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"CHARACTERIZATION OF CELLULOSE AND POLYPEPTIDE POLYMERS"

Technical Report No. 1

(b) "The Molecular Characterization of Sodium Carboxymethylcellulose"

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THE MOLECULAR CHARACTERIZATION OF SODIUM CARBOXYMETHYLCELLULOSE

Paul Doty and Nathaniel Schneider

A light scattering and viscosity study has been made on an unfractionated sample of sodium carboxymethylcellulose (NaCMC), having 1.15 carboxymethyl groups per glucose unit, with the aim of (1) characterizing the stiffness of the molecule and the effect of electrostatic forces on the extension of the cellulose chain, (2) examining the relation between the molecular size and the intrinsic viscosity, (3) determining whether the Donnan effect accounts satisfactorily for the second virial coefficient.

Light scattering and viscosity measurements were carried out on NaCMC in 0.5, 0.05, and 0.01 M NaCl. The refractive index increment, determined in 0.5 M NaCl at λ = 4360 Å, was 0.0776 giving a value of 9.80×10^{-9} for K which occurs in the well-known equation:

$$P(\theta)\frac{Kc}{R_\theta} = \frac{1}{M} + 2BP(\theta)c$$

After a 90 minute centrifugation at 80,000 g, the scattering was measured over the range of 30° to 135° at four concentrations and the results evaluated by means of a Zimm plot. Such a plot is shown in figure 1 for the case of 0.05 M NaCl. The reciprocal of the intercept gives the molecular weight (M) directly while the second virial coefficient (B) is obtained from the slope of the zero angle line and the mean end-to-end distance (R) from the limiting slope of the zero concentration line.

Molarity of NaCl	Molecular Weight	R(Å)	$\frac{R}{L}$	$\frac{R}{\sqrt{DP}}$	$[\eta]$	$\phi_{calc} \times 10^{-21}$	$B \times 10^3$ Expt.	$B \times 10^3$ Calc.
0.5	177,000	2410	0.46	75	7.03	0.17	{2.74 4.00	7.7
0.05	173,000	2590	0.50	82	10.1	0.17	13.8	77
0.01	170,000	3100	0.59	97	15.9	0.14	37.6	385

The molecular weight is found to be constant, within probable experimental error, in the ionic strength range studied. This together with the normal concentration dependence of the scattering show that aggregation is absent.

The high degree of extension of the molecule can best be appreciated by comparing the end-to-end length with the contour length, i.e. the length of the completely extended molecule, preserving the normal valence angle. The contour length is obtained by multiplying the degree of polymerization by the length of the projection of the repeating unit on the direction of the chain. Since NaCMC has a broad distribution of molecular weights resulting from a random degredation process, we must take account of the fact that the light scattering molecular weight is a weight average but the end-to-end distance is a z-average and must be compared with the contour length calculated from the z-average molecular weight. The distribution appropriate to a random degredation process gives a ratio of M_w to M_z of 2 to 3. Thus, we obtain a value of M_z = 260,000 and L_z = 5280 Å from which the ratios of R to L listed in the table have been obtained. These values show that the NaCMC molecule, in this range of ionic strength, is about half extended and, therefore, deviates markedly from the Gaussian coil usually assumed for polymer molecules. The degree of extension is not, however, greatly different from earlier, less accurate measurements on cellulose derivatives. In particular, the value of the ratio $\frac{R}{\sqrt{DP}}$, a useful index of chain stiffness, is 75 for NaCMC in 0.5 N NaCl. This may be compared with a value of 40 for cellulose nitrate in acetone[1], a value of about 40 for cellulose acetate in acetone[2],

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1. Badger and Blaker, J. Phys. Colloid Chem. 53, 1056 (1949)
2. Stein and Doty, J.A.C.S. 68, 159 (1946)

and a value of 10 for polystyrene in toluene[3], all values being for the same DP as NaCMC. Thus, the present measurements confirm the earlier conclusion that cellulose is a very stiff molecule and indicate that the extension of NaCMC is somewhat greater than in the uncharged derivatives.

In keeping with the conclusion that NaCMC is a highly extended non-Gaussian coil, the angular scattering envelope at zero concentration in all the Zimm plots is not a straight line, as heretofore was found for all polymers, but shows a distinct downward curvature. This type of curve, lying intermediate between that for a Gaussian coil and that for a rod, is just what would be expected for a non-Gaussian coil. The curvature has bearing on the comparisons made in the preceeding paragraph since it indicates that dissymmetry is not an adequate characterization of the molecular size. For example, from the dissymmetry for NaCMC in 0.05 N NaCl a value of R = 1650 Å is obtained while the limiting slope of the zero concentration line gives a value of 2590 Å. Consequently, the earlier values for the molecular size in cellulose derivatives, based on dissymmetry measurements, should be higher giving results closer to those for NaCMC. It is also important to point out that the limiting slope of the zero concentration curve is a direct measure of the radius of gyration and not the end-to-end distance. The two quantities are related by a factor of $\sqrt{6}$ for the Gaussian coil and by a factor of $\sqrt{12}$ for the rod while for a non-Gaussian coil the value of the factor must vary continuously between these two limits. The use of the proper factor in the present work would lead to somewhat larger values of the mean end-to-end distance,

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3. B. H. Zimm, J. Chem. Phys. 16, 1099 (1948)

but this has not been attempted and the values reported are actually $\sqrt{6}$ times the radius of gyration.

Like the end-to-end distance, the intrinsic viscosity, $[\eta]$, was found to increase with decreasing ionic strength. As shown in Figure 2, $[\eta]$ varies as the inverse square root of the ionic strength, as previously demonstrated by Pals and Hermans[4]. An extrapolation to infinite ionic strength leads to a value of 5.70 for $[\eta]$ which compares closely with that of non-electrolytic cellulose derivatives of the same DP. This indicates that when the effects of electrostatic interaction are removed in this manner, the molecular configuration of NaCMC is very similar to other cellulose derivatives.

Flory and Fox have recently proposed the following equation relating $[\eta]$ to R and M and have demonstrated its validity for polystyrene and polyisobutylene:

$$[\eta] = \phi R^3/M$$

where ϕ is a universal constant, equal to 2.1×10^{21}. In a more recent paper[5] this equation has been employed to measure R for fractions of two cellulose triesters assuming that ϕ remains unchanged for these polymers. Since the values of R calculated by means of the above equation were only twice those expected for free rotation about the glucosidic bonds, it was concluded that the stiffness of cellulose molecules is a fiction. The viscosity and light scattering measurements on NaCMC offer an opportunity to make a direct check on Flory's assumption of the constancy of ϕ. For NaCMC at three ionic strengths, the values of ϕ recorded in the table are found to be lower than the established

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4. Pals and Hermans, Rec. Trav. Chim. 71, 433 (1952)

5. Flory and Mandelkern, J.A.C.S. 74, 2517 (1952)

value by a factor of more than ten. This demonstrates the inapplicability of this theory to such highly extended systems. Furthermore, the absence of any internal inconsistency, which would indicate that the theory was being misapplied, suggests the need for an independent check on the parameters when this treatment is extended to systems widely different from polystyrene and polyisobutylene.

Finally, we come to a consideration of the second virial coefficient (B). In the region of low ionic strength, where electrostatic interactions are the main contribution to B, it would be expected that the Donnan term should account for the magnitude of B and its variation with ionic strength. However, the values of B in the table indicate that the Donnan term gives the correct order of magnitude only at high ionic strength. With decreasing ionic strength, the Donnan term increases far more rapidly than the experimental values. Furthermore, the results plotted in Figure 2 demonstrate that the ionic strength dependence is well represented by the inverse square root of the ionic strength rather than the inverse ionic strength as would be anticipated from the Donnan term. The recent osmotic pressure measurements of B, at high ionic strength, by Pals and Hermans[4] lead to values comparable to those obtained here. While the authors concluded that the Donnan term adequately represented the variation of B with ionic strength, the results do not actually permit a discrimination between the above two types of dependence on ionic strength. It appears, therefore, that the Donnan term alone does not adequately characterize the electrostatic interactions in this polyelectrolyte system.

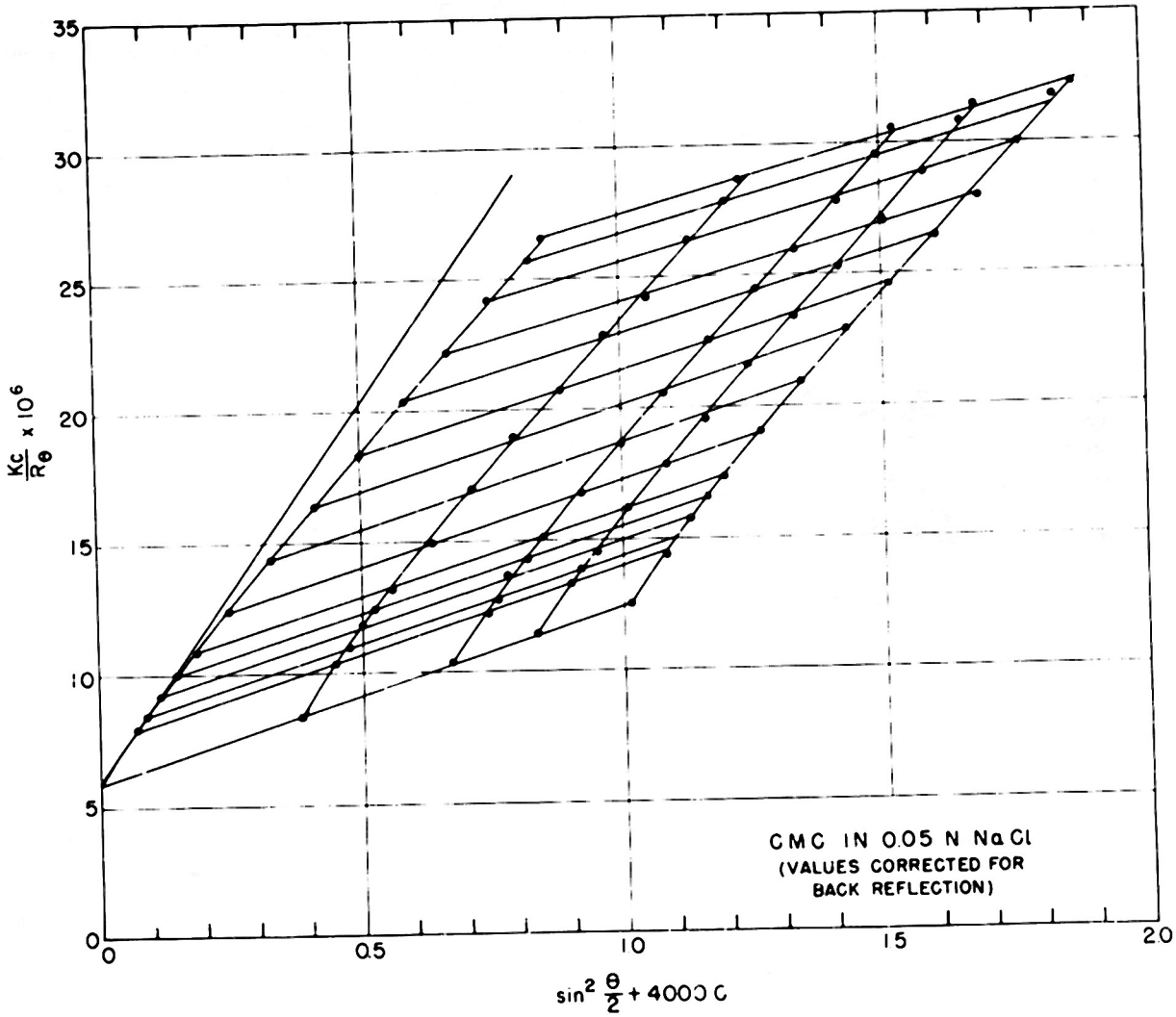
Summary:

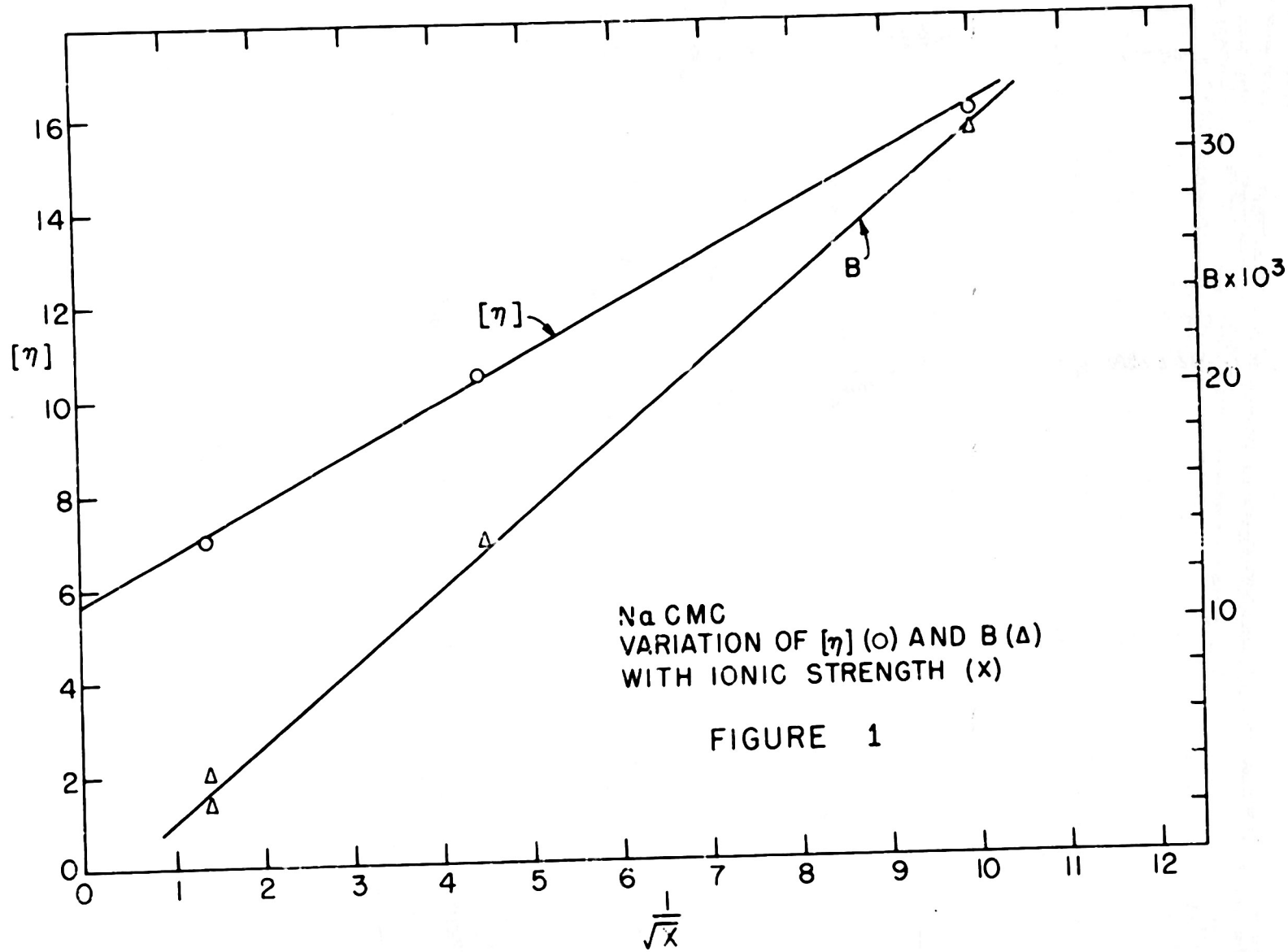
1) The present measurements on NaCMC confirm the conclusion that cellulose is a stiff molecule and show that, except at high ionic strength, NaCMC is more extended than unchanged cellulose derivatives.

2) The dissymmetry coefficient is not an adequate measure of the molecular size for non-Gaussian coils, such as the low molecular weight cellulose derivatives. However, the limiting slope of the angular envelope always gives a direct measure of the radius of gyration, from which the end-to-end distance may be obtained.

3) Direct evaluation of the constant, ϕ, which occurs in the Flory-Fox intrinsic viscosity equation indicates that this theory is not applicable to such highly extended polymers.

4) Examination of the second virial coefficient indicates that the electrostatic interactions in this polyelectrolyte system are not well accounted for by the Donnan term alone.


35
30
25
20
15
10
5
0
$\frac{Kc}{R_\theta} \times 10^6$
0
0.5
1.0
1.5
2.0
$\sin^2 \frac{\theta}{2} + 4000\,C$
CMC IN 0.05 N NaCl
(VALUES CORRECTED FOR
BACK REFLECTION)



Na CMC
VARIATION OF [η] (o) AND B (Δ)
WITH IONIC STRENGTH (X)

FIGURE 1