

Estimation of the Relative Stiffness of the Molecular Chain in Polyelectrolytes from Viscosity Measurements at Different Ionic Strengths. Comparison of Polycations 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.¹ 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

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

Substance	$[\eta]_{0,1}$	S^a	B^b
Dextran sulfate, DS=1.6	1.27	0.30	0.23
Carboxymethyl dextran, DS=1.0	0.22	0.039	0.23
DEAE dextran, DS=0.35	0.95	0.194	0.21
QAE dextran, DS=0.35	0.86	0.166	0.20

$$^a S = \frac{d[\eta]}{d(1/\sqrt{I})}; \quad ^b B = S_{[\eta]_{0,1}=1}$$

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.¹

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

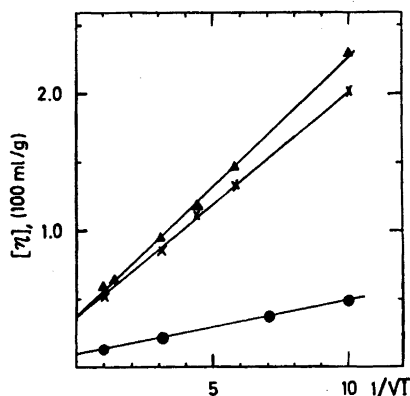


Fig. 1. Intrinsic viscosity as a function of the reciprocal square root of the ionic strength.

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

The carboxymethyl dextran (DS=1.0) was a gift from Pharmacia. The DEAE-dextran (dextran, $M_w = 2.0 \times 10^6$, 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.² 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 ($pK_a = 5.5$) basic tertiary

amino group. From Fig. 1 it is seen that the intrinsic viscosity plotted against $1/\sqrt{I}$ yielded straight lines; the slopes are given in Table 1. The B -values were obtained as before¹ by graphical extrapolation in a plot of $\log S$ against $\log[\eta]_{0,1}$.

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 α -1,6-linkages³ in these samples causes contiguous sugar rings to be well separated, and there is therefore most probably a very small effect of the bulkiness 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 difference between the four B -values is of doubtful significance, it seems, as was the case for polyanions,¹ 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 parameter B may be used as a measure of chain flexibility also for polycations.

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1. Smidsrød, 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, C. E. *J. Am. Chem. Soc.* **78** (1956) 4435.

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Correction

The title of the article on p. 1855, vol. 25 (1971), should read: Covalent Binding of Proteins 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.¹ When the temperature of the sample is raised, most of these spectra change, indicating an exchange process whose activation barrier can be determined by a complete line-shape analysis.

For the simplest of these, the cyclic tripeptide, bromoform was chosen as solvent because of the low solubility in other high-boiling solvents and because bromoform permitted the recording of spectra at temperatures up to 145°C. The coalescence point was found to be as high as 145°C and since bromoform boils at 150°, 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 Titlestad¹ pointed out, they must all be *cis* since they cannot all be *trans*. In bromoform solution cyclotrisarcosyl was unstable at elevated temperatures 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 cyclodisarcosyl.¹ 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 $\kappa = 1$. The parameters of activation are given in Table 1. In the fitting routines the chemical-shift difference Δ_{AB} between the methylene protons was varied and a decrease in Δ_{AB} with increasing temperature was found. The quality of the spectra does not, however, permit any further conclusions to be