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NEW VISCOSITY METHOD FOR ESTIMATING UNPERTURBED CHAIN DIMENSIONS OF MACROMOLECULES WHEN DRAINING EFFECT AND/OR NON-GAUSSIAN NATURE IN THE UNPERTURBED STATE ARE NOT NEGLIGIBLE

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Abstract—An attempt has been made to establish a new method for estimating the unperturbed chain dimensions of macromolecules when the partially free draining effect and/or the non-gaussian nature in the unperturbed state are not negligible, using the Mark–Houwink–Sakurada (MHS) equation. For this purpose, a previous treatment was generalized and an equation was derived. This method was applied to cellulose and amylose derivatives; the results agreed well with those estimated by thermodynamic and other hydrodynamic approaches.

INTRODUCTION

The unperturbed chain dimensions A of macromolecules are one of the most important factors characterizing the intrinsic feature of a chain and are defined by Eqn (1).

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

where $\langle R^2\rangle_0$ is the mean-square end-to-end distance of the chain at an unperturbed state and M is the molecular weight. The A value can be directly determined by light scattering measurements on polymer in a θ solvent. Unfortunately, theta solvents have not been discovered for all polymeric materials and, for a polar polymer in a polar solvent, there is a possibility of a significant variation in A value with the solvent nature. For these reasons, numerous treatments have been proposed for estimation of the unperturbed chain dimensions by analysing the dilute solution properties (e.g. the limiting viscosity number $[\eta]$ and the radius of gyration $\langle S^2\rangle^{1/2}$) in non-ideal solvents.

Kamide *et al.* [1-9] have proposed a series of methods for estimating A values by analysing the parameters K_m and a in the semi-empirical MHS equation:

$$[\eta] = K_m \mathrm{M}^a. \tag{2}$$

Here K_m and a are parameters characteristic of the polymer/solvent combination at a given temperature and the molecular weight range M_1–M_2 in which Eqn (2) is valid.

Equation (3) is a typical equation derived by Kamide and Moore [3, 4]

$$\begin{aligned} -\log K_m - \log\{2(1-a)\}& \\ = -\log K + (a - 0.5)\log \mathrm{M}_0& \end{aligned} \tag{3}$$

with

$$K = \Phi_0(X_0)\,A^3. \tag{4}$$

$\Phi_0(X_0)$ is the Flory viscosity parameter in the unperturbed state with the draining parameter $X = X_0$, M_0 is a parameter depending on the molecular weight range, M_1–M_2, and the geometric mean $(\mathrm{M}_1\mathrm{M}_2)^{1/2}$ can be regarded as a good approximation to M_0. The value of X_0 in Eqn (4) is determined by the equation:

$$v(X_0) = \epsilon(3 - n(X_0)) \tag{5}$$

$v(X)$ and $n(X)$ are the function of X given in the Kurata–Yamakawa theory [10] and X_0 can be well approximated to be 50 as shown previously [1]. K, and accordingly A, can be determined from experimental data on K_m, a and M_0. This method has been referred to as method 2F previously [11] and has been extensively confirmed as applicable to various kinds of polymers, especially vinyl-type polymers [3, 12].

Stockmayer and Fixman (SF) have derived the following equation [13]:

$$[\eta]/\mathrm{M}^{1/2} = K + 2(3/2\pi)^{3/2}\,\Phi_0(\infty)\,B\mathrm{M}^{1/2} \tag{6}$$

where $\Phi_0(\infty)$ is Φ_0 at $X = \infty$ ($2.87 \times 10^{23}\,\mathrm{mol}^{-1}$ for $[\eta]$ in units of cm^3/g), B is the long-range interaction parameter. A method based on Eqn (6) for estimating K [accordingly A; in this case, $\Phi_0(\infty)$ is utilized in place of $\Phi_0(X_0)$ in Eqn (4)] is the most popular method for determining A from $[\eta]$ data in a non-ideal solvent, due to its simplicity; this method was designated as method 2E previously [11].

Equation (3) is, in principle, equivalent to Eqn (6) because both are derived from the Flory–Fox type viscosity equation and Fixman type excluded volume theory (Eqn (11) [14]). The method of Kamide *et al.*, as well as the SF method, which assumes non-free draining [a_Φ (in Eqn (8)) = 0] and the gaussian chain in the unperturbed state [a_2 (in Eqn (9)) = 0], are inapplicable to cases where these assumptions are unacceptable [11, 15]. Almost all solutions of cellulose and amylose derivatives are cases where the Flory viscosity parameter Φ exhibits significant molecular weight dependence and sometimes the unperturbed chain is non-gaussian [11, 15–21].

Recently, Kamide and Miyazaki [11] extended Eqn (6) to the case when the draining effect and/or non-gaussian nature at the unperturbed state are not negligible [see Eqn (19)] showing that the estimated A values are in excellent agreement with those found by a thermodynamic approach, based on $\langle S^2\rangle^{1/2}$, for a number of cellulose and amylose derivatives [11, 15–21].

An attempt to generalize Eqn (3) has failed because of low accuracy of estimation of X [11].

This article extends the method of Kamide *et al.* and tests the applicability of the new method to solutions of cellulose and amylose derivatives.

THEORETICAL BACKGROUND

In general, $[\eta]$ can be expressed by the equation [10]:

$$[\eta] = 6^{3/2}(\langle S^2\rangle_0^{3/2}/\mathrm{M})\,\alpha_s^3 \tag{7}$$

where $\langle S^2\rangle_0^{1/2}$ is the radius of gyration in the unperturbed state, Φ is the Flory viscosity parameter, α_s is the dimensionless expansion factor defined as the ratio of $\langle S^2\rangle^{1/2}$ to $\langle S^2\rangle_0^{1/2}$.

Next we consider the case when Φ and $\langle S^2\rangle_0/\mathrm{M}$ show molecular weight dependence of the forms:

$$\Phi = K_\Phi \mathrm{M}^{a_\Phi} \tag{8}$$

$$\langle S^2\rangle_0/\mathrm{M} = K_0\mathrm{M}^{a_2}. \tag{9}$$

Here K_Φ, a_Φ, K_0 and a_2 are empirical parameters for the polymer/solvent combination and the temperature. We assume that Eqns (2), (8) and (9) are applicable over the same molecular weight range M_1–M_2.

Equation (7) can be transformed by using Eqns (8) and (9) into

$$[\eta] = 6^{3/2}K_\Phi K_0\mathrm{M}^{0.5+a_\Phi+1.5a_2}\alpha_s^3 \tag{10}$$

α_s in Eqn (10) can be given by a closed simple form of an excluded volume parameter z [12]:

$$\alpha_s^3 = 1 + 2z \tag{11}$$

with

$$z = (3/2\pi)^{3/2}BA^{-3}\mathrm{M}^{1/2}. \tag{12}$$

Combination of Eqns (2), (10), (11) and (12) yields

$$\{K_m/(6^{3/2}K_\Phi K_0^{3/2})\}\,\mathrm{M}^{a-0.5-a_\Phi-1.5a_2} = 1 + C\mathrm{M}^{(1-3a_2)/2} \tag{13}$$

where

$$C = (1/4\pi)^{3/2}K_0^{-3/2}B. \tag{14}$$

Writing M_0 for M, taking logarithms and differentiating with respect to $\log \mathrm{M}_0$ gives

$$1 + C\mathrm{M}_0^{(1-3a_2)/2} = (1-3a_2)/\{1 - 3a_2 - 2(a - a_\Phi - 1.5a_2 - 0.5)\}. \tag{15}$$

Substitution of Eqn (15) into Eqn (13) and rearrangement give

$$\begin{aligned}-\log K_m &+ \log\{(1-3a_2)/(2(1-a+a_\Phi))\} + 3/2\log 6 + \log K_\Phi = \\ &-3/2\log K_0 + (a - 0.5 - a_\Phi - 1.5a_2)\log \mathrm{M}_0\end{aligned} \tag{16}$$

when $a_2 = 0$, Eqn (16) reduces to Eqn (17).

$$\begin{aligned}-\log K_m &- \log\{2(1-a+a_\Phi)\} + 3/2\log 6 + \log K_\Phi = \\ &-3/2\log K_0 + (a - 0.5 - a_\Phi)\log \mathrm{M}_0.\end{aligned} \tag{17}$$

Putting $a_\Phi = 0$ and $a_2 = 0$ in Eqn (16) reduces to Eqn (3) derived by Kamide and Moore [3, 4].

We can determine K_0 from K_m, a, K_Φ, a_Φ, a_2 and M_0 by using Eqn (16) without the aid of θ solvent measurements. If K_0 does not vary with the solvent nature, the experimental plots of the left-hand side of Eqn (16) as a function of $a - 0.5 - a_\Phi - 1.5a_2$ for the polymer in various solvents should be linear with a slope of $\log \mathrm{M}_0$, yielding $-3/2\log K_0$ as an intercept. We use the description method 2K for this method. From the K_0 value thus obtained, A can be calculated by Eqn (18)

$$A = (6K_0\mathrm{M}^{a_2})^{1/2}. \tag{18}$$

It should be noted that Eqns (17) and (18) are rigorously valid only at $a_2 = 0$ and should be regarded as being approximate if $a_2 \neq 0$.

Similar relations with Eqn (11), in which α_s^3 is a linear function of z, yield the same equation as Eqn (16).

Equation (11), and so Eqn (16) restrict application to a system of comparatively small z region [22]. Fortunately, in solutions of cellulose and amylose derivatives the excluded volume effect is not large.

Method 2K requires a value of a_2, which can only be estimated from the molecular weight dependence of A. Nevertheless, the determination of A is the final purpose of method 2K. This seems self-contradictory. In order to overcome this difficulty, the rough estimate of a_2 can be made by a thermodynamic approach (method 2B in the previous paper [11]) from the experimental $\langle S^2\rangle^{1/2}$ and α_s values estimated with help of the penetration function ψ (defined as $0.746\times 10^{-25}A_2\mathrm{M}_w^2/\langle S^2\rangle_w^{3/2}$) [23]. As will be demonstrated later, the A value estimated by method 2K is rather insensitive to the magnitude of a_2 and in addition, for solutions of cellulose and amylose derivatives a_2 is usually zero or close to it.

Combining Eqn (10) with Eqn (11), Kamide and Miyazaki [11] have derived the equation:

$$[\eta]/\mathrm{M}^{0.5+a_\Phi+1.5a_2} = 6^{3/2}K_\Phi K_0^{3/2} + 0.66\mathrm{K}_\Phi B\mathrm{M}^{(1-3a_2)/2}. \tag{19}$$

Equation (19) is a straightforward generalization of Eqn (6) in the most versatile form. A graph of $[\eta]/\mathrm{M}^{0.5a_\Phi+1.5a_2}$ as a function of $\mathrm{M}^{(1-3a_2)/2}$ (Kamide–Miyazaki (I) plot) should be linear, having $6^{3/2}K_\Phi K_0$ (accordingly, K_0) as the intercept. This method was referred to as method 2G.

An alternative expression of Eqn (16) is

$$\begin{aligned}-\log K_m &+ \log\{(1-3a_2)/2(1-a+\Delta)\} \\ &+ 3/2\log 6 + \log\Phi_0(X_0) + \log f \\ &= -3/2\log K_0 \\ &+ (a - 0.5 - 1.5a_2)\log \mathrm{M}_0\end{aligned} \tag{20}$$

where

$$\Delta = v(X) - v(X_0) \simeq a_\Phi \tag{21}$$

$$f = X\,F_0(X)/X_0F_0(X_0) \tag{22}$$

$\Phi_0(X)$ and $F_0(X)$ are functions of the draining parameter X defined by Kurata and Yamakawa [10]. Then, Eqn (41) in Ref. [11] should be read as Eqn (20).

Method 2K and 2G need not only viscosity data but also some thermodynamic data, for estimation of K_Φ, a_Φ and a_2. Then, these methods are not, in the strict sense, purely hydrodynamic.

Tanner and Berry [24] have derived, by assuming $a_2 = 0$, $a_\Phi \neq 0$, and $\mathrm{d}\ln\alpha_s/\mathrm{d}\ln \mathrm{M}\ (\equiv a_1/3) = 0$, the following equation for polymers having a non-negligible free draining effect in solutions:

$$\mathrm{M}^{1/2}/[\eta] = \{K'(6\langle S^2\rangle/\mathrm{M})^{3/2}\}^{-1}(1 + A'\mathrm{M}^{-1/2}) \tag{23}$$

where K' and A' are parameters depending on the models used. This method has been designated as method 2H [25].

Kamide and Terakawa [25] have pointed out that Eqn (23) is not valid for $a_1 \neq 0$ and $a_\Phi \neq 0$ and, in place of Eqn (23), the equation

$$\mathrm{M}^{a_1+1.5a_2+0.5}/[\eta] = (K'6^{3/2}K_0^{3/2}K_\alpha')^{-1}(1 + A'\mathrm{M}^{-1/2}) \quad (24)$$

should be utilized when $a_1 \neq 0$, $a_\Phi \neq 0$ and $a_2 \neq 0$. Here,

$$K_\alpha = \alpha_s^3/\mathrm{M}^{a_1}. \quad (25)$$

To employ Eqn (24) for estimating K_0 (and so A), K' and K_α' values should be known in advance, as well as a_1 and a_2. The estimation of K_α' is practically impossible for solutions of cellulose derivative due to small α_s value.

The A value obtained by method 2H is approximately the most probable A value $[A_{(m)}]$ only at $a_1 + 1.5a_2 \simeq 0$ as theory predicts [25]. When $a_1 + 1.5a_2 > 0$, the Tanner–Berry (TB) plot (i.e. plot of $\mathrm{M}^{1/2}/[\eta]$ vs $\mathrm{M}^{-1/2}$) overestimates the A value and when $a_1 + 1.5a_2 < 0$, the TB plot underestimates it [25].

The unperturbed chain dimensions A can also be evaluated by using the frictional coefficient ξ as well as $[\eta]$. Kamide and Miyazaki [25] derived, for $a_\Phi \neq 0$ and $a_2 \neq 0$, the equation:

$$\xi/\eta_0 = 6^{1/2}K_\mathrm{p}K_0^{0.5}\mathrm{M}^{0.05+0.5a_2+a_\mathrm{p}} \times (1 + 0.0144\,BK_0^{-1.5}\,\mathrm{M}^{0.5-1.5a_2}) \quad (26)$$

where

$$\mathrm{P} \equiv (\xi/\eta_0)/(6^{1/2}\langle S^2\rangle^{1/2}) = K_\mathrm{p}K^{a_\mathrm{p}}. \quad (27)$$

η_0 is the viscosity of solvent. A graph of $(\xi/\eta_0)/\mathrm{M}^{0.5+0.5a_2+a_\mathrm{p}}$ against $\mathrm{M}^{0.5-1.5a_2}$ (Kamide–Miyazaki (KM) (II) plot), based on Eqn (26), enables $6^{1/2}K_\mathrm{p}K_0^{1/2}$ to be evaluated from the intercept at $\mathrm{M}^{0.5-1.5a_2} = 0$. This method has been referred to as method 2J [26].

When $a_2 = a_\mathrm{p} = 0$, Eqn (26) reduces to

$$\xi/\eta_0 = \mathrm{P}_0(\infty)\,A\,\mathrm{M}^{0.5}(1 + 0.211\mathrm{B}A^{-3}\mathrm{M}^{-0.5} - \ldots) \quad (28)$$

where $\mathrm{P}_0(\infty)$ is P_0 at $X = \infty$. Equation (28) is almost the same as the equation of Cowie and Bywater [27] (CB). The A value can be determined from the plot of $(\xi/\eta_0\mathrm{M}^{0.5})$ vs $\mathrm{M}^{0.5}$ (CB plot) as the ordinate. This method has been referred to as method 2I [26].

In this paper, method 2K is compared with other so-called hydrodynamic approaches: Eqn (3) (method 2F), Eqn (6) (method 2E), Eqn (19) (method 2G), Eqn (23) (method 2H), Eqn (26) (method 2J) and Eqn (28) (method 2I).

In addition to the hydrodynamic approaches, the thermodynamic approaches are employed for the comparison. The basic equations of the latter approaches are as follows:

Method 2B [11]:

$$\langle S^2\rangle_0^{1/2} = \langle S^2\rangle^{1/2}/\alpha_s \quad (29)$$

α_s is estimated through use of the penetration function ψ from the second virial coefficient A_2, M and $\langle S^2\rangle$ data.

Method 2C (Baumann plot [28]):

$$\langle S^2\rangle^{3/2}/\mathrm{M}^{3/2} = A^3/6^{3/2} + (1/4\pi^{3/2})\,B\mathrm{M}^{1/2}. \quad (30)$$

Method 2D (Baumann–Kamide–Miyazaki plot [11]):

$$\langle S^2\rangle^{3/2}/\mathrm{M}^{3(1+a_2)/2} = K_0^{3/2} + (1/(4\pi^{3/2}))\,B\mathrm{M}^{(1-3a_2)/2}. \quad (31)$$

APPLICATION TO EXPERIMENTAL DATA

In order to test the reliability of method 2K, Eqn (16) was applied to experimental data for cellulose,

Table 1. Various parameters employed for evaluation of the unperturbed chain dimensions of cellulose and amylose derivatives

Polymer	Solvent	Sample No.	$\bar{\mathrm{M}}_w/\bar{\mathrm{M}}_n$	K_m	a	$K_\Phi \times 10^{-20}$	a_Φ	a_2	$\mathrm{M}_0 \times 10^{-5}$	Ref.
Cellulose	Cadoxen	6	1.8–2.3	0.0264	0.792	4.55	0.304	−0.216	4.61	11 [28]
	FeTNa	9	2.0	0.0494	0.779	5.01	0.429	−0.296	2.01	11 [29]
Cellulose nitrate (N = 12.9%)	Acetone	4	1.2	0.0048	0.916	29	0.274	0	1.55	11 [30, 31]
Cellulose trinitrate (N = 13.9)	Acetone	6	1.2	0.0076	0.903	6.36	0.379	−0.024		
Cellulose diacetate	Acetone	9	1.2–1.3	0.133	0.616	0.226	0.716	−0.471	1.27	16, 17
(DS = 2.46)	THF	6	1.2–1.3	0.0513	0.688	573	0.105	0	1.49	16, 17
Cellulose triacetate (DS = 2.92)	DMAc	10	1.3–1.5	0.0264	0.750	350	0.106	0	2.09	18
Cellulose	DMF	4	1.03–1.5	0.268	0.495	4.17	0.377	−0.248	2.86	11 [32]
tricaproate	1-Cl-N	4	1.03–1.5	0.159	0.515	4.17	0.377	−0.248	2.86	11 [32]
Cellulose	Acetone	6	1.76–2.4	0.0012	0.912	60.6	0.21	0	8.26	11 [33, 34]
tricarbanilate	Dioxane	4	1.76–2.4	0.0008	0.971	1.52	0.462	0	8.26	11 [33, 34]
Methylcellulose (DS = 2)	Water	5	2.4–2.9	0.473	0.508	2.01	0.464	−0.280	2.64	11 [35]
Hydroxyethyl cellulose (DS = 1)	Water	5	1.5–1.7	0.0074	0.890	0.54	0.608	−0.128	2.23	11 [37]
Ethylhydroxy ethylcellulose (DS = 2)	Water	4	3.07–3.23	0.0406	0.754	0.207	0.688	−0.256	3.02	11 [38]
Sodium cellulose xantate (DS = 0.78)	1 M NaOH	3	1.25	0.0477	0.679	0.088	0.568	−0.24	4.18	11 [39, 40]
Sodium carboxy methyl cellulose (DS = 0.88)	NaCl (I → ∞)	4	2.1–3.7	0.173	0.604	1880	0.192	−0.072	3.95	11 [36]
Sodium cellulose sulphate (DS = 1.9)	0.5 M aq. NaCl	8	3.53–5.27	7.17×10^{-4}	0.931	5.74	0.40	0	3.28	21
Amylose	DMSO	9	1.5	0.0013	0.868	0.018	0.794	−0.336	8.19	11 [41]
Amylose triacetate	Nitromethane	12	1.5	0.0012	0.862	6.75	0.379	0	7.53	11 [42]

Table 2. The unperturbed chain dimensions estimated by various methods for solutions of cellulose derivatives

							$A \times 10^8$ cm				
		Thermodynamic approach					Hydrodynamic approach				
Polymer	Solvent	2B Eqn (29) χ_s from ψ	2C (Baumann) Eqn (30) $a_2 = 0$	2D (BKM)[a] Eqn (31) $a_2 = 0$	2E (SF)[b] Eqn (6) $a_2 = a_\Phi = 0$	2F (Kamide) Eqn (3) $a_2 = a_\Phi = 0$	2G [KM(I)][c] Eqn (19) $a_2 = 0, a_\Phi = 0$	2H (TB)[d] Eqn (23) $a_1 = 0, a_\Phi = 0$	2I (CB)[e] Eqn (28) $a_2 = a_p = 0$	2J [KM(II)][f] Eqn (26) $a_2 = 0, a_p = 0$	2K (KS)[g] Eqn (16) $a_2 = 0, a_\Phi = 0$
Cellulose	Cadoxen	1.53	1.83		1.21	1.20	1.57	2.15	1.43(s_0) 1.18(D_0)	1.92 2.04	1.56
	FeTNa	1.96	2.31	2.27	1.31	1.29	2.17	2.34			2.07
CN (N = 12.9%)	Acetone	1.84	1.84	1.85	0.52	0.74	1.91	3.33			1.96
CN (N = 13.9%)	Acetone	2.41	2.43		0.79	1.02	2.45	3.33			2.50
CA (DS = 2.46)	Acetone	1.68	2.14	1.77	1.10	1.12	1.75	1.45	1.11	1.72	1.76
	THF	1.23	1.24		0.99	1.00	1.23	1.37			1.26
CA (DS = 2.92)	DMAc	1.43	1.49		0.89	1.00	1.47	1.59			1.46
CTC_p	DMF		2.14	1.94	0.96	0.92	1.99	1.03			2.00
	1-Cl-N	1.75	2.14	1.94	0.90	0.85	1.82	0.96			1.80
CTC	Acetone	1.43	1.43		0.56	0.56	1.25	1.99			1.23
	Dioxane	1.88	1.85		0.55	0.47	1.83	2.35			1.82
MC (DS = 0.2)	Water	2.05	2.56	2.34	1.23	1.25	2.31	1.34			2.34
NaCS (DS = 1.9)	0.5 M NaCl	1.20	1.23	1.47	0.46	0.53	1.44	2.37			1.25
NaCMC (DS = 0.88)	NaCl (1 → ∞)	1.42	1.50	1.47	1.26	1.25	1.44	1.55			1.44
HEC (DS = 1)	Water	2.10	2.40	2.25	0.93	0.96	2.26	2.63			2.26
EHEC (DS = 1)	Water	2.10	2.41	2.37	1.24	1.22	2.32	2.06	1.08(s_0) 0.84(D_0)	2.16 2.47	2.40
NaCX	1N NaOH	3.30	4.04	3.86	1.03	1.03	3.96	1.47	0.73	3.63	3.97
Amylose	DMSO	1.48	1.33	1.62	0.60	0.56	1.76	1.52			1.80
ATA	Nitromethane	1.04	1.14		0.55	0.55	1.06	1.29			1.14

[a]Baumann–Kamide–Miyazaki; [b]Stockmayer–Fixman; [c]Kamide–Miyazaki (I); [d]Tanner–Berry; [e]Cowie–Bywater; [f]Kamide–Miyazaki (II); [g]Kamide–Saitoh.

amylose and their derivatives as follows: cellulose/cadoxen [29], cellulose/iron sodium tartrate (FeTNa) [30], cellulose nitrate (CN)/acetone [31, 32], cellulose trinitrate (CTN)/acetone [31, 32], cellulose diacetate (CDA)/acetone [17], CDA/tetrahydrofuran (THF) [17], cellulose triacetate (CTA)/dimethylacetamide (DMAc) [18], cellulose tricaproate (CTC_p)/dimethylformamide (DMF) [33], CTCp/1-chloronaphthalene (1-Cl-N) [33], cellulose tricarbanilate (CTC)/acetone [34, 35], CTC/dioxane [34, 35], methylcellulose (MC)/water [36], sodium carboxymethylcellulose (NaCMC)/aq. NaCl [37], sodium cellulose sulphate (NaCS)/0.5 aq. NaCl [21], hydroxyethyl cellulose (HEC)/water [38], ethyl hydroxyethyl cellulose (EHEC)/water [39], sodium cellulose xanthate (NaCX)/1M NaOH [40, 41], amylose/dimethylsulphoxide (DMSO) [42] and amylose triacetate (ATA)/nitromethane [43]. For these systems, except for CDA, CTA and NaCS, all parameters necessary for estimating A by Eqn (16) have been determined by Kamide and Miyazaki [11] and for CDA/acetone, CDA/THF, CTA/DMAc and NaCS/aq. NaCl systems, the parameters were estimated in the original literature, as summarized in Table 1.

Table 1 shows that, for all the systems employed here, the partially free draining effect cannot be neglected ($a_\Phi \neq 0$) and for some systems the unperturbed chain is obviously non-gaussian ($a_2 < 0$).

The A values estimated by method 2K are tabulated in Table 2, together with those obtained by other methods. Table 3 summarizes the correlation coefficient r between the A values for cellulose, amylose and their derivatives obtained by the two methods arbitrarily chosen. As shown in Fig. 1, the A values obtained by methods 2B, 2C, 2D, 2G, 2J and 2K are highly correlated ($r > 0.95$) with each other (with the exception of a combination of methods 2C and 2D) and to be accurate within 6%. The correlation coefficient r between method 2C and 2D is estimated as 0.912. This value is significantly smaller than those corresponding to any combination among the methods 2B, 2C (or 2D), 2G and 2K because, for solutions of cellulose and amylose derivatives, a_2 often deviates from zero. Of course, the A values obtained by method 2D agree well with those by methods 2B, 2G and 2K; r value (0.960) between methods 2C and 2K is smaller than that (0.986) between methods 2D and 2K.

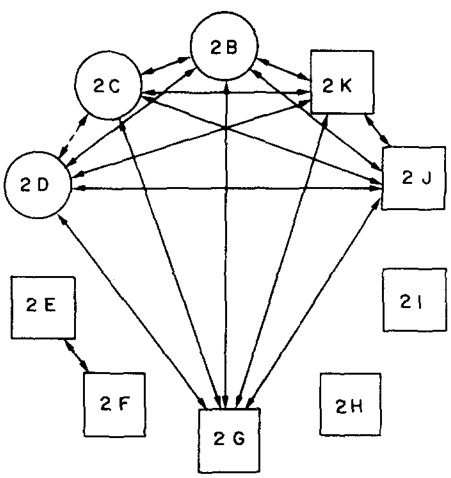

Fig. 1. Correlation coefficient r of A between the two methods arbitrarily chosen. Circle; thermodynamic method, rectangle; hydrodynamic method, solid line; $r > 0.95$, dotted line; $0.95 > r > 0.90$.

The A values determined by methods 2E and 2F coincide. In the last line of Table 3, the A values estimated by a given method averaged over these systems are collected. The A values estimated by the former group [2B, 2C (or 2D), 2G, 2J and 2K] are some twice those by methods 2E and 2F, in which $a_2 \neq 0$ and/or $a_\Phi \neq 0$ are not taken into consideration.

In the past, conclusions with respect to chain rigidity of cellulose derivatives and the polymer–solvent interaction in these solutions differed greatly according to the method [thermodynamic approach or hydrodynamic approach (2E and 2F)] employed for the analysis [11]. This disagreement has been resolved completely by using methods 2G and 2J [11, 26]. Method 2K is consistent with the thermodynamic approach.

From the theoretical point of view, for $a_\Phi \neq 0$ method 2B, method 2C ($a_2 = 0$), method 2D ($a_2 \neq 0$), method 2G, method 2J and method 2K are reasonable and are recommended for use. Method 2K is apparently a great improvement over method 2F.

As predicted, method 2H overestimates A in the region $a_1 + 1.5a_2 < 0$ and underestimates in the

Table 3. Correlation coefficient r between the A values estimated for cellulose, amylose and their derivatives by the two methods arbitrarily chosen

	Thermodynamic approach			Hydrodynamic approach							
Method	2B	2C	2D	2E	2F	2G	2H	2I	2J	2K	
Correlation coefficient r		0.965	0.993	0.302	0.349	0.984	0.223	−0.830	0.963	0.981	2B
			0.912	0.444	0.461	0.967	0.043	−0.813	0.950	0.960	2C
				0.207	0.212	0.993	−0.025	−0.839	0.987	0.986	2D
					0.958	0.336	−0.274	0.447	−0.569	0.316	2E
					–	0.366	−0.086	0.512	−0.668	0.350	2F
							0.112	−0.393	0.963	0.998	2G
								0.501	−0.403	0.116	2H
									−0.793	−0.841	2I
									–	0.958	2J
										–	2K
Averaged A value $A \cdot 10^8$ (cm)	1.77	1.97	1.91	0.90	0.92	1.88	1.90			1.90	

Table 4. The unperturbed chain dimensions estimated by various methods for poly(α-methyl styrene) (PαMS)/toluene and poly (*p*-methyl styrene) (P*p*MS)/toluene

Polymer	Solvent	$K_m \times 10^3$	a	$K_\Phi \times 10^{-23}$	a_Φ	a_2	$A \times 10^8$ (cm)					
							2B	2C	2E	2F	2G	2K
P(αMS)	Toluene	5.98	0.754	1.22	0.024	0	0.861	0.837	0.712	0.712	0.873	0.875
P(*p*MS)	Toluene	8.86	0.74	1.29	0.043	0	—	0.790	0.680	0.729	0.771	0.829

region $a_1 + 1.5a_2 > 0$. This fact indicates that, for solutions of cellulose and its derivatives, the excluded volume effect and/or the non-gaussian properties can never be ignored, when estimating unperturbed chain dimensions.

Besides the A value, the B value can also be indirectly determined by use of methods 2C, 2D, 2E, 2G, 2I and 2J [11, 26]. Methods 2G and 2J give the same B value as estimated by method 2C (when $a_2 = 0$) or 2D (when $a_2 \neq 0$) and moreover, the A_2 values calculated from A and B values (estimated by methods 2G and 2J) agree with the experimental values [11, 17, 18, 26]. In contrast, the B values estimated by methods 2E and 2I are remarkably larger than those by method 2C, 2D, 2G and 2J giving too large A_2 values, and not accommodated by the experimental A_2 value, as demonstrated before [11, 26].

Applicability of Eqn (16) is not limited to cellulose, amylose and their derivatives in solution. Kamide and Miyazaki have found $a_\Phi \neq 0$ for some vinyl-type polymer solutions, including poly(α-methyl styrene) in toluene [11] and poly(*p*-methyl styrene) in toluene [11]. In fact, in these systems the A values estimated by methods 2E and 2F are smaller than those by methods 2B and 2C and much better agreement between A values estimated by method 2G and those by methods 2B and 2C has been observed. In this paper Eqn (16) was applied to the above systems. The parameters K_m, a, K_Φ, a_Φ and a_2 have already been calculated by Kamide and Miyazaki [11] from published data [44–46]. The results are given in Table 4, which contains the A values estimated by other methods [11]. Obviously, method 2K is preferable to method 2F and the A values obtained by the former agree well with the averaged values of methods 2B, 2C and 2G.

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