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Viscosity

On the Viscosity of Sodium Alginates in the Presence of External Salt

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SUMMARY

This paper concerns a series of experimental results obtained on sodium alginates with various molecular weights. The dependence of the intrinsic viscosities $[\eta]$ as a function of the ionic concentration (Cs) is discussed ; the persistence length is given for Cs extrapolated to infinite. The dependence of the specific viscosity as a function of the overlap parameter C $[\eta]$ is discussed ; it is independent of Cs as long as Cs is lower than 0.5 M.

INTRODUCTION

The alginates under sodium form are highly charged polyelectrolytes characterized by a chemical composition mannuronic/guluronic units depending on the origin. This composition is related to the ability to form gels in presence of Ca counterions ; it is less important in presence of monovalent counterions. The properties of alginic acid were mainly investigated by Haug et al. (1) and more recently by Smidsrõd (2,3). The aim of this paper is to give some new experimental data on the viscosity of dilute and semi-dilute solutions of Na-alginates with different molecular weights.

EXPERIMENTAL

The samples were kindly given by CECA (France) ; A was extracted from Ascophyllum nodosum and B from Laminaria digita ; the different molecular weights were obtained by progressive acid hydrolysis of the sample B.

All the samples were purified and isolated under sodium form. The ratio mannuronic/guluronic was around 1.3 for samples A and B.

The molecular weight distributions were established by size exclusion chromatography on diol-silica gel columns 250-4 RT from Merck (2 x 1000 Å ; 1 x 500 Å, 1 x 100 Å).

The eluent was $NaNO_3$ 0.1 M with 1 % ethyleneglycol ; a light scattering detector CMX 100-Chromatix (USA) and a differential refractometer IOTA from JOBIN YVON (France) were adapted on line. The average molecular weights ($\overline{Mn}$ and $\overline{Mw}$) were deduced from the molecular weights distribution ; these characteristics are given in Table I.

The intrinsic viscosities were obtained in solvent with ionic concentration from 5.10^{-2} M to 0.5 M NaCl ; the viscosities were determined in an automatic viscometer FICA (France) equipped with an Ubbelhode capillary at a temperature 25± 0.1°C.

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TABLE I : Characteristics of the samples

Samples	$\overline{Mw}$	$\overline{Mn}$	$[\eta]$ ml/g*
A	69 500	20 900	104
B1	143 500	58 700	226
B2	261 400	107 000	373
B3	495 000	369 000	690
B4	528 100	361 500	796
B5	629 200	427 000	843

* in NaCl 10^{-1}M.

RESULTS AND DISCUSSION

A/ Relation between the molecular weight and the intrinsic viscosity as a function of the ionic strength.

The intrinsic viscosities in NaCl are given in Table II. From these values, the K and a parameters from MARK-HOUWINK empirical equation are determined using the weight average molecular weights (Table I). Our results are in good agreement with that obtained by Smidsrød (3).

TABLE II Intrinsic viscosities in NaCl with different concentrations.

Solvents	0.05 M		0.1M		0.2M		0.5M		
Samples	$[\eta]$*	k'	$[\eta]$*	k'	$[\eta]$*	k'	$[\eta]$	k'	$[\eta]_\infty$
A	106	0.38	104	0.39	-	-	102	0.50	100
B1	234	0.39	226	0.33	218	0.46	213	0.51	200
B2	462	0.35	373	0.37	-	-	296	0.54	216
B3	713	0.40	690	0.42	638	0.44	578	0.52	530
B4	860	0.42	796	0.35	740	0.43	627	0.51	550
Average k'		0.39		0.37		0.44		0.52	

* $[\eta]$ in ml/g.

These values allow to determine the parameter $[\eta]_\infty$, the intrinsic viscosity extrapolated to infinite ionic concentration (Cs) from the equation :

$$[\eta] = [\eta]_\infty + k\ Cs^{-1/2} \qquad [1]$$

This variation is in agreement with that predicted from the model proposed by ODIJK (4).

From the Table II, it is clear that the HUGGINS constant k'increases from 0.37 to 0.52 when the ionic strength increases. In the same time, the parameters from MARK-HOUWINK equation K increases from 1 to 11.10^{-3} and a decreases from 1.04 to 0.82.

In NaCl 0.1 M, the relation between $[\eta]$ and $\overline{Mw}$ becomes :

$$[\eta] = 2.10^{-3} \times \overline{Mw}^{0.97} \qquad [2]$$

This result is in good agreement with data given in the literature (2) :

$$[\eta] = 2.10^{-3}\ \overline{Mw}^{1} \qquad [3]$$

From the data $[\eta]_{\infty}$, the persistence length of the alginate chain was determined from the YAMAKAWA FUJII treatment (5).

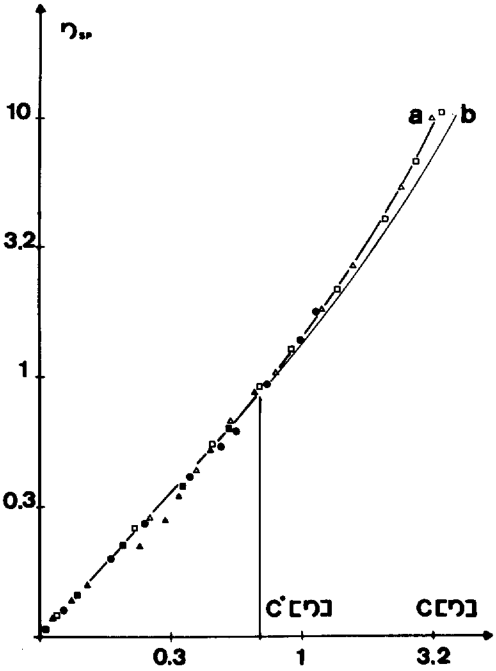

Figure 1 : Variation of the specific viscosity with the overlap parameter C[η] in NaCl 0.1 M.

a) experimental data

A ■	B3 □
B ▲	B4 △
B2 ●	B5 ○

b) Huggins relation.

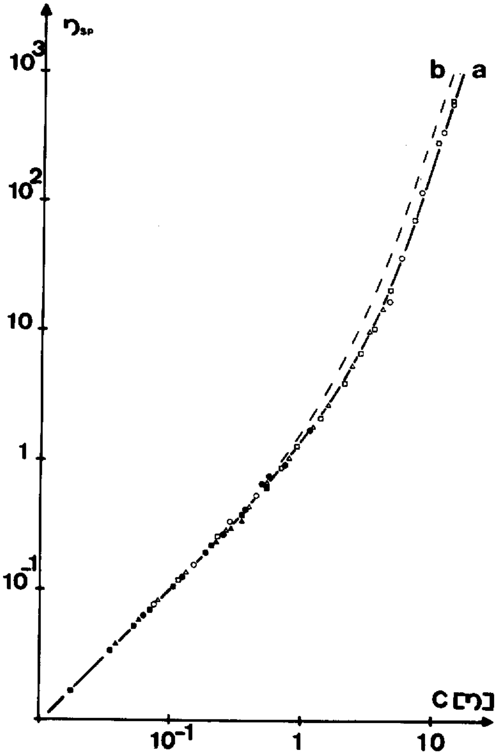

Figure 2 : Variation of the specific viscosity with the overlap parameter C[η] (sample references see figure 1).

a) ionic concentration from 5.10^{-2} to 0.1 M NaCl.

b) ionic concentration 0.5 M NaCl.

One finds a persistence length q = 100 Å in absence of electrostatic contributions and q = 130 Å in 0.5 M ; this value is in agreement with the value 75 Å given in the literature by Smidsröd for infinite ionic strength (3). This value reflects the relative stiffness of the alginate molecule. It must be pointed that the dependence of [η] with the ionic concentration is moderate compared with synthetic polyelectrolytes.

B/ Relation between the specific viscosity and the overlap parameter C [η].

As generally found, the specific viscosity can be expressed as :

$$\eta_{sp} = \sum_{1}^{n} B_n \, (C[\eta])^n \qquad [4]$$

in which C[η] is the overlap parameter equal to the product of the weight concentration and of the intrinsic viscosity [η] . This development can be reduced to :

$$\eta_{sp} = C[\eta] + k'(C[\eta])^2 + B_n \, (C[\eta])^n \qquad [5]$$

The experimental results are given in Figure 1,a ; the two first terms of relation [5] correspond to the HUGGINS relation plotted on Figure 1,b.

The divergence between both curves may be in first approximation considered as the critical value of C* [η] in which C* corresponds to the transition from dilute to semi-dilute domains. One obtains C* [η] ≃ 0.8 in agreement with the theoretical value from Graessley (6)

The figure 2 gives the dependence of log η_{sp} as a function of log C [η] for solvents with different ionic concentrations ; the curve is unique as soon as Cs is lower than 0.5 M ; then it dissociates as found by Kuliche and Kniewske on polystyrene in different solvents (7) ; it is in agreement with the decrease of the thermodynamic quality of the solvent. The parameters characterizing the curves a and b (relation 5) are respectively :

0.1 M k' = 0.37	B_n = 0.1	n = 3.2
0.5 M k' = 0.52	B_n = 0.13	n = 3.4

It must be pointed that the curve a (Figure 2) looks like that obtained recently for xanthan, a stiff microbial polysaccharide (8).

CONCLUSION

The experimental results concerning the viscosity of alginic acid in sodium form demonstrates a behaviour η_{sp} (C[η]) very analogous with that of other polymers as polystyrene in organic solvent or xanthan in NaCl aqueous solutions.

The dependence of the intrinsic viscosities with the ionic strength confirms the large stiffness of this linear chain and allows to determine the persistence length (q = 100 Å) in agreement with the value given in the literature.

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