller than that of cellulose–6 wt % aq LiOH at least in the range 0.6—46.0°C. In the range of temperature below 35°C, [η] in aq NaOH decreases linearly with an increase in temperature as in the case of cellulose aq LiOH and CDA–acetone systems. d[η]/dT was found to be $-1.2\,\text{cm}^3\text{g}^{-1}\text{K}^{-1}$ for aq NaOH, of which the absolute magnitude was slightly larger than that for aq LiOH ($-1.02\,\text{cm}^3\text{g}^{-1}\text{K}^{-1}$) and CDA–acetone ($-1.01\,\text{cm}^3\text{g}^{-1}\text{K}^{-1}$). [$\eta$] in aq NaOH decreased drastically in the range 35—41°C, suggesting that a certain conformational change of cellulose chain might occur in this narrow temperature range. Similar change in [η] was observed in the region of helix–coil transition of the poly(γ-benzyl L-glutamate)–dichloroacetic acid–ethylene dichloride system.[27] Huggins coefficients in aq NaOH and aq LiOH are about 0.8 and 0.6, respectively, being not so sensitive to the temperature, slightly decreasing with increaseing temperature, whereas the CDA–acetone system exhibited a positive temperature dependence of k'.

Figures 3a and 3b show the temperature dependences of n_0 and $(\partial n/\partial c)_{\phi N}$ of cellulose in aq NaOH. n_0 and $(\partial n/\partial c)_{\phi N}$ can be empirically represented by eq 1 and 2, respectively.

$$n_0 = 1.3535 - 2.17 \times 10^{-4}\ (T\text{-}25) \quad (1)$$

$$(\partial n/\partial c)_{\phi N} = 0.154 - 3.0 \times 10^{-4}\ (T\text{-}25)\ (\text{cm}^3\text{g}^{-1}) \quad (2)$$

Here T is expressed by the °C unit. The value of $(\partial n/\partial c)_{\phi N}$ at 25°C (0.154) is *ca.* 13% larger than that for the undialyzed cellulose (SA3)–6 wt% aq LiOH solution system[24] ($(\partial n/\partial c)_{\phi L} = 0.134$) at the same temperature. The CDA–
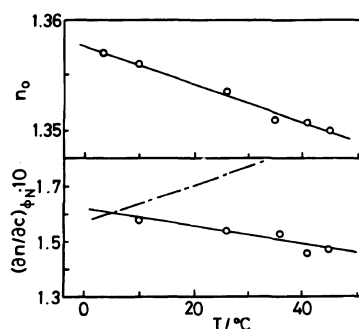

Figure 3. Refractive index n_0 of 8% NaOH aq solution (a) and refractive index increment $\partial n/\partial c$ of cellulose–8% NaOH aq solution (circle and solid line) and cellulose diacetate–acetone system[21] (broken line) (b) as a function of temperature T.
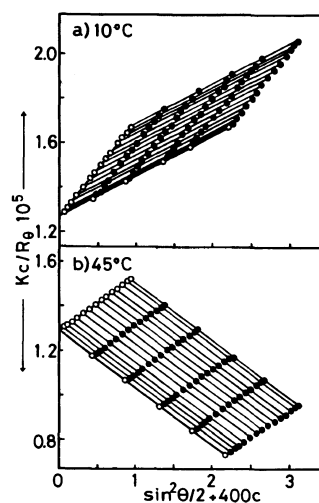

Figure 4. Zimm plots of cellulose–8% NaOH aq solution system at temperature of 10°C (a) and 45°C (b). ●, experimental data; ○, extrapolated value from the experimental data at scattering angle $\theta = 0$ and a concentration $C = 0$.

acetone system has a positive temperature dependence of $(\partial n/\partial c)$,[21] whereas cellulose–aq NaOH system shows a negative temperature coefficient of $(\partial n/\partial c)_{\phi N}$.

Figures 4a and 4b show some typical Zimm plots of the cellulose sample code SA3 in aq NaOH. At any temperature of measurements ranging 3.5—45°C, no significant distortion was observed in the Zimm plots. This means that the solutions prepared in this study

Table I. Results of light scattering measurements on cellulose-8% NaOH aq solution and hydro- and thermo-dynamic parameters in 8% NaOH aq solution at temperatures ranging from 3.5 to 45°C

| Temp °C | Light scattering | | | | | | | Hydro-, thermo-dynamic parameters | |
| | 8% NaOH aq solution | | | 6% LiOH aq solution[a] | | | Cadoxen[a] | 8% NaOH aq solution | |
	$\bar{M}_w{}^*$ $\times 10^{-4}$	$\langle S^2 \rangle_z^{1/2\,b}$ $\times 10^6$	$A_2{}^{*c}$ $\times 10^4$	$\bar{M}_w{}^*$ $\times 10^{-4}$	$\langle S^2 \rangle_z^{1/2}$ $\times 10^6$	$A_2{}^*$ $\times 10^4$	$\bar{M}_w$ $\times 10^{-4}$	Φ $\times 10^{-22}$	α_s
3.5	8.10	3.66	4.79 (4.91)[d]	—	—	—	—	4.14	1.005
10	7.89	3.61	3.75	—	—	—	—	3.95	1.004
25	—	—	—	12.1	3.25	11.0	(8.0)[e]	—	—
26	7.89	3.14	3.33	—	—	—	—	5.46	1.006
35	7.98	3.01	2.75	—	—	—	—	5.55	1.005
41	7.98	2.69	−0.58	—	—	—	—	6.10	0.999
45	7.81	2.64	−3.06	—	—	—	—	6.28	0.992

[a] Reference 24. [b] cm. [c] $cm^3 mol g^{-1}$, $A_2{}^* \simeq A_2$, except 3.5°C. [d] True A_2.
[e] Estimated value using light scattering data on two dialysed cellulose–cadoxen solutions.

had no undissolved material or gel over a wide range of measuring temperature.

Table I summarizes $\bar{M}_w{}^*$, $\langle S^2 \rangle_z^{1/2}$ and $A_2{}^*$ of cellulose in aq NaOH, all evaluated from the Zimm plots. Here, the above quantities at 3.5°C were determined using the value of $(\partial n/\partial c)_{\phi N}$ calculated by eq 2.

Figure 5a shows the temperature dependence of $\bar{M}_w{}^*$. Evidently, $\bar{M}_w{}^*$ of cellulose dissolved in aq NaOH remains almost constant ($\sim 7.9 \times 10^4$) above 10°C. $\bar{M}_w{}^*$ of the same sample in aq LiOH (undialyzed) at 25°C was 1.2×10^5 [24] and is shown as the filled circle in the figure. This value is 1.5 times larger than that in aq NaOH. $\bar{M}_w$ for cellulose (SA3) in cadoxen (8×10^4), indirectly evaluated by linear interpolation of two $\bar{M}_w$ data directly determined by the light scattering method for two other samples in dialyzed cadoxen,[24] is in fairly good agreement with $\bar{M}_w{}^*$ in aq NaOH. Then, we can consider $\bar{M}_w{}^* \simeq \bar{M}_w$ in aq NaOH. In other words, the selective adsorption does not occur essentially above 10°C for cellulose–aq NaOH system, but this can never be ignored for cellulose–aq LiOH system. We can also conclude that cellulose dissolves molecularly into aq NaOH, at least over a tem-
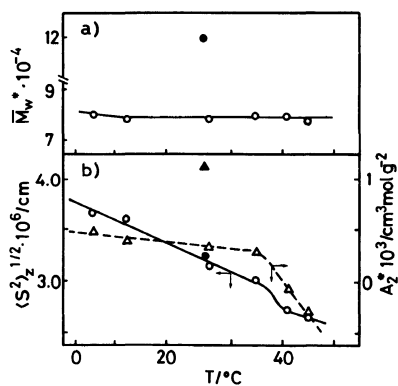

Figure 5. Plots of apparent weight-average molecular weight $\bar{M}_w{}^*$ (a) and apparent second virial coefficient $A_2{}^*$ and z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$ (b) against temperature T. Open marks, cellulose–8% NaOH aq solution and closed marks, cellulose–6% LiOH aq solution system.[24]

perature range of 10—45°C and the discussion on "solubility" of cellulose in aq NaOH by Kamide et al.[25] is absolutely acceptable.

Now we can evaluate a parameter representing selective adsorption, Γ, quantitatively from the equation[28]

$$\Gamma = \{\bar{M}_w{}^*/\bar{M}_w)^{1/2} - 1\}d_N(\partial n/\partial c)_{\phi N}/(\partial n_0/\partial \phi_N)$$

(3)

1177

to be 0.007 at 3.5°C, where d_N is the density of 8 wt% aq NaOH solution (ca. 1.09) and $\partial n_0/\partial \phi_N$ is an increment of refractive index of aq NaOH (0.31 cm^{3}g^{-1} at 3.5°C near 8 wt% NaOH concentration). Γ of cellulose in aq NaOH is almost 10% of those of cellulose in aq LiOH at 25°C[29] (i.e., $\Gamma = 0.095$ for $\bar{M}_w = 5.26 \times 10^4$ and 0.126 for $\bar{M}_w = 1.2 \times 10^5$).

Figure 5b shows the temperature dependence of A_2^* (unfilled triangle) and $\langle S^2 \rangle_z^{1/2}$ (unfilled circle) of cellulose in aq NaOH.

The true second virial coefficient A_2 can be calculated from A_2^* by[28]

$$A_2 = (\bar{M}_w^*/\bar{M}_w)A_2^* \qquad (4)$$

Using eq 4 $A_2 = 4.91 \times 10^{-4}$ cm^{3}molg^{-1} was obtained at 3.5°C and is shown in parenthesis in the fourth column of Table I. Of course, at the temperature equal to or above 10°C, A_2^* can be regarded as A_2, because $\bar{M}_w^* \simeq \bar{M}_w$ holds. For comparison, the A_2 data on cellulose (sample code SA3)–aq LiOH at 25°C are shown. The cellulose–aq NaOH system has a remarkably smaller A_2 than the cellulose–aq LiOH system, suggesting that aq NaOH is poor compared with aq LiOH. The temperature dependence of A_2 for cellulose–aq NaOH system can be approximately represented by two straight lines; with an increase in the temperature below 35°C, A_2 decreases slowly, but above 35°C A_2 decreases remarkably, becoming zero at $T \simeq 40$°C. In other words, the 8 wt% aq NaOH system is a Flory theta solvent found for cellulose. $\langle S^2 \rangle_z^{1/2}$ decreases also with an increase in temperature. A decrease in $\langle S^2 \rangle_z^{1/2}$ with temperature is significantly larger in the range $35 \sim 41$°C than those in other temperature ranges (i.e., $5 \leq T \leq 35$°C and $T \geq 41$°C). The value of $\langle S^2 \rangle_z^{1/2}$ of the cellulose (SA3)–aq NaOH system at 26°C is about 4% smaller than that of the same sample (SA3)– aq LiOH system at 25°C. $\langle S^2 \rangle_z^{1/2}$ of cellulose– aq NaOH at 40°C (i.e., the unperturbed z-average radius of gyration, $\langle S^2 \rangle_{z,o}^{1/2}$) was estimated, from Figure 5b, to be 2.77×10^{-6} cm.

Flory viscosity parameter Φ is defined by
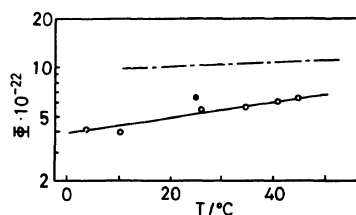

Figure 6. Plots of Flory's viscosity parameter Φ against temperature T. $\bigcirc$ and solid line, cellulose–8% NaOH aq solution; $\bullet$, cellulose–6% LiOH aq solution[24] and chain line; cellulose diacetate–acetone system.[21]

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

Here, $q_{w,z}$ is the polymolecularity correction factor, prerequisiting the molecular weight distribution (MWD) function and breadth of MWD of the sample. The literature data[16,22] suggest that when the acid-hydrolysis of cellulose proceeds to a greater extent, the products have $\bar{M}_w/\bar{M}_n = 2$. Then, in this study we estimated $q_{w,z}$ (= 1.955) assuming the Schulz-Zimm distribution for MWD of sample code SA3 and 2 for its $\bar{M}_w/\bar{M}_n$. In the ninth column of Table I, the values of Φ calculated by eq 5 from $[\eta]$, $\langle S^2 \rangle_z^{1/2}$ and $\bar{M}_w$ data are summarized. Figure 6 shows the plot of Φ vs. temperature. In the figure, the data point for cellulose– aq LiOH is included. The Φ value for cellulose–aq NaOH, including the value at 40°C (theta solvent), is slightly smaller than that for cellulose–aq LiOH and is only 1/5 the theoretical value for the unperturbed non-draining chain (2.87×10^{23}). This means that the cellulose chain is partially free draining in aq NaOH, as in the case of cellulose in aq LiOH[24] and various cellulose derivatives in solvents.[1,30,35] Φ for cellulose–aq NaOH increases monotonically with temperature as found for CDA–acetone system. $d \ln \Phi/d T$ was found to be 1.0×10^{-2} deg^{-1} for cellulose– aq LiOH,[24] which is 3.5 times larger than that $(2.8 \times 10^{-3}$ deg$^{-1})$ for CDA–acetone.[21]

The penetration function ψ is defined by[31]

$$\psi \equiv \bar{z}h_0(\bar{z}) = 7.45 \times 10^{-26}A_2\bar{M}_w^2/\langle S^2 \rangle_w^{1/2} \qquad (6)$$

$$\text{with} \quad \bar{z} = z/\alpha_s^3 \qquad (7)$$

z is the excluded volume effect parameter and α_s ($\equiv \langle S^2 \rangle_w^{1/2} \langle S^2 \rangle_{w,o}^{1/2}$; subscripts w and o denote the weight average and unperturbed state, respectively) is the linear expansion factor. According to the theory of Kurata–Fukatsu–Sotobayashi–Yamakawa,[32] $\bar{z}h_0$ ($\bar{z}$) in eq 6 is a function of $\bar{z}$, given by

$$\bar{z}h_0(\bar{z}) = (1/5.047)\{1 - (1 + 0.683\bar{z})^{-7.39}\} \quad (8)$$

In the vicinity of $z \simeq 0$, the following relation holds between z and α_s[33]

$$\alpha_s^3 = 1 + 1.78z \quad (9)$$

Combining eq 6—9 enables us to estimate α_s, when α_s is not far from unity, using the light scattering data. The tenth column of Table I lists the α_s values determined thus. Here, $\langle S^2 \rangle_z^{1/2}$ was converted to $\langle S^2 \rangle_w^{1/2}$, assuming the Schulz–Zimm distribution and $\bar{M}_w/\bar{M}_w = 2$. α_s of cellulose in aq NaOH solution below 35°C lies between 1.00 and 1.01 almost independent of temperature. We can conclude that the excluded volume effect is extremely small in the cellulose–aq NaOH system even below 35°C.

The unperturbed chain dimension A is generally given by

$$A = (6 \langle S^2 \rangle_{o,w}/\bar{M}_w)^{1/2} \quad (10)$$

Equation 10 is valid only when the unperturbed chain is Gaussian and is only approximately valid when the unperturbed chain is not Gaussian, but the extent of departure from the Gaussian nature is not remarkable. Although, in the strict sense, the Gaussian nature of cellulose dissolved in aq NaOH solution has not been experimentally confirmed yet, it is well-known that the cellulose chain behaves as a Gaussian chain in cellulose–aq LiOH systems and we can apply eq 10 for cellulose in aq NaOH solution. Here, $\langle S^2 \rangle_{o,w}$ was evaluated from $\langle S^2 \rangle_z$ and α_s (method 2B[1]). Table II summarizes the A values estimated thus at 25°C together with the literature data for cellulose in aq LiOH,[24] cadoxen[16] and FeTNa.[23]

Table II. · Unperturbed chain dimension A estimated using method 2B[1], conformation parameter σ, and characteristic ratio C_∞ of cellulose in various solvents at 25°C

| Solvent | A | σ | C_∞ |
	$\times 10^8$/cm		$\times 10^{-1}$
8% NaOH aq solution	2.2	3.6	3.14
6% LiOH aq solution[a]	2.2	3.6	2.97
Cadoxen	1.9[b]	3.1[b]	—
FeTNa[c]	2.7[d]	4.4[d]	—

[a] Reference 24.
[b] Value at $\bar{M}_w = 8 \times 10^4$ estimated using the data in ref 16.
[c] Iron sodium tartarate.
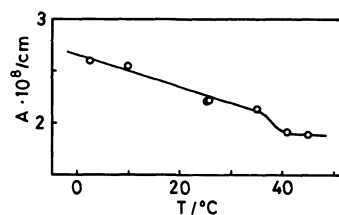[d] Value at $\bar{M}_w = 8 \times 10^4$ estimated using the data in ref 23.

Figure 7. Plots of unperturbed chain dimension A of cellulose aq alkaline solvents against temperature T. ○ and solid line, 8% NaOH aq solution; ●, 6% LiOH aq solution.[24]

Figure 7 shows the temperature dependence of A. The temperature dependence of A is almost the same as that of $\langle S^2 \rangle_z^{1/2}$ below 35°C, becuase α_s is practically independent of the temperature. In the figure, the value of A for cellulose in aq LiOH at 25°C is shown by the filled circle. A in aq NaOH is nearly the same as that in aq LiOH.

In Table II are shown the conformation parameter σ ($\equiv A/A_f$, A_f is A of hypothetical free rotating chain) and the characteristic ratio C_∞ ($\equiv A_\infty^2 M_b/l^2$, A_∞ is A for $M = \infty$, M_b, the molecular weight per skeletal bond, l, the mean bond length). The flexibility of cellulose chain in aq alkali solutions lies between those in cadoxen and iron sodium tartarate. Comparing the values of σ for cellulose in

1179

these solvents with those of typical flexible polymers,[1] we can conclude that the cellulose chain dissolved in any solvent belongs to a category of semi-flexible chains.

$[\eta]$ can be represented in the form[34]

$$[\eta] = 6^{3/2}\Phi(\langle S^2\rangle_{o,w}^{3/2}/\bar{M}_w)\alpha_s^3 \quad (11)$$

Equation 11 can be readily transformed by differentiating the logarithm of the both side of the equation into

$$d\ln[\eta]/dT = d\ln\Phi/dT$$
$$+ 1.5\,d\ln(\langle S^2\rangle_{o,w}/\bar{M}_w)/dT$$
$$+ 3\,d\ln\alpha_s/dT \quad (12)$$

Each term in the right hand side of eq 12 can be estimated for cellulose–aq NaOH below 35°C

$$d\ln[\eta]/dT = -7.42\times10^{-3} \quad (13)$$

$$d\ln\Phi/dT = 1.0\times10^{-2} \quad (14)$$

$$d\ln(\langle S^2\rangle_{o,w}/\bar{M}_w)dT = -1.26\times10^{-2} \quad (15)$$

$$d\ln\alpha_s/dT \simeq 0 \quad (16)$$

Putting the values in eq 14—16 into the right hand side of eq 12, we obtain -8.90×10^{-3}, which agrees fairly well with the experimental $d\ln[\eta]/dT$ value ($= -7.42\times10^{-3}$). Inspection of eq 14—16 shows that the temperature dependence of the unperturbed chain dimension is a main factor governing the negative temperature coefficient of $[\eta]$ for cellulose–aq NaOH, as was found by Suzuki et al.[21] for the CDA–acetone system.

The remarkable decrease in $[\eta]$ at the temperature range of 35—41°C can also be explained by the large negative temperature dependence of the unperturbed chain dimensions. Kamide and Saito[35] indicated that there exists a strong correlationship between the number of solvent molecules solvated per a pyranose ring at infinite dilution s_0 and A for the CDA–acetone system and the solvation makes the cellulose chain rigid. The negative temperature dependence of A, observed also

for cellulose–aq NaOH system, can be speculated to be due to the negative temperature dependence of the solvation.

The conclusions reached in the previous paper[24] for cellulose–aq LiOH have not changed for cellulose–aq NaOH systems:

(1) Cellulose dissolves molecularly in aq NaOH

(2) Cellulose is semi-flexible in aq NaOH

(3) The excluded volume effect is small or zero (at 40°C)

(4) Partially free drainage effect is not negligibly small.

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