Molecular Parameters of Sodium Carboxymethyl Amylose in Dilute Solution

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ABSTRACT

Carboxymethyl amylose was fractionated and the fractions were characterized by light scattering and viscometry. The viscosity and the molecular weight data have been used to evaluate the Mark-Houwink's constant a, expansion factor α, Flory's universal constant ϕ_0, and unperturbed dimension of the chain. The configurational parameters, e.g., effective bond length b, Kuhn-Kuhn chain segment length A_m, and steric factor σ have also been determined and compared with those of similar cellulose derivatives obtained in our laboratory.

INTRODUCTION

A number of conformational and thermodynamic studies on cellulose and cellulose derivatives, e.g., hydroxymethyl cellulose [1], ethyl hydroxyethyl cellulose [2], and carboxymethyl cellulose [3], have been made recently. But so far little attention has been paid to similar investigations on amylose and its derivatives. This work was therefore

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undertaken to evaluate the configurational parameters of sodium carboxymethyl amylose in 0.5 $\underline{M}$ NaCl solution by means of viscosity and light scattering.

EXPERIMENTAL

Preparation of Sodium Carboxymethyl Amylose (NaCMA)

Amylose was separated from amylopectin from the two samples of starch viz. high molecular weight potato starch (Sample I) and an industrially processed low molecular weight amylose (Sample II) by the standard method [4]. Carboxymethylation of amylose, its purification, and the determination of degree of substitution were carried out in the usual way [5]. The degree of substitution of the two samples was found to be 0.62 and 0.56, respectively. The samples were fractionated into well-defined fractions, acetone being used as the nonsolvent. The fractions were dried under vacuum and dissolved in 0.5 $\underline{M}$ NaCl solution.

Viscosity Measurement

All viscosity measurements were made with a standard Ostwald viscometer havin a flow time of 142.5 sec for 5 ml of 0.5 $\underline{M}$ NaCl solution at 30 ± 0.1°C Kinetic energy corrections were considered to be negligible.

Light-Scattering Measurement

Light-scattering measurements were made as previously described [5] using green mercury line (λ = 5460 Å). The data were graphed according to the method of Zimm [6], a typical plot being shown in Fig. 1. The root-mean square radius of gyration was calculated from the slope of line of zero concentration as

$$(\overline{S}^2)_z^{1/2} = \frac{\lambda}{n}\left(\frac{3}{16\pi^2} \ \frac{\text{initial slope}}{\text{Intercept}}\right)^{1/2}$$

where n is the refractive index of the solvent. The second virial coefficient (A_2) was obtained from the slope of the zero angle line. The refractive index increment was determined at 5460 Å by using Brice-Phoenix differential refractometer at 30°C.
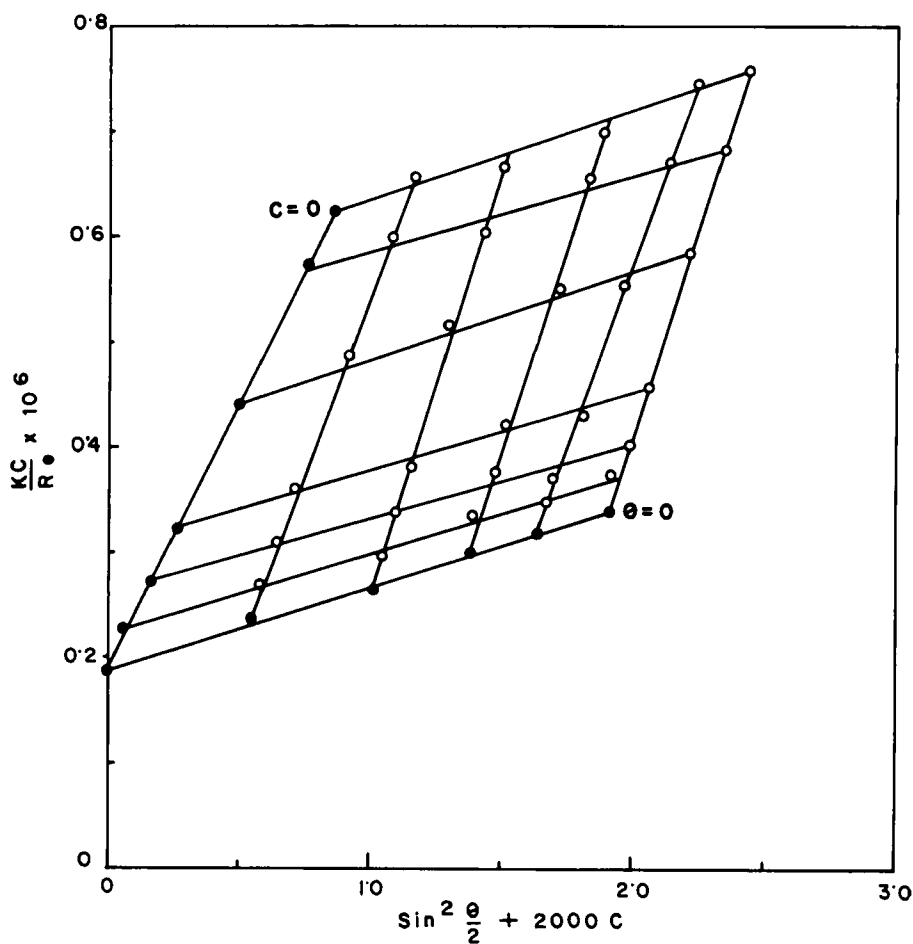
FIG. 1. Zimm plot for sodium carboxymethyl amylose (Sample lb) in 0.5 $\underline{M}$ NaCl.

RESULTS AND DISCUSSION

Intrinsic Viscosity-Molecular Weight Relationship

The variation of intrinsic viscosity with molecular weight for linear polymer chains is expressed by the Mark-Houwink relationship [7]

$$[\eta] = KM^a$$
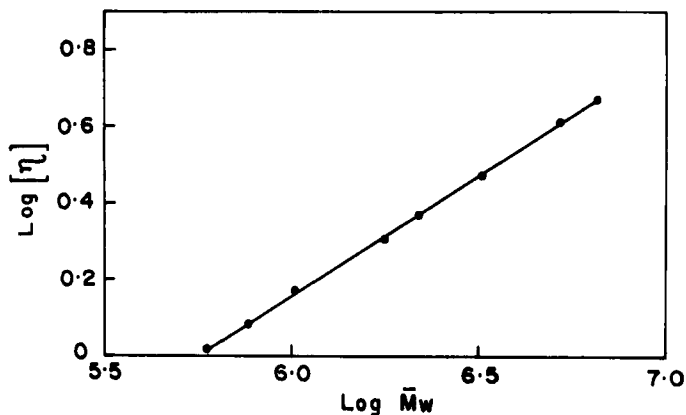
FIG. 2. Log-log plot of $[\eta]$ vs M_W for sodium carboxymethyl amylose.

where K and a are constants independent of molecular weight for a specific polymer-solvent system. From the log-log plot of intrinsic viscosity and molecular weight (Fig. 2), the value of a for sodium carboxymethyl amylose in 0.5 M NaCl has been found to be 0.66, which indicates that the shape of this amylose derivative lie in between free-draining and the solvent immobilizing forms.

Expansion Factor, α

The expansion factor α was calculated by use of the relationship due to Orofino and Flory [8]:

$$A_2 = 16 \left(\frac{\pi}{3^{3/2}} \right) \left[N_A \, (\overline{S}^2)_Z^{3/2} / \overline{M}_W^2 \right] \ln \left[1 + \left(\frac{\pi}{2} \right)^{1/2} (\alpha^2 - 1) \right]$$

The values of α shown in Table 1 seemed to be of a somewhat lower magnitude. Such lower magnitudes of expansion factors have also been reported for cellulose derivatives [9, 10] such as hydroxyethyl cellulose (HEC) and NaCMC in aqueous solvents. The inherent stiffness of the amylose chain might be responsible for this negligible expansion ($\alpha - 1$).

TABLE 1. Molecular Parameters of Sodium Carboxymethyl Amylose in 0.5 $\underline{M}$ NaCl Solution

Sample no.	Mol wt $M_W \times 10^{-6}$	$[\eta]$ (dl/g)	a	$(\overline{S^2})_Z^{1/2}$ (Å)	α	$(\overline{R^2})_Z^{1/2}$ (Å)	$(\overline{S_0^2})_Z^{1/2}$ (Å)	$(\overline{R_0^2})_Z^{1/2}$ (Å)	A_2, (cm^3/g^2)	$\phi_0 \times 10^{-21}$
1a	6.40	4.78		1132.0	1.20	2773	943.2	2311	6.77×10^{-5}	2.81
1b	5.24	4.10		1040.0	1.19	2549	874.4	2142	7.45×10^{-5}	2.54
1c	3.25	3.00		765.4	1.12	1875	683.4	1674	5.00×10^{-5}	2.88
1d	1.80	2.03		531.4	1.08	1302	492.0	1205	3.70×10^{-5}	3.17
			0.66							
2a	2.20	2.30		600.3	1.09	1471	550.8	1350	3.90×10^{-5}	3.09
2b	1.25	1.64		450.4	1.07	1104	428.9	1051	1.40×10^{-5}	2.97
2c	0.78	1.20		352.2	1.05	862.5	335.5	823	3.60×10^{-5}	2.84
2d	0.59	1.02		298.6	1.03	731.6	290.0	710	1.88×10^{-5}	2.99

Flory's Universal Parameter, ϕ_0

According to Flory and Fox [11], the intrinsic viscosity of polymer molecules is related to their dimensions according to the relationship

$$[\eta] = \phi_0 \, (\overline{R}^2)_z^{3/2}/\overline{M}_w$$

where ϕ_0 is a universal constant independent of the solvent and polymer, $(\overline{R}^2)_z^{1/2}$ is the root-mean-square end-to-end distance of the polymer molecule, and $\overline{M}_w$ is the weight-average molecular weight. For this equation to be valid, it is necessary for the molecule to coil sufficiently so as to approach spherical symmetry and for the internal hydro-dynamic resistance to be great enough for ϕ_0 to approach its asymptotic value [10].

In order to simplify calculation from light-scattering data, a alternative relation was proposed:

$$[\eta] = \left(\frac{\phi_0}{q'}\right) \, (\overline{R}^2)_z^{3/2}/\overline{M}_w$$

where q' is a factor correcting for sample heterogeneitry according to

$$q' = \frac{\Gamma(y + 1)\,[\Gamma(y + 3)/\Gamma(y + 2)]^{3/2}}{(y + 1)[\Gamma(y + 3/2)]}$$

where $\overline{M}_z:\overline{M}_w:\overline{M}_n = (y + 2):(y + 1):y$. In the present case y = 1 and thus q' = 1.95. A discussion of this factor is given by Krigbaum and Sperling [12].

The ϕ_0 values (Table 1) show a tendency to decrease with increasing molecular weight. However, in order to isolate the causes of the variation in ϕ_0, the equation was recast into the equivalent form

$$\phi_0 = q' \, \frac{\overline{M}_w}{(\overline{S}^2)_z} \, \frac{[\eta]}{(\overline{S}^2)_z^{1/2}} \, \frac{1}{6^{3/2}}$$

since $\overline{S}^2 = R^2/6$. In the present case, the values of the ratio $(\overline{S}^2)_z/\overline{M}_w$ were observed to be approximately constant. The values $[\eta]/(\overline{S}^2)_z^{1/2}$, however, decrease with a decrease in molecular weight. This then reflects on the hydrodynamic behavior of the molecule, so that its permeability increases with a decrease in molecular weight.

The values of ϕ_0, however, show a larger scattering, which makes it difficult to define the exact relation between ϕ_0 and molecular weight. This scattering may arise from the effects of both experimental error and the interpretation of the theory. The largest experimental error may be associated with the determination of the radius of gyration $(\overline{S}^2)_z^{1/2}$. Again, in terms of excluded volume parameter Z, the radius of the macromolecule [13] (α) and that of its effective hydrodynamic radius [14] (α_η) are expressed as

$$\alpha^3 = 1 + 2.0Z$$

and

$$\alpha_\eta^3 = 1 + 1.55Z$$

Thus when the excluded volume effect is not negligible, the parameter ϕ_0 is not constant. Hence in a system in which there is both a variable free draining and an excluded volume effect, the parameter ϕ_0 is subjected to two opposing tendencies—with decreasing molecular weight, increasing permeability causes ϕ_0 to decrease, whereas the excluded volume effect causes it to increase. The interpretation of the experimental values of ϕ_0 is therefore difficult.

Evaluation of Unperturbed Dimension, $(\overline{R}_0^2/M_w)^{1/2}$

A number of graphical procedures [13, 15, 16] are available for the determination of unperturbed dimensions of polymer molecules from intrinsic viscosity and molecular weight measurements in non-ideal solvents. All these methods, in general, involve determination of the constant K_0 of the expression

$$[\eta] = K_0 \overline{M}_w^{1/2} \alpha^3$$

where

$$K_0 = \phi_0 (\overline{R}_0^2/M_w)^{3/2}$$

In the present case, the unperturbed dimension of carboxymethyl amylose in 0.5 $\underline{M}$ NaCl solution was determined using the Stockmayer-Fixman relation [13].

$$[\eta]/\overline{M}_w^{1/2} = K_0 + 0.51\phi_0 B \overline{M}_w^{1/2}$$

Thus, from the graph of $[\eta]\overline{M}_w^{-1/2}$ vs $\overline{M}_w$, a value of K_0 of 1.10×10^{-3} was obtained from the intercept of the ordinate (Fig. 3). By using the
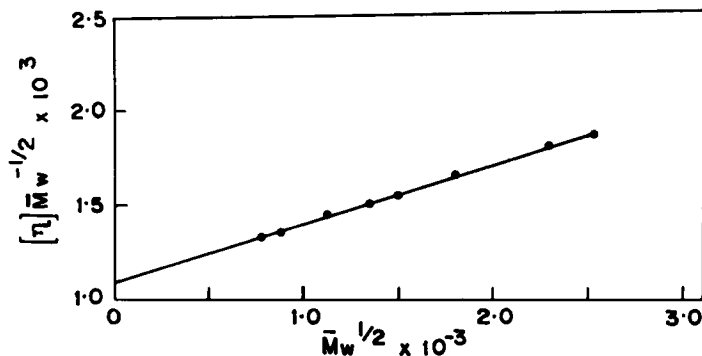
FIG. 3. Stockmayer-Fixman plot for sodium carboxymethyl amylose.

Kurata-Yamakawa [14] value of $\phi_0 = 2.87 \times 10^{21}$, a value of 0.726×10^{-8} was obtained for the unperturbed dimension.

Configurational Parameters

Important parameters for designating a polymer coil as flexible or stiff in solution are b, the effective bond length; A_m, the Kuhn-Kuhn chain segment length; and δ, the steric factor. All these parameters were calculated by using relationships as previously stated [17]. The values of these parameters are shown in Table 2 together with those for some cellulose derivatives and polystyrene for comparative study.

TABLE 2. Configurational Parameters of Sodium Carboxymethyl Amylose in 0.5 M NaCl and Those of Other Polymeric Chains in Appropriate Solvents

System	b (Å)	A_m (Å)	δ	Ref.
Sodium cellulose xanthate in 1 N NaOH	29	-	3.8	17
Sodium carboxymethyl cellulose in NaCl	37.4	-	-	17
Sodium carboxymethyl amylose in 0.5 M NaCl	12.5	30.4	2.04	Present work
Polystyrene in toluene	8.6	-	2.2	

The effective bond length of sodium carboxymethyl amylose (12.5 for Sample 1b) is seen to be higher than that of polystyrene (8.6) but smaller than those of sodium cellulose xanthate and sodium carboxymethyl cellulose (NaCMC), which shows that NaCMA is more flexible than NaCX and NaCMC in this solvent. Again, considering the values of A_m of NaCMA (30.4 A) and those of cellulose derivatives, it could be concluded that NaCMA in 0.5 M NaCl is considerably less extended than the cellulose derivatives. The low value of δ (2.04) for NaCMA (the same sample) further signifies the highly flexible nature of the amylose chain.

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