Estimation of the Relative Stiffness of the Molecular Chain in Polyelectrolytes from Viscosity Measurements at Different Ionic Strengths. Comparison of Polymers and Polyanions

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Recently a method was developed that allowed comparison of the stiffness of the molecular chain in different polyelectrolytes from measurements of viscosity at different ionic strengths. It has so far been tested on polyanions, only. This communication reports experiments which show that it may equally well be applied on polycations. A comparison of both weakly and strongly acidic and basic dextran derivatives was made for this purpose. A sample of dextran sulfate (Pharmacia AB, Uppsala, Sweden) has previously been studied with results as shown in Table 1. The parameter of stiffness, $B$, is the slope, $S$, of the straight line relating the intrinsic viscosity to the inverse square root of the ionic strength for the case when the intrinsic viscosity is 1.0 (100 ml/g) at ionic strength, $I = 0.1$. The $B$-value has been found to be inversely related to accepted parameters of stiffness and is, for example, 0.44 for the very flexible polyphosphate chain and 0.0055 for the stiff, double-stranded DNA chain.

The intrinsic viscosities of three dextran derivatives in their fully ionized forms were determined, as before, in solutions containing different amounts of sodium chloride, and the results are given in Fig. 1.

![Fig. 1. Intrinsic viscosity as a function of the reciprocal square root of the ionic strength.](image)

- ▲: DEAE-dextran, DS = 0.33, pH = 4.8
- ×: QAE-dextran, DS = 0.35, pH = 7.2
- ●: Carboxymethyl dextran, DS = 1.0, pH = 7.

Table 1. Comparison of viscosity data for different dextran derivatives.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$[\eta]_{k,1}$</th>
<th>$S^a$</th>
<th>$B^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dextran sulfate,</td>
<td>1.27</td>
<td>0.30</td>
<td>0.23</td>
</tr>
<tr>
<td>DS = 1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxymethyl dextran,</td>
<td>0.22</td>
<td>0.039</td>
<td>0.23</td>
</tr>
<tr>
<td>DS = 1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEAE dextran,</td>
<td>0.95</td>
<td>0.194</td>
<td>0.21</td>
</tr>
<tr>
<td>DS = 0.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QAE dextran,</td>
<td>0.86</td>
<td>0.166</td>
<td>0.20</td>
</tr>
<tr>
<td>DS = 0.35</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$S = \frac{A[\eta]}{D(1/\sqrt{I})};$ $B = S[\eta]_{k,1} = 1$

The carboxymethyl dextran (DS = 1.0) was a gift from Pharmacia. The DEAE-dextran (dextran, $M_w = 2.0 \times 10^5$, reacted with 2-chloroethyl-diethylammonium chloride to a nitrogen content of 3.2 %, corresponding to one charged group for every third sugar unit) was a commercial sample from Pharmacia. The QAE-dextran, was made by quaternizing DEAE-dextran as follows: DEAE-dextran (15 g) was dispersed in toluene (75 ml), and water (37.5 g) containing sodium hydroxide (320 mg) and propyleneoxide (18 ml) was added under strong agitation. The reaction was allowed to proceed for 16 h at 50°C. After cooling and neutralization with 1 M HCl, the polymer was precipitated with acetone, washed with acetone and ether, and dried. By potentiometric titration it was found that the product contained less than 10 % of the weakly (p$K_a = 5.5$) basic tertiary groups.

amino group. From Fig. 1 it is seen that
the intrinsic viscosity plotted against
$1/\sqrt{T}$ yielded straight lines; the slopes are
given in Table 1. The $B$-values were ob-
tained as before by graphical extrapola-
tion in a plot of $\log B$ against $\log[\eta]_0$.

The high and similar $B$-values in Table 1
indicate that all the dextran derivatives
are very flexible molecules. This is to be
expected because the presence of 95% or
more of $\alpha,1,6$-linkages in these samples
causes contiguous sugar rings to be well
separated, and there is therefore most
probably a very small effect of the bulki-
ness of the substituents upon the stiffness
of the molecule. The two basic dextran
derivatives have considerably lower charge
density than the acidic ones. Since the dif-
fERENCE between the four $B$-values is of
doubtful significance, it seems, as was the
case for polyanions, that the effect of the
charge density of the polycation on the $B$-
value is very small. The present results,
therefore, strongly suggest that the param-
eter $B$ may be used as a measure of chain
flexibility also for polycations.

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1. Smidtedal, O. and Haug, A. Biopolymers 10
(1971) 1213.
2. British patent No. 1, 133 (1968) 847.
3. Van Cleve, J. W., Schaefer, W. C. and Rist,

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Correction

The title of the article on p. 1855, vol. 25
(1971), should read: Covalent Binding of Pro-
tiens to Polysaccharides . . .

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Ring Inversion in Cyclotrisarcosyl

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Several cyclic oligopeptides of sarcosine
have been synthesized recently and their
NMR-spectra analyzed. When the tem-
perature of the sample is raised, most of
these spectra change, indicating an ex-
change process whose activation barrier
can be determined by a complete line-shape
analysis.

For the simplest of these, the cyclic tri-
peptide, bromoform was chosen as solvent
because of the low solubility in other high-
boiling solvents and because bromoform
permittted the recording of spectra at tem-
peratures up to $145^\circ C$. The coalescence
point was found to be as high as $145^\circ$ and
since bromoform boils at $150^\circ$, only spectra
on the low-temperature side of the coalescence
point could be recorded. The NMR-spectrum of cyclotrisarcosyl consists
at room temperature of five lines, four of
which form an AB-quartet centered at
$\delta = 4.27$ ppm with $\delta_{AB} = 1.30$ ppm and
$|J| = 15.3$ cps. The fifth line is a singlet
positioned at $\delta = 3.10$ ppm. The structure
of the spectrum and the integrated areas
indicate that the quartet is due to all three
methylene groups and that the singlet is
due to all three $N$-methyl resonances. This
means that the amide groups are identical
and, as Dale and Titestad pointed out, they
must all be cis since they cannot all
be trans. In bromoform solution cyclotris-
arcosyl was unstable at elevated tem-
peratures and a decomposition took place.
Two new temperature invariant singlets
with chemical shifts $\delta = 2.96$ ppm and $\delta = 3.94$ ppm, intensity ratio 3:2, appeared
after some time; these correspond to cyclo-
disarcosyl. The singlet positioned at $\delta = 3.94$ ppm is in the region of the AB-
quartet of the trimer, but is very sharp and
interferes therefore little with the line-
shape analysis. The activation energy $E_a =
17.7$ kcal/mol was computed assuming a
transmission coefficient $x = 1$. The param-
eters of activation are given in Table 1. In
the fitting routines the chemical-shift dif-
ference $\delta_{AB}$ between the methylene pro-
tons was varied and a decrease in $\delta_{AB}$
with increasing temperature was found.
The quality of the spectra does not, how-
ever, permit any further conclusions to be