Molecular weight and conformational characteristics of carboxymethyl cellulose and its nitroesters

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Carboxymethyl cellulose (CMC) and its derivatives are widely used in different sectors of the national economy: in the food industry, in agriculture, and in medicine. Therefore, the need to know its molecular weight and conformational characteristics is quite obvious. On the one hand the molecular parameters determine the specific properties of the polymers, and on the other hand these characteristics make it possible to control production processes in terms of the output of a particular polymer product.

In spite of the large number of publications related to the molecular weight characteristics of polymer derivatives based on CMC, work on determining the molecular weight (MW) of nitrocellulose is rare [1]. The present work gives the results of investigating the hydrodynamic properties of Na-CMC and nitroesters based on it by methods of viscometry, gel permeation chromatography, sedimentation, and diffusion.

Chromatographic investigations were carried out on a KhZh-1304 high-speed liquid chromatograph. Use was made of stainless steel columns of 0.3 m length and 4 × 10⁻³ m internal diameter, packed with sorbent G-40-OH (produced in the Czech Republic) with a pore diameter of 240 Å and an average particle size of 3–5 µm. The eluent was a 0.5N aqueous solution of NaNO₃, and the eluant feed rate was 10 ml/h. Gel chromatograms were recorded using a refractometric detector.

Sedimentation analysis was carried out on a 3180 ultracentrifuge (MOM, Hungary) in single- and two-sector trays with a rotor rotational speed of 44 000 r/min. The sedimentation coefficients of the specimens, S, were determined from the slope of the dependence of ln x on time t (Figure 1). The coefficients of forward diffusion were measured on a V. N. Tsvetkov polarisation diffusometer [3] by the area and maximum ordinate method. Figure 2 gives the dependences of the variance of diffusion curves, Δ², on time t, from the slope of which the coefficients of diffusion were determined.

Viscometer measurements were carried out on an Ubelohde viscometer. All measurements were carried out at a temperature of 25 ± 0.1°C. The molecular weights of all the specimens were calculated from sedimentation and diffusion data by means of the Svedberg equation.

Figure 1. Dependences of ln x (the x coordinate of the sedimentation curve maximum) on sedimentation time for specimens of Na-CMC (a) and nitro-Na-CMC (b) in water–methanol–KCl mixture (66.67%:32%:1.33%): 1 – DP = 500; 2 – DP = 300; 3 – DP = 130; 4 – DP = 60; 5 – DP = 20
with a value of the partial volume \( v = 0.55 \text{ cm}^3/\text{g} \).

Experimental values of the hydrodynamic characteristics and molecular weights are given in Table 1.

By means of hydrolysis, four specimens with a degree of polymerisation (DP) of 300, 130, 60, and 20 were obtained from the initial Na-CMC specimen with a DP of 500. Hydrolytic breakdown was carried out under heterogeneous conditions in ethyl alcohol in the presence of hydrochloric acid with a molar ratio of Na-CMC to HCl of 1:3.

Specimens differing in DP were obtained by controlling the duration of the hydrolysis process. The average value of the degree of substitution of specimens was 0.8 ± 0.01. For the specimens, the intrinsic viscosities \( \eta \) were measured in two solvents: a mixture of water with methanol with the addition of KCl in a mass ratio of 66.7:32.1:33 (time 174 s), and also in an aqueous 0.5M solution of NaN03 (time 90.5 s). The \( [\eta] \) values of nitrated specimens were measured in an aqueous methanol solution. The results are given in Table 1.

As can be seen from Table 1, the \( [\eta] \) values for Na-CMC in the different solvents practically coincide. This means that methanol added to eliminate film formation has practically no effect on the conformation of Na-CMC and Na-nitro-CMC macromolecules. Therefore, their comparative investigations were carried out in aqueous methanol solutions.

From the data in Table 1, the hydrodynamic invariant \( A_0 = \frac{D[\eta]/T[M[\eta]/100]^{1/3}}{1 - \nu v_0} \) with a value \( \eta_0 = 1.9 \times 10^{-2} \text{ cP} \)

This value differs appreciably from the \( A_0 = (3.15 \pm 0.23) \times 10^{-10} \) obtained for CMC in Cadoxen + H2O [4] but falls in the range of values \( A_0 = (3.5 \pm 0.8) \times 10^{-10} \) obtained for cellulose derivatives in aqueous and buffer solvents [5]. In a study of CMC in 0.1M NaCl, a value of 4.9 \times 10^{-10} was obtained for \( A_0 \) [6].

Figure 3 presents dependences of the Mark–Kuhn–Houwink type \( (C_i = K_i M_i^{1/2}) \), where \( C_i = [\eta] \) or \( S_0 \) or \( D_0 \).

The corresponding equations obtained by the least-squares method have the following form:

water–methanol + KCl

\[ [\eta]^* = 1.73 \times 10^{-3} M_1^{0.04} \text{ cm}^3/\text{g} \]

water + 0.5M NaN03

\[ [\eta]^** = 1.99 \times 10^{-3} M_1^{0.3} \text{ cm}^3/\text{g} \]

water–methanol + KCl

\[ D = 5.78 \times 10^{-4} M_1^{0.73} \text{ cm}^3/\text{g} \]

### Table 1. Molecular weight characteristics of Na-CMC and Na-nitro-CMC

<table>
<thead>
<tr>
<th>Specimen</th>
<th>([\eta]^* \text{ dl/g})</th>
<th>([\eta]_1 \text{ dl/g})</th>
<th>(D \times 10^7, \text{ cm}^2 \text{s}^{-1})</th>
<th>(S \times 10^{13}, \text{s})</th>
<th>(M_{SD} \times 10^{-3})</th>
<th>(A_0, \text{ erg K}^{-1} \text{ mol}^{-1/3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-CMC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP = 500</td>
<td>3.9</td>
<td>4.0</td>
<td>0.8</td>
<td>1.7</td>
<td>115</td>
<td>4.2</td>
</tr>
<tr>
<td>DP = 300</td>
<td>0.96</td>
<td>0.93</td>
<td>1.72</td>
<td>1.4</td>
<td>45</td>
<td>4.0</td>
</tr>
<tr>
<td>DP = 130</td>
<td>0.53</td>
<td>0.55</td>
<td>3.5</td>
<td>1.3</td>
<td>21</td>
<td>5.1</td>
</tr>
<tr>
<td>DP = 60</td>
<td>0.40</td>
<td>0.46</td>
<td>3.75</td>
<td>1.0</td>
<td>15</td>
<td>4.5</td>
</tr>
<tr>
<td>DP = 20</td>
<td>0.29</td>
<td>0.28</td>
<td>5.0</td>
<td>0.91</td>
<td>10</td>
<td>4.8</td>
</tr>
<tr>
<td>Na-nitro-CMC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NK-228-500</td>
<td>0.134</td>
<td></td>
<td>5.9</td>
<td>0.75</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>NK-231-300</td>
<td>0.126</td>
<td></td>
<td>6.2</td>
<td>0.75</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>NK-230-130</td>
<td>0.092</td>
<td></td>
<td>5.6</td>
<td>0.70</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>NK-241-60</td>
<td>0.088</td>
<td></td>
<td>8.7</td>
<td>0.71</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>NK-240-20</td>
<td>0.076</td>
<td></td>
<td>13.9</td>
<td>0.80</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

* Determined in an aqueous solution of methanol with the addition of KCl
† Determined in a 0.5M aqueous solution of NaN03
A value of $\alpha$ close to unity for CMC in Cadoxen and in Cadoxen + water was obtained in [4]. For Na-CMC in 2%NaCl, $\alpha = 1.28$, while in 6%NaOH the value of $\alpha$ decreases to 0.93. Such a change in $\alpha$ is due to weakening of the interaction between chain charges owing to their screening and a certain reduction in chain rigidity [7].

The difference in the exponents from 0.5 for Na-CMC is due to leakage of the chain, since for cellulose derivatives the volume effects play no appreciable role [8]. To determine the size of the Na-CMC molecules in solution, use was made of theories taking into account the leakage of the polymer molecules. According to Table 1, and also from the dependence of the coefficients of forward and rotational frictions on the molecular weight or the unit length $L$ of the macromolecular chains described by the equations given in [4, 9], the following conformational data were obtained:

$$A_f = 243 \text{ Å}, \quad d_f = 1.7 \text{ Å}, \quad A_\eta = 200 \text{ Å}, \quad d_\eta = 36 \text{ Å}$$

where $A_f$ and $A_\eta$ are the lengths of a Kuhn segment, and $d_f$ and $d_\eta$ are the chain diameters. The mass of a unit chain length that was used in calculations of $M_t$ for Na-CMC with a degree of substitution of 0.8 has the value $M_t = M_0/\lambda = 44.7 \text{ amu/Å}$.

These data correlate with data for Na-CMC molecules in Cadoxen + H$_2$O ($A_f = 280 \text{ Å}$) but are markedly greater than the value of $A$ in Cadoxen ($A_\eta = 140 \text{ Å}$) [4].

Figure 4 presents chromatograms of the exclusion separation of the initial cellulose ester Na-CMC-500 and products of different degrees of hydrolysis of Na-CMC. From Figure 4 it can be seen that the selected conditions ensure a sufficient degree of resolution and make it possible to draw the preliminary curve of the investigated specimens in a wide range of molecular weights.

The molecular weight on switching from Na-CMC-500 to Na-CMC-60 decreases by an order of magnitude. The investigated CMC esters are discernible chromatographically, and therefore further investigations of the given specimens after the procedure of their nitration are justified. Comparative results are presented in Figure 5. It can be seen that nitrated Na-CMC specimens obtained from corresponding hydrolysed specimens of Na-CMC with DP = 500, 300, 130, 60, and 20 emerge with considerably greater volumes of retention than the initial specimens of Na-CMC of the same degrees of polymerisation. Moreover, the retention volumes for practically all the specimens are the same and correspond to a molecular weight range of the order of 5000–6000.

A comparison of the value of $[\eta]$ of the initial Na-CMC specimens of different DP and the products of their nitration indicates that, in the process of nitration, there is a great fall in viscosity (see Table 1). As can be seen from Table 1, the coefficients of diffusion of Na-CMC
nitroesters is 2–3 times greater, while the coefficient of sedimentation is 2–3 times lower by comparison with those of the initial Na-CMC specimens. Here, the values of $[\eta]$, $S$, and $D$ of Na-CMC nitroesters have roughly identical values irrespective of the DP of the initial Na-CMC specimens. These data are in good agreement with data obtained from chromatographic studies. Such a change in the hydrodynamic parameters of Na-CMC may be due to change in the molecular weight of the initial specimens during nitroester production.

To make a clear judgement concerning the causes of the sharp change in the hydrodynamic parameters of Na-CMC during nitration, the intrinsic viscosities $[\eta]$ for nitrated Na-CMC (DP = 500) were also measured after denitration. As shown by the studies carried out, the values of $[\eta]$ of Na-nitro-CMC specimens and denitrated specimens remain unchanged. Gel chromatographic investigations showed that the peaks corresponding to Na-nitro-CMC and to denitrated specimens have the same retained volume.

Thus, from the above analysis it follows that, under nitration conditions, there is a sharp reduction in the molecular weight of Na-CMC, irrespective of the DP of the initial specimens. The reduction in molecular weight of Na-CMC during nitration is due to degradation of the polymer chain [1].

The conducted investigations make it possible to draw the following conclusions:

1. In the process of the nitration of Na-CMC, there is a change in the hydrodynamic characteristics of the esters, connected with changes in the molecular weight of the initial specimens.
2. The reduction in the molecular parameters of Na-CMC under nitration conditions is due to degradation of the macrochain of the cellulose ester.
3. The molecular weight of nitration products has roughly the same low values (5000–7000) irrespective of the degree of polymerisation of the initial cellulose esters.

REFERENCES